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THEORETICAL STUDIES OF RELATIVELY RIGID POLYMER CHAINS
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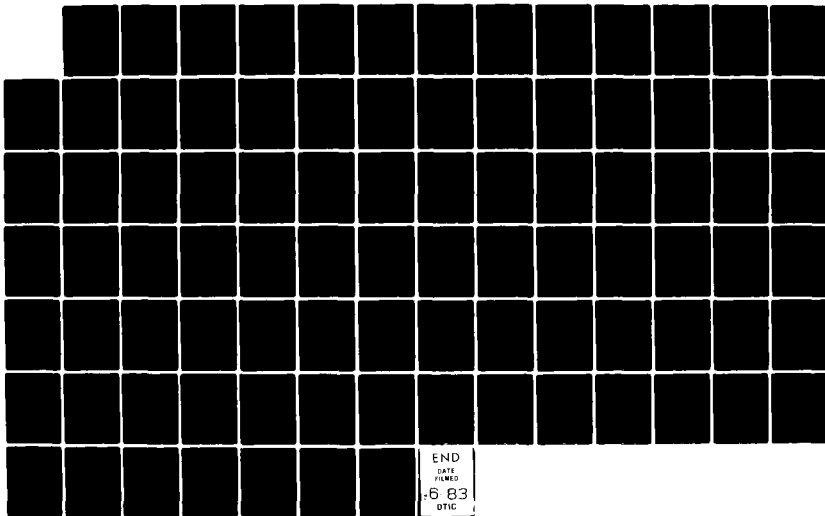
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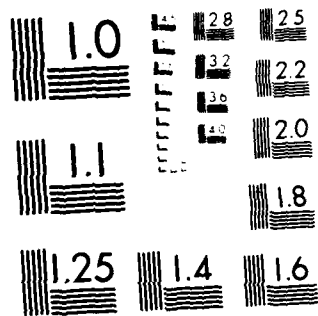
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THEORETICAL STUDIES OF RELATIVELY RIGID POLYMER CHAINS

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Final Report, August 1, 1978 - October 31, 1982

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) <p>Various theoretical approaches were applied to elucidate the structure and properties of rigid rodlike polymer chains which are of interest as high-performance polymeric materials. First, semi-empirical molecular mechanics methods were used to calculate the intramolecular and intermolecular energies pertinent to conformational flexibility and chain packing effects, and to characterize the rotational flexibility of various molecular</p>		

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"swivels" which could be inserted into these rodlike chains to facilitate their processing. Second, geometry optimized CNDO/2 molecular orbital calculations were carried out to investigate the structure and conformational characteristics of the rodlike polymers and of wholly aromatic swivels, in both the unprotonated and protonated states. Third, several theoretical approaches were used to calculate the molecular polarizabilities of the rodlike chains and of several analogous aliphatic and aromatic hydrocarbons. Fourth, electronic band gap calculations within the extended Hückel approximation were carried out in both the axial and perpendicular directions to elucidate the packing and electronic properties of these chains in the crystalline state. Some of these same methods were also used to investigate a variety of molecular species possessing structural features similar to those of the rodlike polymers.

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FOREWORD

This report was prepared at the Department of Chemistry of the University of Cincinnati, under Grant AFOSR 78-3683. The research described herein was administered under the direction of the Air Force Office of Scientific Research, Bolling Air Force Base, Washington, D.C., 20332.

The report covers work carried out between August 1, 1978, and October 31, 1982, and was prepared in December, 1982.

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A. RESEARCH OBJECTIVES

The research was carried out in order to obtain an understanding of the properties of relatively stiff polymer chains, and to provide guidance on how these properties can be exploited to obtain high-performance polymeric materials. More specifically, one primary goal was to use semi-empirical and quantum-mechanical methods to obtain information on the physical properties of rigid-rod benzobisoxazole (PBO) and benzobisthiazole (PBT) polymers which are of importance to the Air Force because of their high mechanical strength and excellent thermal stability. Such calculations involve energy calculations on both intramolecular (conformational) effects and interchain interactions for the polymers in both the unprotonated and protonated states. Of particular interest is the extent to which the various ring structures in the chains deviate from coplanarity, and how these deviations affect the ordering of the chains in the crystalline state. A related feature is the protonation of these chains, which occurs in the strongly acidic media used as solvents, and its effect on structure and deviations from coplanarity.

A second area of importance is the nature and magnitudes of the interchain interactions, and how they relate to the excellent mechanical properties of these materials. Also of great interest are the effects of oxygen, sulfur, and wholly aromatic "swivels"

on the processability of these materials, the ordering of the chains, and the mechanical strength of the resulting films or fibers. The basic goals are thus a molecular understanding of unusually high strengths of these materials, and knowledge regarding how currently available structures could be modified to improve these strengths. Also important is sufficient information on intermolecular interactions to provide guidance on improving processability by modification of the structure and rigidity of the chains, or by incorporation of a suitably chosen diluent or plasticizer. Polarizability calculations were carried out in support of various experimental studies of the polymers in solution, and calculations of the electronic band structures were explored with regard to the types of conductivity which may be of interest for electronic applications of these materials. Similar calculations were carried out on relatively small molecules having structural features in common with the PBO and PBT polymers.

Some theoretical and experimental investigations were also carried out on more tractable random-coil polymers such as the polyoxides, polyformals, and polysulfides in order to obtain more insight into the properties of the structurally related rigid-rod polymers.

Status of Research

Intramolecular (conformational) energy calculations using semi-empirical molecular mechanics techniques were carried out on

PBO and PBT repeat units in order to characterize deviations from coplanarity (see Reprint 1). The results indicated that PBO should be planar, in agreement with experimental results on model compounds. The PBT was correctly predicted to be nonplanar but its degree of nonplanarity was overestimated. Inclusion of intermolecular interactions improved agreement between theory and experiment. These intermolecular interaction energies were very large (see Reprint 2), suggesting that the failure mechanism in these materials might generally be bond breakage rather than bond slippage. Predicted densities and details of chain packing were in good agreement with experimental results.

Similar techniques were used to calculate the intramolecular energies of various molecular "swivels", which are inserted into the rodlike chains to impart flexibility, in order to characterize their flexibilizing ability (see Reprint 3). Wholly aromatic swivels were found to excel in this regard, particularly those containing ring nitrogen atoms adjacent to the rotatable bond. Three theoretical approaches were used to calculate the repeat unit polarizabilities of the polymers (see Reprint 4). Two of these gave comparable values of the polarizabilities, and corresponding values of the anisotropic ratio qualitatively agreed with experiment. The third method seriously underestimated the polarizabilities for PBO and PBT (see Reprint 4) and for the n-alkanes (see Reprint 5) but gave good agreement with experiment for benzene and biphenyl (see Reprint 5). Geometry-optimized CNDO/2 (Complete Neglect of Differential Overlap) molecular

orbital calculations were carried out to further characterize the structure and flexibilizing ability of the wholly aromatic molecular swivels, both as unprotonated and protonated species (see Reprint 6). The results confirm that both rotational flexibility and preference for coplanarity increased with the number of ortho-CH groups replaced by N atoms. Similar techniques were applied to characterize the structure and conformational profiles of PBO and PBT model compounds (see Abstract 1). Both cis- and trans-PBO preferred the coplanar form while trans-PBT preferred a conformation ca. 20° from coplanarity, and these theoretical results are in excellent agreement with experiment. Strain energies associated with the bowing observed in the cis-PBT model compound were estimated to be extremely large relative to those typically associated with bond length and bond angle deformations. Similar calculations were also carried out to predict both the effect (see Abstract 2) and sequence (see Reprint 7) of protonation of PBO chains. The preference for planarity was found to increase with successive protonation, and protonation was preferred at the N atoms rather than the O atoms within a repeat unit.

Electronic band gap calculations based on the extended Huckel approximation were carried out on PBO and PBT to investigate the possibility of electrical conductivity in these polymers (see Abstracts 3 and 4). Calculated band gaps in the axial direction are very similar to those obtained for the promising semiconductor trans-polyacetylene while conductivity in a

direction perpendicular to the chain axis was predicted to be negligible.

Similar calculations were frequently carried out on relatively small molecules having structural features in common with the PBO and PBT polymers. Some theoretical and experimental investigations were also carried out on more tractable random-coil polymers such as the polyoxides, polyformals, and polysulfides in order to obtain more insight into the properties of the structurally related rigid-rod polymers.

Phenylene Group Rotations and Nonplanar Conformations in Some *cis*- and *trans*-Poly(benzobisoxazoles) and -Poly(benzobisthiazoles)

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ABSTRACT: Planarity, or departures therefrom, can be of considerable importance in the formation of either crystalline or liquid-crystalline phases in rigid-rod polymeric systems. Of the four aromatic heterocyclic polymers *cis*- and *trans*-poly(benzobisoxazoles) (PBO) and -poly(benzobisthiazoles) (PBT), the *cis*-PBO and *trans*-PBT are known to form such phases, and the present investigation involves energy calculations carried out to characterize any deviations from planarity arising from *p*-phenylene group rotations along these chain backbones. Intramolecular (conformational) energy calculations indicate that the two PBO polymers should be planar, and this conclusion is in agreement with experimental results obtained on pertinent model compounds. Similar calculations on the PBT polymers correctly predict nonplanarity but overestimate its magnitude. Inclusion of intermolecular contributions (chain-packing effects) in this case considerably improves the agreement between theory and experiment.

Introduction

A number of aromatic heterocyclic polymers¹⁻¹² have been found to have exceedingly attractive properties, including very high mechanical strength, excellent thermal stability, and unusual resistance to most common solvents. Of particular interest have been the para-catenated polymers of the type illustrated in Figure 1. The poly(benzobisoxazole) (PBO) shown here is designated the *cis* form on the basis of the relative locations of the two oxygen atoms in the repeat unit. Other related polymers of interest are the *trans*-PBO and the *cis* and *trans* forms of the corresponding poly(benzobisthiazole) (PBT), in which the two oxygen atoms are replaced by sulfur atoms. Chains of this type are relatively rigid and frequently form liquid-crystalline¹³⁻¹⁹ as well as crystalline phases. In spite of the rigidity of the molecules, however, there is some conformational flexibility in that rotations should be permitted (at least to some extent) about the *p*-phenylene groups in each repeat unit. Such rotations ϕ are illustrated in the chain segment shown in Figure 2. The associated flexibility could be important with regard to solubility characteristics of the polymer and chain-packing effects in the crystalline and liquid-crystalline states.

The present theoretical investigation was undertaken in an attempt to characterize and elucidate this type of conformational flexibility in PBO and PBT polymers. Calculations of intramolecular (conformational) energies were carried out by using standard semiempirical potential energy functions, with contributions for nonbonded, torsional, and Coulombic interactions.^{20,21} Of primary interest are the identification of the conformations of lowest energy and their comparison with known crystalline-state conformations of relevant model compounds.^{22,23} If a predicted conformation is nonplanar, the estimated energy difference between it and the planar conformation, and the rotational energy profile in general, becomes of considerable importance. Also, in such cases the calculations will be extended to take approximate account of intermolecular interactions, which one would intuitively expect to increase the accessibility of the planar conformation.

Theory

Conformational and Intermolecular Energies. The energy calculations pertain to the chain segment shown in Figure 2 and were carried out as a function of the rotational angle ϕ . As is customary in conformational analyses,²⁰ $\phi = 0^\circ$ corresponds to the coplanar conforma-

tional state, with positive values of ϕ corresponding to the direction that would advance a right-handed screw. The total energy E associated with a given conformation was considered to be the sum of the steric or van der Waals energy E_{vdw} , the torsional contribution E_t , and the Coulombic energy E_C . Interactions not dependent on ϕ are of no interest in the present calculations and were therefore not included.

The van der Waals interactions between a pair of atoms i and j separated by the distance d_{ij} were treated by using the Buckingham potential function²⁰

$$E_{vdw} = \sum_{i < j} [a_{ij} \exp(-b_{ij}d_{ij}) - c_{ij}/d_{ij}^6] \quad (1)$$

with the parameters a , b , and c differing, of course, for different atom pairs. The parameter c characterizing the attractions was calculated from atomic polarizabilities²⁴ by application of the Slater-Kirkwood equation.²⁵ Values of b for a like atom pair were taken from Scott and Scheraga^{26,27} while values for an unlike pair were given by $b_{ij} = (b_i b_j)^{1/2}$. The corresponding values of the parameter a were then determined by minimizing eq 1 at $r_{min} = r_1 + r_2$, where r_1 and r_2 are the van der Waals radii, taken from crystal structure data.²⁸ (In these calculations of conformational energies, the values of r_1 and r_2 were augmented by 0.1 Å, as suggested by Flory²⁰ and others.²⁹ The increase is introduced to compensate for the absence, in this application, of long-range attractive forces that are operative in the crystal.)

Our choices for some of the Buckingham parameters a , b , and c require additional comments. It is particularly important to distinguish between aliphatic and aromatic carbon atoms. The basis for the difference can be understood by considering two overlapping, parallel benzene molecules. Due to the presence of π -electron clouds above and below each molecule, the equilibrium intermolecular carbon-to-carbon distances are greater than they would be if the carbon atoms were aliphatic. To account for this enhanced thickness in a direction perpendicular to the plane of the ring, aromatic carbon atoms are frequently assigned a larger van der Waals radius ($r = 1.85$ Å) than the value given for an aliphatic carbon (1.70 Å).²⁸ However, these assignments increase the size of the carbon atom in all directions, i.e., spherically, and ignore the fact that the increase in thickness is directional. An improvement would be to regard an aromatic carbon as "aromatic" only in a direction nearly perpendicular to the ring and as

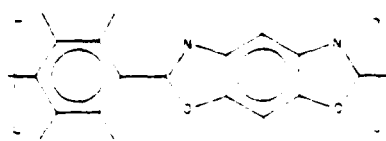
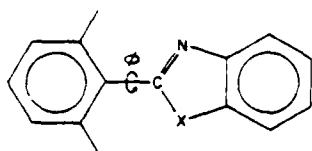
Figure 1. *cis*-PBO repeat unit.

Figure 2. Rotatable segment in PBO (X = O) and PBT (X = S).

Table I
Values of the Parameters^a for the
van der Waals Interactions

atom pair	r_{\min} , Å	$10^{-3}a$	b	c
C...C	3.60	908.6	4.59	363.0
C...N		755.3	4.59	445.9
C...O		432.2	4.59	275.5
C...S		1163	4.25	1158
C...H		86.10	4.57	127.0
N...H		75.43	4.57	156.0
O...H		41.75	4.57	92.2
S...H		123.3	4.22	407.0
H...H	2.60	10.37	4.54	47.1

^a Units are such as to give E in kcal/mol when d_{ij} is in Å.

"aliphatic" in a direction more nearly parallel to the ring.³⁰ This was the approach taken in the present investigation. The oxygen parameters are those given for a hydroxyl oxygen in a typical organic acid.³¹ This choice was based on the similarity in length of the C-O bond in such acids (1.36 Å)³² and in the PBO model compounds (1.325 Å for *cis*, 1.37 Å for *trans*).^{22,23} The nitrogen parameters are those given for a nitrogen atom in a polypeptide backbone, again based upon the similarity in the length of the C-N bond in a polypeptide (1.32 Å)^{20,33} and those observed in model compounds for both PBO (1.325 Å for *cis*, 1.30 Å for *trans*)^{22,23} and PBT (1.30 Å for *cis*, 1.292 Å for *trans*).^{22,23} These comments pertain to the intramolecular interactions, but only slight modifications, described elsewhere,^{34,35} are required for the intermolecular energy calculations. Illustrative values of the parameters for the most important case of augmented values of r_1 and r_2 and aliphatic-type carbon atoms are given in Table I.³⁴⁻³⁷

The torsional contributions were calculated from the standard representation^{20,21}

$$E_t = (E_0/2)(1 - \cos 2\phi) \quad (2)$$

where E_0 is the intrinsic barrier height for the specified rotation. The required value of E_0 was obtained from experimental studies of small molecules, on the perfectly reasonable assumption that such information is transferable to polymeric chains.²⁰

Coulombic energies were represented by the equation^{20,21}

$$E_C = \sum_{i < j} 332.072 q_i q_j / \epsilon d_{ij} \quad (3)$$

where q_i and q_j are, respectively, the partial charges on atom i and atom j , separated by distance d_{ij} , in a medium having a bulk dielectric constant ϵ . (The conversion factor 332.072 gives E_C in units of kcal/mol when d_{ij} is in Å and q is in units of electron charge.) Since Coulombic energies are frequently of only minor importance,³⁷ ϵ was assigned

Table II
Detailed Information on the
Conformational Energies^a of the *cis*-PBO Segment

ϕ , deg	E_{vdW}	E_t	E_C	E	d , ^b Å
0	-0.233	0.000*	-1.090	-1.32*	2.56
10	-0.009	0.139	-1.114	-0.984	2.57
20	-0.433	0.538	-1.120	-1.01	2.62
30	-0.620	1.150	-1.126	-0.596	2.68
40	-0.810	1.900	-1.165	-0.075	2.77
50	-0.960	2.699	-1.170*	0.569	2.88
60	-1.070	3.450	-1.145	1.23	2.99
70	-1.140	4.062	-1.120	1.80	3.12
80	-1.180	4.461	-1.100	2.18	3.24
90	-1.200*	4.600	-1.096	2.30	3.37

^a Energies are in kcal/mol, with asterisks specifying minimum values. ^b Distance between the O atom and the closer phenylene H atom separated from it by four bonds (see Figure 2).

the value unity to determine the maximum possible contribution from this source. The values of the (conformation-dependent) partial charges q were determined as a function of ϕ by the CNDO/2 (complete neglect of differential overlap) method.³⁸ Typical results, those calculated for the *cis*-PBO segment shown in Figure 1 (X = O), are given in Table IA (supplementary material). The Coulombic energies thus calculated for *cis*-PBO and *trans*-PBT were assumed also to apply to *trans*-PBO and *cis*-PBT, respectively.

In one case, where nonplanarity was predicted, additional calculations were carried out to investigate the effect of intermolecular interactions on the rotational angle, as described elsewhere.^{34,35} These calculations were based on three chain segments, each of which was assigned the same, specified value of ϕ . Different parallel arrangements of the chains at various spacings were investigated in order to find the one of lowest intermolecular energy. An entire series of calculations was carried out in this manner for ϕ varied in increments of 10°. For each value of ϕ , this approximate intermolecular contribution was added to the conformational part already calculated to give the total energy as a function of ϕ .

Structural Information. The bond lengths and bond angles of the molecular segments were those obtained in the X-ray studies of Fratini and co-workers on the PBO and PBT model compounds.^{22,23} The values are typical of aromatic heterocyclic compounds, and some information of this type is cited in the preceding section. The torsional barrier E_0 was assigned the value 4.6 kcal/mol, which corresponds to that found in gaseous benzaldehyde.³⁹ This value is in satisfactory agreement with the values 3.7 and 4.0 kcal/mol used by Birshtein and co-workers⁴⁰ and by Flory and co-workers,⁴¹ respectively, for similar types of bonds. As expected, the phenylene groups had perfect or near-perfect twofold symmetry. The only values of ϕ of relevance were therefore in the range 0-90°.

Results and Discussion

As described above, values were calculated for the van der Waals, torsional, and Coulombic energies and the sum of these (the total conformational energy) as a function of the rotational angle ϕ . Typical results, those for *cis*-PBO and *trans*-PBT, are given in Tables II and III, respectively. The corresponding results for *trans*-PBO and *cis*-PBT are given in Tables IIA and IIIA, respectively, as part of the supplementary material. Also included in these tables are values of the distance between the heteroatom X and the closer phenylene H atom separated from it by four bonds, as illustrated in Figure 2. The interaction between these

Table III
Detailed Information on the
Conformational Energies^a of the *trans*-PBT Segment

ϕ , deg	E_{vdw}	E_t	E_C	E	$d,^b$ Å
0	4.457	0.000*	-0.508*	3.95	2.66
10	4.100	0.139	-0.500	3.74	2.68
20	3.154	0.538	-0.496	3.20	2.73
30	1.913	1.150	-0.330	2.73	2.80
40	0.672	1.900	-0.350	2.22	2.91
50	-0.376	2.699	-0.290	2.03	3.03
60	-1.154	3.450	-0.311	1.98*	3.18
70	-1.670	4.062	-0.220	2.12	3.32
80	-1.965	4.461	-0.200	2.29	3.50
90	-2.071*	4.600	-0.191	2.34	3.62

^a Energies are in kcal/mol, with asterisks specifying minimum values. ^b Distance between the S atom and the closer phenylene H atom separated from it by four bonds (see Figure 2).

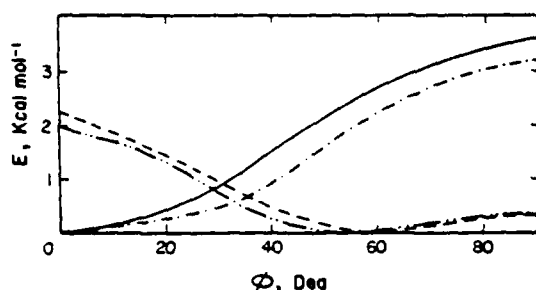


Figure 3. Conformational energy shown as a function of rotation angle for *cis*-PBO (—), *trans*-PBO (---), *cis*-PBT (-·-·-), and *trans*-PBT (···). In each case, the energies are expressed relative to zero for the energy minimum.

two atoms is of considerable importance because of the possibility of steric repulsions interfering with the attainment of coplanarity between the two parts of the repeat units. This is, of course, particularly important with regard to possible differences in conformational behavior between PBO and PBT.

The most important results are summarized in Figure 3, which shows the total conformational energy as a function of ϕ for all four chains. In the case of *cis*-PBO, the lowest energy form is seen to correspond to $\phi = 0^\circ$, and this is in excellent agreement with the planarity found for the corresponding model compound in the crystalline state.²² *trans*-PBO is also predicted to be planar, as one might anticipate, and preliminary results²² are consistent with this expectation.

Significant nonplanarity is predicted for *trans*-PBT, with ϕ estimated to be approximately 55° . The nonplanarity predicted for the PBT, but not for the PBO polymers, is due to the fact that the S atom has a much larger van der Waals radius than the O atom (~ 1.85 vs. 1.40 Å).^{20,28} Since the van der Waals radius of an H atom is ~ 1.15 Å, repulsions should become important when the smaller phenylene H—O distance becomes significantly less than 2.55 Å or the corresponding H—S distance less than 3.00 Å. As shown in Tables II and IIA, this H—O separation in the planar conformation of *cis*-PBO and *trans*-PBO is almost exactly this critical value of 2.55 Å. The corresponding separation in *trans*-PBT is 2.66 Å, which is ~ 0.34 Å less than the critical value of 3.00 Å.

The pertinent experimental ϕ value, obtained from a crystalline *trans*-PBT model compound, is 23.2° .^{22,23} The lack of quantitative agreement between theoretical and experimental results is less significant than the numerical differences in ϕ might suggest. First, the energy changes

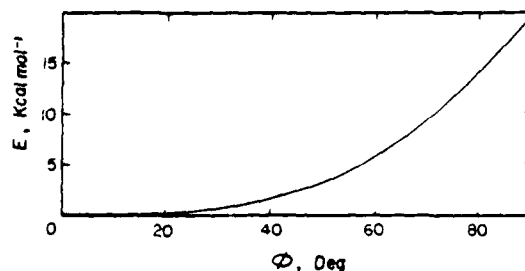


Figure 4. Sum of the conformational energy and an estimate of the intermolecular interaction energy for *trans*-PBT shown as a function of the rotation angle.

only gradually with ϕ near the minimum; specifically, the entire range $\phi = 25$ – 90° gives energies within 1 kcal/mol of the minimum value, and this indicates considerable rotational flexibility. Second, the torsional barrier $E_0 = 4.6$ kcal/mol chosen in these calculations may underestimate the true barrier to rotation. In the rigid-rod polymer, the coplanar conformation may be favored by long-range resonance stabilization which is absent in benzaldehyde, the model compound used for the estimate of E_0 . Some evidence for this possibility exists in that the length of this bridging bond in the polymers of interest is 1.46 Å, which is smaller than the lengths of corresponding bonds in analogous low molecular weight species,³² such as benzoic acid (1.49 Å), diethyl terephthalate (1.48 Å), and benzamide (1.50 Å). The smaller bond length in PBO and PBT does suggest some partial double-bond character in these C—C bonds. Third, and possibly most important, the discrepancy between theory and experiment in this case could be due to intermolecular forces, which could strongly favor a more nearly planar conformation for more efficient chain packing. The effect of including intermolecular interactions in the total energy is shown in Figure 4. Although these results are extremely approximate, it is important to note that this combined energy does show a broad minimum between $\phi \approx 0^\circ$ and $\phi \approx +25^\circ$, a region which includes the experimentally observed angle of $\sim 23^\circ$.^{22,23} These results strongly suggest that intermolecular interactions can have a significant effect on chain conformation.

The *cis*-PBT chain is also predicted to be significantly nonplanar, but the experimental results^{22,23} indicate a deviation of only 2.8 – 5.8° from planarity. Molecules of this type are much more complicated than the three others in that they have considerable "bowing" within the repeat unit, presumably due to strain arising from the S atoms located *cis* to one another.²³ In any case, calculations of conformational and intermolecular energy are greatly complicated by this bowing²³ and will therefore have to be the subject of a separate theoretical investigation.

The conformational energy profiles shown in Figure 3 indicate that the phenylene groups in the PBT chains should have somewhat greater flexibility than those in the PBO chains. This could be of importance with regard to the properties of these chains in solution and in the liquid-crystalline state. The results also furnish information concerning the nature of the barriers to rotation. For both the *cis*-PBO and *trans*-PBO segments, the torsional term dominates in that it shows the greatest change over the range $\phi = 0$ – 90° ; the change in E_t is 4.6 kcal/mol compared with 1.20 kcal/mol for E_{vdw} and 0.09 kcal/mol for E_C . However, for the *cis*-PBT and *trans*-PBT segments, E_{vdw} makes the largest contribution. The changes are 6.5 – 6.9 kcal/mol for E_{vdw} compared with 4.6 kcal/mol for E_t and 0.32 kcal/mol for E_C . The differences can be traced to the larger size of the S atom in the case of repulsions occurring

at small distances of separation and to higher polarizability³⁷ in the case of attractions at larger distances. It is also interesting to note that Coulombic interactions are not very important with regard to the conformational energy. Since they are also relatively unimportant with regard to interchain interactions,³⁵ these observations suggest that the dielectric constant of a solvent should have relatively little effect on this type of rotational flexibility. Protonation of the chain, however, would be expected to have an effect,⁴² as could also any "specific solvent interaction"⁴³⁻⁴⁵ with the chain segments.

Acknowledgment. It is a pleasure to acknowledge the financial support provided by the Air Force Office of Scientific Research (Grant AFOSR 78-3683, Chemical Structures Program, Division of Chemical Sciences). We also acknowledge, with gratitude, the very useful information, help, and advice provided by Professors A. V. Fratini of the University of Dayton, P. J. Flory of Stanford University, and H. H. Jaffé of The University of Cincinnati.

Supplementary Material Available: Partial charges for the *cis*-PBO segment and detailed conformational energy information on *trans*-PBO and *cis*-PBT (4 pages). Ordering information is given on any current masthead page.

References and Notes

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Interchain Interactions in Some Benzobisoxazole and Benzobisthiazole Rigid-Rod Polymers

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ABSTRACT: Interaction energies between relatively rigid benzobisoxazole and benzobisthiazole polymers were calculated in an attempt to gain insight into the very high mechanical strength and unusual solvent resistance of these materials. The predicted details of the chain packing and the corresponding densities were found to be in good agreement with experimental results obtained on relevant model compounds in the crystalline state. The interaction energies are estimated to be very large, with van der Waals contributions being far more important than Coulombic ones. Additional calculations indicate that protonation of the chains should greatly decrease the intermolecular attractions, even at very high dielectric constant. This conclusion is consistent with the fact that only extraordinarily strong acids are solvents for these types of chain molecules.

Introduction

Para-catenated benzobisoxazole and benzobisthiazole polymers are relatively rigid chain molecules which can be used in fabricating materials having very high strength and unusual resistance to most common solvents.¹⁻¹⁶ One poly(benzobisoxazole) (PBO) of particular interest in this regard is shown in Figure 1; an alternate form, in which the O atoms are trans to one another is of comparable interest. The poly(benzobisthiazole) (PBT) related to the *trans*-PBO is shown in Figure 2. Although it and the alternate *cis* modification are both in this category, only the *trans* form has been extensively studied up to the present time.

One goal of foremost importance in this area is the elucidation of the unusual properties of these materials in molecular terms. Of obvious importance are intramolecular (conformational) effects,^{15,16} particularly as they relate to the rigidity of the chains. Also of importance are intermolecular effects, and these are the focus of the present investigation. It deals with interchain interactions, both van der Waals and Coulombic, as estimated by standard methods based on semiempirical potential energy functions. The specific goals are elucidation of the nature of the chain packing and estimation of the corresponding densities, the magnitude of the total interaction energies, the relative importance of van der Waals and Coulombic contributions, and the extent to which the intermolecular interactions are modified by protonation of the chains, which occurs in the strongly acidic media used as solvents for these polymers.

Theory

The three polymers investigated were *cis*-PBO, *trans*-PBO, and *trans*-PBT. The bond lengths and bond angles characterizing their repeat units were obtained from the X-ray structural studies carried out on model compounds by Fratini and co-workers.^{13,14} The values are typical of aromatic heterocyclic compounds.¹⁷ In the case of the two PBO polymers the repeat units are planar, but the *trans*-PBT repeat unit has the *p*-phenylene group rotated by 23.2°. Values of the atomic partial charges q were determined by the CNDO/2 (complete neglect of differential overlap) method.¹⁸ In the case of the protonated chains, each repeat unit was given two protons, the number indicated by freezing-point depression measurements.¹⁹ These protons were placed on the nitrogen atoms at a distance corresponding to the usual N—H bond length and at an orientation bisecting the C=N—C bond angle. This is shown diagrammatically in Figure 3. In some illustrative calculations, two additional protons were added to the two O or two S atoms in an analogous manner. In all

cases, increasingly long sequences of repeat units were investigated until the charges calculated for the central repeat unit were seen to converge. Typical charge distributions thus obtained are given in Figures 1-3.

The total intermolecular interaction energy E was considered to be the sum of the steric or van der Waals energy E_{vdw} and the Coulombic energy E_C . The van der Waals interactions between a pair of atoms i and j separated by the distance d_{ij} were treated by using the Buckingham potential function²⁰

$$E_{vdw} = \sum_{i < j} [a_{ij} \exp(-b_{ij}d_{ij}) - c_{ij}/d_{ij}^6] \quad (1)$$

with the parameters a , b , and c differing, of course, for different atom pairs. The parameter c characterizing the attractions was calculated from the effective number N_{eff} of electrons and atomic polarizabilities²¹ α by application of the Slater-Kirkwood equation.²² Values of b for a like atom pair were taken from Scott and Scheraga²³ while values for an unlike pair were given by $b_{ij} = (b_i b_j)^{1/2}$. The corresponding values of the parameter a were then determined by minimizing eq 1 at $r_{min} = r_1 + r_2$, where r_1 and r_2 are the van der Waals radii, taken from crystal structure data.²⁴ Distinctions were made between aliphatic and aromatic carbon atoms, with the latter being assigned an increased thickness in directions nearly perpendicular to the aromatic ring,²⁵ as described elsewhere.¹⁶ In addition, carbon atoms in N=C—O and N=C—S bond sequences were assigned the parameters found to be most suitable for carbon atoms of this type in peptide linkages, as suggested by Brant, Miller, and Flory.²⁶ A summary of the set of parameters employed is given in Table I.^{15,16,27,28}

The Coulombic interaction energies were estimated from^{20,29}

$$E_C = \sum_{i < j} 332.072 q_i q_j / \epsilon d_{ij} \quad (2)$$

where q_i and q_j are, respectively, the partial charges on atom i and atom j , separated by the distance d_{ij} . The dielectric constant ϵ of the medium was assigned a value of 3.0 (in cgs units) for the unprotonated, undiluted chains²⁰ and the range of values 10-100 in the case of the protonated chains in very strong acids.¹⁹

Because of the complexity of these systems, the calculations were of necessity very approximate, being based on only a pair of the chains of a given type in their planar or nonplanar conformations,^{13,14} as mentioned above. The first chain was one repeat unit long, with the second being assigned a series of lengths in an attempt to make the interaction energies (per repeat unit) as realistic as possible without making the calculations impracticable. Four re-

Table I
Parameters for the Buckingham Potential Functions

atom pair	N_{eff}^a	$10^{24} \alpha_i^b$, cm ³	r_{min}^c , Å	$10^{-1} a^d$	b^d	c^d
C...C ^e	5.0	0.93	3.4	541.4	4.59	363.0
C...C ^f	5.0	1.23	3.7	1820	4.59	556.7
C...C ^g	5.0	1.30	3.4	395.6	4.59	600.5
N...N	6.0	1.15	3.1	393.2	4.59	547.3
O...O	7.0	0.59	3.0	135.8	4.59	217.2
S...S	14.8	3.04	3.6	906.3	3.90	3688
H...H	0.9	0.42	2.4	7.323	4.54	47.1

^a Effective number of electrons. ^b Polarizability. ^c Sum of van der Waals radii. ^d Units are such as to give E in kcal/mol when d_{ij} is in Å. ^e Aliphatic carbon atoms. ^f Aromatic carbon atoms. ^g Carbon atoms in NCO peptide-type linkages.

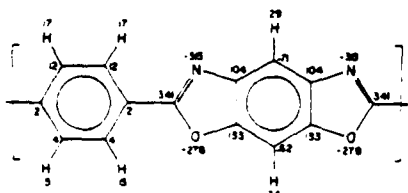


Figure 1. *cis*-PBO (unprotonated) repeat unit. In this and the following two figures, the charges shown were calculated by the CNDO/2 method and are in units of 10^{-3} of the electron charge.

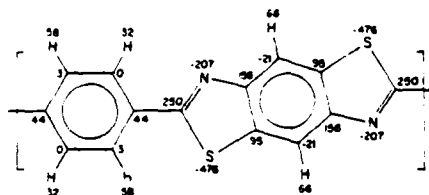


Figure 2. *trans*-PBT (unprotonated) repeat unit arbitrarily shown in the planar conformation; see legend to Figure 1.

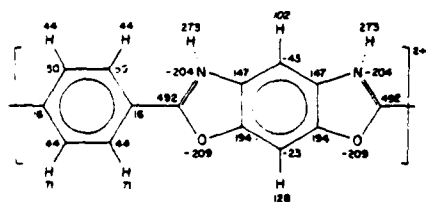


Figure 3. *cis*-PBO repeat unit with two protons. Two additional protons could possibly be added to the two (negatively charged) O atoms.

peat units were found to be appropriate in this regard. A Cartesian coordinate system was defined about the longer chain so that the x , y , and z coordinates lay along the length, width, and thickness, respectively, of the repeat units. (In the case of the nonplanar *trans*-PBT unit, the plane of the phenylene ring was taken to be the plane of the molecule.) In the initial series of calculations the chains were first placed in parallel arrangements, one above the other, and then one chain was rotated along its x , y , and z axes. The rotations invariably increased the energy,¹⁵ and such arrangements were therefore not considered further. Thus, the calculations to determine minimum-energy arrangements were based primarily on two parallel chains shifted relative to one another along the x , y , and z axes. In the case of the density estimates, there are two specific sets of calculations which are relevant, one for a pair of chains above one another ($\Delta y = 0$) and the other for a pair alongside one another ($\Delta z = 0$).

Results and Discussion

The characteristics of the minimum-energy arrangements thus identified are summarized in Table II. For pairs of chains above one another the predictions are that

Table II
Interchain Spacings and Energies in Minimum-Energy Arrangements

polymer	spacings, Å			energy, kcal/mol	
	Δx	Δy	Δz	total	Coulombic
<i>cis</i> -PBO ^a	3.0	0.0	3.5	-22.44	0.07
<i>cis</i> -PBO ^b	2.0	6.2	0.0	-4.48	-0.02
<i>trans</i> -PBO ^a	3.0	0.0	3.5	-22.33	0.01
<i>trans</i> -PBO ^b	3.5	6.1	0.0	-6.81	-0.17
<i>trans</i> -PBT ^a	1.5	0.0	3.7	-29.44	0.57
<i>trans</i> -PBT ^b	1.0	6.1	0.0	-6.83	-0.23

^a Chains above one another at a spacing of Δz .

^b Chains alongside one another at a spacing of Δy . The shift parallel to the chain axes is Δx .

the chains are out of register by $\Delta x = 3.0$ Å in the case of the two PBO polymers (which would place a phenylene group of the upper chain over the bond bridging the two ring systems of the repeat unit of the lower chain) and by 1.5 Å in the case of the *trans*-PBT. These are rather approximate results, in part because of the large number of energy minima occurring as the chains are slid by one another.¹⁵ The latter displacement is predicted to be smaller than the former because of the large size of a sulfur atom relative to oxygen and the much more irregular cross section of the nonplanar PBT molecule. These results are in at least qualitative agreement with the results of X-ray structural studies. The experimental values of these axial shifts were found to be approximately 4.5 Å in the case of model compounds for all three types of molecules.^{13,14} The agreement between theoretical and experimental values of Δx could, of course, be considerably better for the polymeric chains, which have not yet been studied experimentally in this regard. In the case of the vertical spacings, the theoretical results are in excellent agreement with the experimental finding that $\Delta z \approx 3.5$ Å for all three types of model compounds.^{13,14} For the pairs of chains alongside one another, the spacing Δy is predicted to be approximately 6.1 Å. Although there are no experimental values of this quantity available for comparison, it is important for density estimates, which are to be discussed below.

The interaction energies are seen to be rather large, with contributions from only a few repeat units adding up to values approaching typical bond dissociation energies. This suggests that the failure mechanism in such materials might generally be bond breakage rather than bond slippage. The attractions are somewhat larger for the *trans*-PBT chain because S atoms give rise to larger van der Waals attractions than do O atoms because of their much higher polarizability (see Table I). Analogous differences are found in comparisons between poly(ethylene sulfide) (PES) and poly(ethylene oxide) (PEO).²⁸ The Coulombic

Table III
Densities of PBO and PBT Chains
in the Crystalline State

polymer	densities, g/cm ³	
	calcd	exptl ^a
cis-PBO	1.46	1.38
trans-PBO	1.49	1.41
trans-PBT	1.55	1.44

^a References 13 and 14.

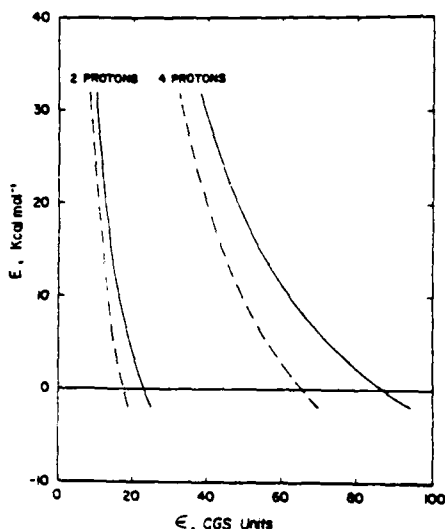


Figure 4. Total interaction energy per repeat unit shown as a function of degree of protonation and dielectric constant of the medium. The solid line refers to both cis- and trans-PBO and the broken line refers to trans-PBT.

contributions to the total interaction energy are seen to be very small, as was also observed in the case of PES and PEO.²⁸ This suggests that the dielectric constant of a potential solvent for these (unprotonated) polymers should be of no importance, and this is in agreement with experiment.³⁰

The above information also permits estimation of the densities of the PBO and PBT polymers in the crystalline state. The two polymers were represented as having elliptical cross sections, with dimensions based on the results given in Table II and with six such ellipses closely packed around a central ellipse. The densities thus estimated are given in the second column of Table III. They are seen to be in good agreement with the experimentally obtained densities of the model compounds,^{13,14} particularly in the way they vary with changes in the structure of the repeat unit. The results indicate that the higher density for the PBT polymer is due to the higher atomic weight of S relative to O rather than to more efficient chain packing.

The results of the calculations on the protonated chains are summarized in Figure 4. It is difficult to relate such results quantitatively to the polymer-solvent dissolution process, which is, of course, controlled by changes in free energy. They are nonetheless of considerable interest in that they indicate that protonation of the chains should

greatly decrease the intermolecular attractions, even at the very high dielectric constants characteristic of strong, undiluted acids.¹⁹ This conclusion is consistent with the fact that only extraordinarily strong acids are solvents for these types of polymers.³⁰

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The Flexibility of Various Molecular Swivels Used to Control the Rigidity and Tractability of Aromatic Heterocyclic Polymers

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ABSTRACT

Some aromatic heterocyclic polymers are rigid or rodlike and form liquid-crystalline phases which can be used to prepare films and fibers having unusual strength and thermal stability. They are, however, very nearly intractable unless some atoms or groups of high flexibility are introduced along the chains. The present theoretical investigation employs semiempirical methods to calculate intramolecular energies of various conformations about such "molecular swivels" in order to characterize their flexibility. In addition, simple geometric arguments are used to determine which swivels have one or more conformations exhibiting the parallel or collinear chain continuation which is characteristic of liquid-crystalline phases and apparently essential to the unusual mechanical properties of these materials.

INTRODUCTION

The effect of the stiffness of a polymer chain on its solubility and solution behavior in general has been predicted by Flory [1-4] and has been studied experimentally in some detail [5-12]. Of particular interest has been the case of relatively rigid ("rod-like") polymers, since their solutions undergo phase separation as a consequence of the particle asymmetry, with some contributions from the intermolecular interactions between the chains [4]. Films and fibers formed from such materials, in particular the paracatenated polybenzobisoxazoles and polybenzobisthiazoles shown in Fig. 1, have very high mechanical strength and excellent thermal stability and are affected relatively little by most common solvents. These polymers are therefore of considerable interest whenever high-performance characteristics are required. They are, for example, an important part of the U.S. Air Force's program to develop polymeric materials which exhibit superior mechanical properties through molecular organization [11-16].

Unfortunately, such chains of relatively high rigidity are very nearly intractable, being insoluble in all but the strongest acids and very difficult to process into utilizable films and fibers [11-16]. These materials may be made more tractable, however, by the insertion of a limited number of atoms or groups chosen so as to impart a controlled amount of additional flexibility to the chains. For example, the introduction of oxygen atoms into a typical aromatic heterocyclic backbone should decrease the rigidity of the chain, thereby increasing its solubility and decreasing its viscosity in both the bulk (undiluted) state and in solution. This decrease in rigidity is due to the fact that O atoms are relatively small and therefore relieve congestion between chain atoms [17]. Also, the C-O-C bond angle is approximately tetrahedral [18], thus putting a "kink" into the otherwise approximately linear rigid rod, as is illustrated in Fig. 2. It is obviously of considerable

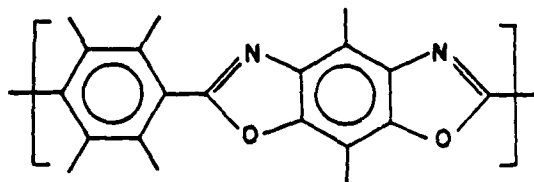


Fig. 1. A typical aromatic heterocyclic polymer, a polybenzobisoxazole in which the two oxygen atoms in the repeat unit are *cis* to one another. Some related molecules of interest are the *trans* modification of this polymer and both the *cis* and *trans* forms of the corresponding polybenzobisthiazole (in which the oxygen atoms are replaced by sulfur atoms).

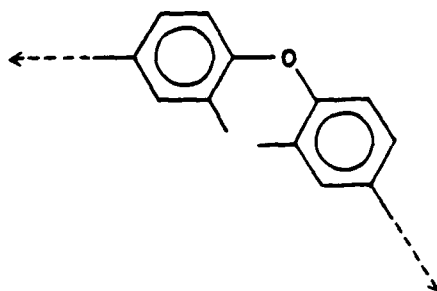


FIG. 2. A single oxygen para-phenylene swivel.

importance to investigate the effect of the structure, number, and spacing of such swivels along the chain. For example, two closely spaced swivels would decrease the rigidity of the chains but still permit occurrence of nearly parallel conformations conducive to the formation of the desired molecular alignment or organization. This is illustrated in Fig. 3.

The general goals of this theoretical investigation were therefore to determine the effects of such swivels on the intramolecular interactions in these systems, and thus on their physical properties. In order to assess the flexibility of such swivel linkages, conformational-energy calculations were carried out. The first series of swivels were of the type R_1-X-R_2 , where the R represents the para form of either phenylene (Ph) ($-C_6H_4-$) or pyridylene (Pyr) ($-C_5H_3N-$) and the linkage species X are the single atoms oxygen ($-O-$), sulfur ($-S-$), selenium ($-Se-$), or tellurium ($-Te-$), or the groups carbonyl ($-\overset{O}{\parallel}C-$), sulfonyl ($-\overset{O}{\parallel}S-$), methylene ($-CH_2-$), and difluoromethylmethylene [$-C(CF_3)_2-$]. As might be expected, all the above atoms and groups tend to decrease the stability of the chains at very high temperatures [19]. There is now

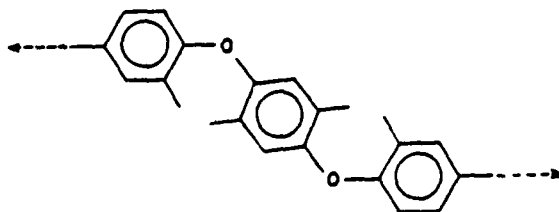


FIG. 3. Two adjacent oxygen para-phenylene swivels.

growing interest, therefore, in wholly aromatic swivels of the type R_1-R_2 , and such groups are included in the present calculations.

THEORY

Calculation of the Conformational Energy

A typical molecular swivel is sketched in Fig. 4, which also shows the bond angle θ and the rotational angles of relevance ψ and ϕ . As is customary in conformational analyses [20], $\psi = \phi = 0^\circ$ corresponds to the (coplanar) conformational state, with positive values of ψ and ϕ corresponding to the direction that would advance a right-handed screw. The total energy E associated with these angles is considered to be the sum of the steric or van der Waals energy E_{vdw} and the torsional contribution E_t . In these swivel flexibility calculations, the groups moving relative to one another are generally quite nonpolar and shielded from one another by the high dielectric constant medium in which they would be dispersed. Coulombic interactions could therefore be ignored at the present level of approximation.

The van der Waals interactions between a pair of atoms i and j separated by the distance d_{ij} were treated using the Buckingham potential function [20]

$$E_{vdw} = \sum_{i < j} a_{ij} \exp(-b_{ij} d_{ij}) - c_{ij} / d_{ij}^6 \quad (1)$$

with the parameters a , b , and c differing of course for different atom pairs. The parameter c characterizing the attractions was calculated from atomic polarizabilities [21] by application of the Slater-Kirkwood equation [22]. Values of b for a like atom pair were taken from Scott and Scheraga [23, 24] while values for an

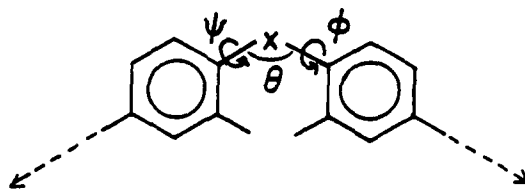


FIG. 4. Illustration of an R_1-X-R_2 swivel having $R_1 = R_2 = \text{Ph}$ (phenylene group). The bond angle θ and the rotation angles ψ and ϕ are shown, and the short line segments locate the H atoms in steric conflict in the coplanar arrangement.

TABLE 1
 Values of the Parameters^a for the Potential
 Energy Functions

Atom pair	r_{\min} (Å)	$10^{-3} a$	b	c
C...C	3.60	908.6	4.59	363.0
C...N	-	755.3	4.59	445.9
C...H	-	86.10	4.57	127.0
N...N	3.30	635.7	4.59	547.3
N...H	-	75.43	4.57	156.0
H...H	2.60	10.37	4.54	47.1

^aUnits are such as to give E in kcal/mol when d_{ij} is in Å.

unlike pair were given by $b_{ij} = (b_{ii}b_{jj})^{1/2}$. The corresponding values of the parameter a were then determined by minimizing Eq. (1) at $r_{\min} = r_1 + r_2$, where r_1 and r_2 are the van der Waals radii, taken from crystal structure data [17], and augmented by 0.1 Å, as suggested by Flory [20] and others [25]. (This increase is introduced to compensate for the absence, in the present application, of long-range attractive forces that are operative in the crystal.) The parameters are summarized in Table 1, with r_{\min} in Å and a, b, and c in units so as to give energies in kcal/mol when d_{ij} is in Å. The summation of the energies specified in Eq. (1) was taken over all atom pairs that change their distance of separation with change in ψ or ϕ .

Our choice of the Buckingham parameters a, b, and c for the carbon atom requires some additional comments. Specifically, the parameters chosen are those for an aliphatic carbon rather than for an aromatic one. Justification for the selection can be seen by considering two overlapping, parallel benzene molecules. Due to the presence of π electron clouds above and below each molecule, the equilibrium intermolecular carbon-to-carbon distances are greater than they would be if the carbon atoms were aliphatic. To account for this enhanced thickness in a direction perpendicular to the plane of the ring, aromatic carbon atoms are frequently assigned a larger van der Waals radius ($r = 1.85$ Å) than the value given for an aliphatic carbon (1.70 Å) [17]. However, these assignments increase the size of the carbon atom in all directions,

i.e., spherically, and ignore the fact that the increase in thickness is directional. An improvement would be to regard an aromatic carbon as "aromatic" only in a direction nearly perpendicular to the ring, and as "aliphatic" in a direction nearly parallel to the ring [20]. In the present calculations, the intramolecular interactions involving ring carbons lie on a line that is more nearly parallel than perpendicular to the ring. Consequently, parameters pertaining to an aliphatic carbon were considered more appropriate in this type of calculation.

It should also be mentioned that a slight alteration in the Buckingham potential function was found to be necessary in these calculations. Specifically, Eq. (1) possesses a spurious maximum at a very small value d' of d_{ij} . This anomaly in the Buckingham function rarely presents a problem since in most applications d_{ij} is much larger than d' . However, interactions at $d_{ij} < d'$ do occur in the present calculations. These interactions involve the 2, 2', 6, and 6' hydrogens as the two rings joined to the swivel approach coplanarity, and for these conformations Eq. (1) erroneously gives attractive energies. The problem was remedied by invoking a linear function $E = k + md_{ij}$ for $d_{ij} < d'$, with the constants k and m calculated for each atom pair from E values given by Eq. (1) at its steepest slope in the region $d_{ij} > d'$.

The torsional contributions were calculated from the standard representation [20, 27]

$$E_t = (E_o^\psi/2)(1 - \cos 2\psi) + (E_o^\phi/2)(1 - \cos 2\phi) \quad (2)$$

where E_o^ψ and E_o^ϕ are the barrier heights for the two specified rotations. Values of the barrier heights are generally obtained from experimental studies of small molecules in the gaseous phase; the fact that effective barrier heights may be somewhat different in condensed phases [26] could possibly be taken into account in refined calculations on molecules for which there is sufficient reliable experimental data.

The effects of bond angle deformation were estimated in a preliminary manner. More elaborate calculations involving totally relaxing molecules (with bonds as well as bond angles being deformable) will be carried out subsequently for those swivels found to be most promising with regard to ease of synthesis, degree of flexibility, capability of giving collinear or parallel chain continuation, and level of thermal stability.

FLEXIBILITY OF VARIOUS MOLECULAR SWIVELS

65

TABLE 2
Bond Lengths and Bond Angles for the Molecular Swivels [18]

	r (Å)		θ (deg)
C-O	1.28	C-O-C	123
C-S	1.75	C-S-C	109
C-Se	1.92	C-Se-C	106
C-Te	2.05	C-Te-C	101
C-CO	1.49	C-CO-C	126.5
C-SO ₂	1.84	C-SO ₂ -C	100
C-CH ₂	1.53	C-CH ₂ -C	111
C-C(CF ₃) ₂	1.53	C-C(CF ₃) ₂ -C	111
C-C _{Ar}	1.48		

All other bond angles
assumed to be 120°

Structural Information

The bond lengths and bond angles employed in the calculations are summarized in Table 2. The values of the torsional barrier E_0 for the C-O and C-S bonds were taken from measurements on anisole [C₆H₅OCH₃] and thiophenol [C₆H₅SH], respectively, both in the gaseous state. These values are 3.6 [28] and 0.80 kcal/mol [29], respectively. Values of E_0 for the C-Se and C-Te bonds were not available at all, but the bond lengths given in Table 2 suggest that they are small and probably no larger than the value obtained for the C-S bond; they were therefore assigned the value 0.8 kcal/mol. The E_0 values used for the multiatom swivels are 3.1 kcal/mol [28] for C-C^O (taken from measurements on gaseous benzophenone [C₆H₅COC₆H₅]), 0.0 kcal/mol [28] for both C-CH₂ and C-C(CF₃)₂ (taken from measurements on gaseous toluene [C₆H₅CH₃]), and 0.0 kcal/mol [30] for C-S^O (taken from a CNDO/2 calculation on benzene sulfonic acid [C₆H₅SO₃H], since experimental values were not available). Only theoretical values of E_0 were available for the

C-C bonds in the wholly aromatic swivels, and these are 4.0 [31] and 6.2 kcal/mol [32], respectively. In all of these calculations, Pyr-X and Pyr-Pyr bonds were assumed to have the same values of E_0 as the corresponding Ph-X and Ph-Ph bonds, and thus $E_0^\psi =$

E_0^ϕ . In some cases, the values of E_0 were varied in the calculations in order to illustrate the effect of this quantity on the conformational energy.

RESULTS AND DISCUSSION

The results of the above conformational energy calculations were represented in the usual form of contour energy maps [20, 27], consisting of lines of equal energy shown as a function of ψ and ϕ . The features of particular importance are (1) the preferred (lowest-energy) conformations; (2) the relative accessibility of the coplanar conformation ($\psi = \phi = 0^\circ$); (3) the amount of ψ - ϕ space of sufficiently low energy to be accessible; and (4) the energy barriers separating the preferred conformations.

Single-Atom Swivels

Ph-O-Ph and Ph-S-Ph Swivels

Swivels of the type Ph-X-Ph-X-Ph, with X being either an oxygen atom or a sulfur atom, are currently being incorporated into aromatic heterocyclic chains in laboratory-scale syntheses, and the resulting polymers are undergoing preliminary evaluations [33, 34]. The phenylene linkages are of the para type, as shown in Figs. 2-4, which keeps the two chain segments relatively far apart. The two pairs of rotational angles should therefore be independent to good approximation. The energy contour maps obtained for these two swivels are presented in Figs. 5 and 6 and reveal that the O and S swivels are very similar in their conformational energy profiles. First, both swivels display considerable flexibility. Second, both swivels assume "propeller" orientations as their preferred conformations at the energy minima. The minima occur at ± 42.5 , $\mp 42.5^\circ$ (or their supplements). These values, for both Ph-O-Ph and Ph-S-Ph, agree well with the result $\phi = \pm 40^\circ$ obtained by x-ray analyses on crystalline poly(phenylene oxide) [35] and poly(phenylene sulfide) [36]. Third, for both swivels, the coplanar ($0, 0^\circ$) state is of high energy. Preliminary calculations indicate that these very high estimates of the energy at the coplanar conformation would be reduced by a factor of approximately 10 if bond angle deformation is taken into account. Even these reduced values of the energy, however, would probably be too high for the coplanar conformation to be readily

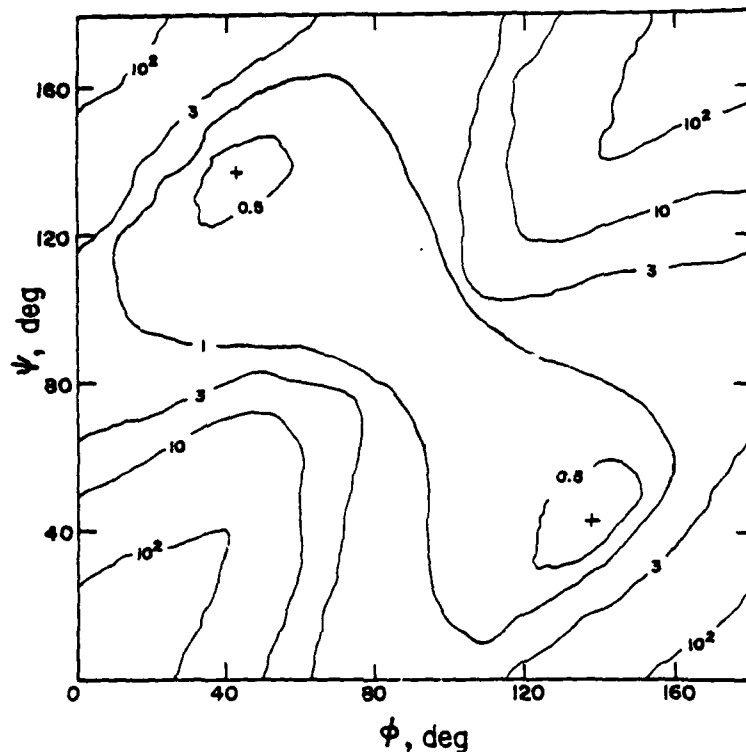


FIG. 5. Conformational energy map for the Ph-O-Ph swivel.

accessible at ambient temperatures. In any case, all of the other areas of the maps correspond to sufficiently low energy to permit bond angle and bond length deformations to be ignored.

The two swivels do seem to differ somewhat, however, with respect to overall flexibility. The Ph-S-Ph swivel is slightly greater both in equilibrium flexibility (more low-energy—and thus accessible—regions in configuration space) and in dynamic flexibility (lower barriers between energy minima). For Ph-O-Ph, the smallest barrier is 1.0 kcal/mol, but for Ph-S-Ph it is only 0.55 kcal/mol. Also, as may be seen from Figs. 5 and 6, the Ph-S-Ph swivel has a larger fraction of the ψ - ϕ map that is energetically accessible. On these grounds, it would appear to have some advantages over the Ph-O-Ph swivel from the standpoint of improving overall flexibility. This indicates that the longer bonds and smaller torsional energies in the Ph-S-Ph swivel are more important than the larger bond angle in the Ph-O-Ph swivel. Nevertheless,

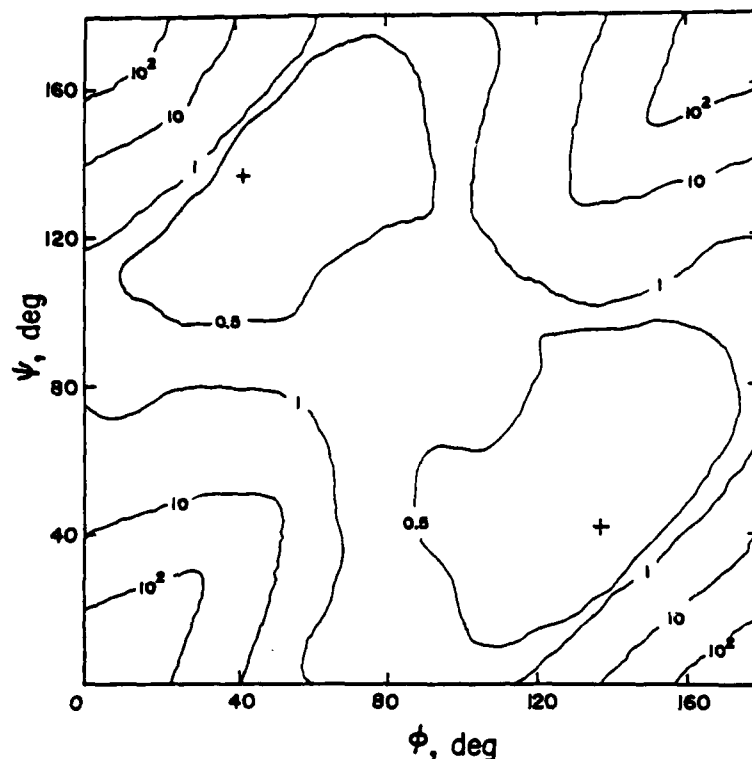


FIG. 6. Conformational energy map for the Ph-S-Ph swivel.

inasmuch as the coplanar conformation is probably strongly suppressed in both swivels, incorporation of either one into a rigid-rod chain could have undesirable effects both on chain alignment and packing and on any long-range resonance stabilization that might be present in the polymer. The latter effect has in fact been mentioned in the literature as a possible explanation for the reduced stability found for some substituted aromatic heterocyclic polymers [15].

These results agree in general with similar theoretical analyses of these groups by other investigators [37-40]. Birshtein and co-workers [38], however, have concluded on the basis of both classical and quantum mechanical calculations that the Ph-O-Ph swivel is somewhat more flexible than the Ph-S-Ph. Since this conclusion is in disagreement with the results of the present investigation, the two sets of calculations were compared in some detail [41]. There are three differences between the parameters employed.

and in each case the Birshtein choice of parameters would tend to make the O swivel appear more flexible. The first is the use [38] of a C-O bond length, 1.36 Å, somewhat larger than that employed in the present investigation. The other structural parameters were essentially the same in the two studies, and the cited difference in bond length was found to be relatively unimportant. Of greater importance are the values chosen for the barrier heights. On the basis of semiempirical quantum mechanical calculations, Birshtein and coworkers [38] chose the same value, 3 kcal/mol, for E_0 of the Ph-O and Ph-S bonds. This is clearly inconsistent with pertinent experimental results, which show that E_0 for thiophenol is very much smaller than that of anisole (as documented in the previous section), and is also much smaller than that of phenol itself [29]. The difference of greatest importance, however, was found to be the potential functions for nonbonded interactions employed by Birshtein and coworkers [42]; they are very different from the functions usually employed in conformational analyses. For example, their function for the C...C interaction gives a maximum attraction far greater than those given by potential functions adjusted to give the correct energy difference between gauche and trans states in a series of n-alkanes, including polyethylene [20].

It is important to note also that results of other investigations reported in the literature support the present finding that swivels with sulfur atoms are more flexible than those with oxygen. As a recent example, Abe's conformational analyses [43, 44] of the aliphatic polymers poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO), poly(ethylene sulfide) (PES), and poly(propylene sulfide) (PPS) clearly demonstrate that the sulfur-containing analog in both cases is the more flexible. These conclusions [43, 44] are based upon comparisons between the pairs PEO-PES and PPO-PPS with regard to both configurational partition functions and unperturbed dimensions [20].

Ph-Se-Ph and Ph-Te-Ph Swivels

The difficulty in achieving the coplanar conformations for Ph-O-Ph and Ph-S-Ph swivels prompted a search for other swivels for which the coplanar conformation might not be energetically suppressed. It was recognized that these deviations from the desired coplanar conformation are chiefly due to steric repulsions involving the 2, 2', 6, and 6' hydrogens, as can be seen in Fig. 4. Consequently, it was hoped that repulsions might be reduced by increasing the bond length C-X by appropriate choice of X.

The swivels Ph-Se-Ph and Ph-Te-Ph appeared promising in that the trend toward greater flexibility in switching from an oxygen swivel to a sulfur swivel might continue in going down the

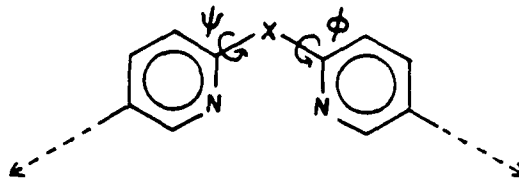


FIG. 7. Illustration of an R_1 -X- R_2 swivel for $R_1 = R_2 = \text{Pyr}$ (2-pyridyl group).

same column in the periodic table. The increase in bond-length C-X might, for the Se and/or Te swivel, more than compensate for the reduction in C-X-C bond angle to yield a net increase in rotational flexibility. The relevant structural information is summarized in Table 2. Comparison of the conformational-energy maps for the Ph-Se-Ph and Ph-Te-Ph swivels with that for Ph-S-Ph revealed, however, that the former two swivels are no more flexible than the latter in terms of either overall flexibility or accessibility of the coplanar conformation.

Pyr-O-Ph, Pyr-S-Ph, Pyr-O-Pyr, and Pyr-S-Pyr Swivels

A more direct way to reduce these offending H...H repulsions would be to eliminate the atoms responsible altogether. As an example, one or both of the phenylenes in the swivel could be replaced with a pyridyl group in which the nitrogen in the ring is located α with respect to the C-X bond, as shown in Fig. 7. This would, of course, remove at least one of the potentially conflicting H atoms.

Conformational-energy maps for the four swivels Pyr-O-Ph, Pyr-S-Ph, Pyr-O-Pyr, and Pyr-S-Pyr are shown in Figs. 8 through 11, respectively. It is seen that when even only one of the phenylenes is thus replaced, as in Pyr-O-Ph and Pyr-S-Ph, the repulsions in the coplanar arrangement are greatly reduced. Replacement of both Ph groups reduces the energy still further. The corresponding energies are 80 and 34 kcal/mol respectively in the case of Ph-O-Ph and Ph-S-Ph swivels, but only 8 and 3 kcal/mol respectively for the Pyr-O-Pyr and Pyr-S-Pyr swivels. Although taking into account bond angle deformation would decrease these differences, the desired coplanar conformation would still be more accessible in the case of the swivels containing Pyr groups. In addition, as can be seen from Figs. 5, 6, and 8-11, these groups seem to increase the flexibility in general of the molecular swivels. They thus merit a much more detailed analysis, including quantum mechanical calculations of the effects of the nonbonding pairs of electrons on the N atoms.

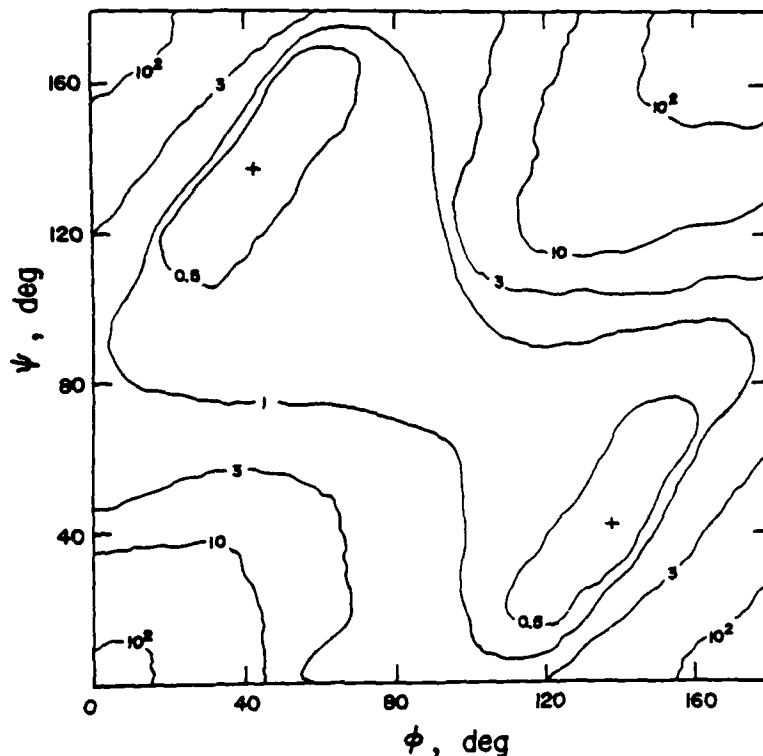


FIG. 8. Conformational energy map for the Pyr-O-Ph swivel.

Various aromatic groups other than pyridylene could conceivably replace the phenylenes in Ph-X-Ph with similar success in terms of increased accessibility of the coplanar conformation and improved flexibility. The requirement that these groups contain an unsubstituted hetero atom in the ring-situated α to the swivel bond is met, for example, by pyrimidine, quinoline, isoquinoline, furan, thiophene, and imidazole. While furan, thiophene, and imidazole by themselves are not nearly as stable as pyridine, these structures could be fused to a benzene ring to give a variety of highly stable bicyclic compounds [45].

Geometric Characterization of Various Isomeric Swivels

There is now considerable interest [34] in "double" swivels of the type Ph-X-Ph-X-Ph, where X is either O or S. Particular interest has centered on the meta, para, meta (MPM) geometric isomer since molecular models reveal that this isomer has a

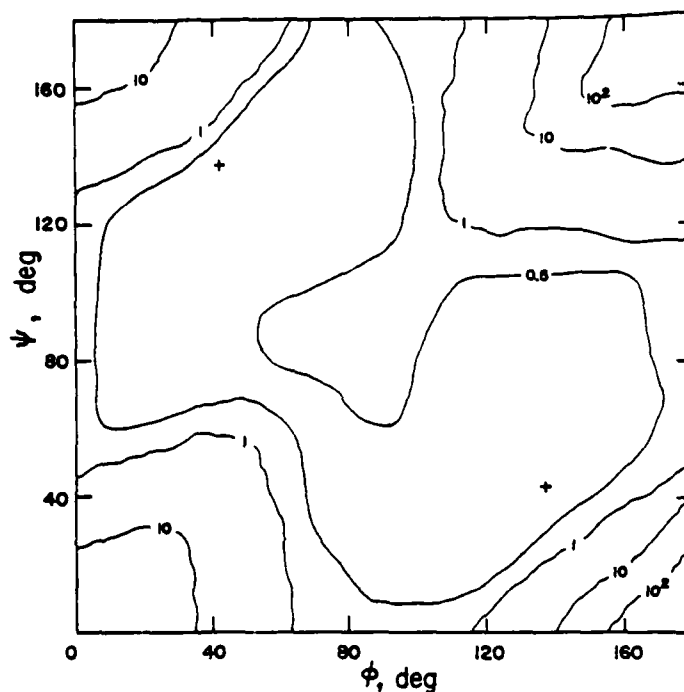


FIG. 9. Conformational energy map for the Pyr-S-Ph swivel.

conformation (shown in Fig. 12) which permits nearly collinear continuation of the chain backbone, in a type of "crankshaft" arrangement. (For purposes of convenience, all swivels have arbitrarily been drawn in the relevant coplanar conformation. This is not meant to suggest that the coplanar conformation is preferred or even achievable; in fact, as already pointed out, the coplanar conformation is generally of rather high energy.) This aspect of the conformational analysis of the swivels was pursued by sketching the 18 different geometrical isomers of the Ph-O-Ph-O-Ph segment. The objective was to identify all isomers that have one or more conformations which maintain nearly parallel or collinear continuation of the rigid-rod chain segments bracketing the swivel region. Of these 18, only 3 can give near collinearity; these are the MPM, POP, and MMP isomers shown in Fig. 13 (where O here represents an ortho placement). Hence, the POP and MMP isomers possess the same desirable feature of collinearity discovered for MPM [34] and, in fact, the relevant conformation of the POP isomer also resembles the crankshaft arrangement. With regard to

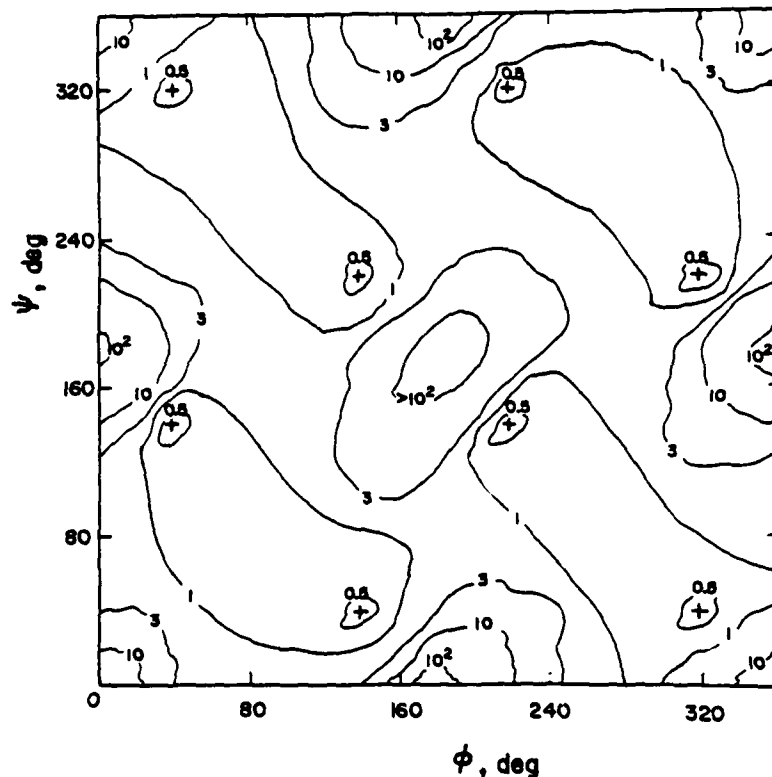


FIG. 10. Conformational energy map for the Pyr-O-Pyr swivel.

efficiency of chain packing, the POP isomer may be advantageous in that it contains more atoms along the backbone than the other two. Since the coplanar conformation generally corresponds to high energy, it is important to point out that collinearity can be maintained if the middle phenylene groups rotate by approximately 60° , which gives a conformation having an energy within 1 kcal/mol of the minimum. Of the three collinear isomers this is possible only with the MPM and POP isomers, since the middle phenylene in the MMP one is chemically locked into place.

Only seven isomers permit nearly parallel continuation of the chain: PPP, OPP, OOP, OPO, OOO, MMO, and MOM. Of these seven, three (OOP, OOO, and MOM) have very severe steric interferences in the conformations of interest and were therefore not considered further. The remaining four acceptable ones are listed in Table 3, along with the extent to which each segment shifts the axis of the polymer chain.

TABLE 3
Extent to Which the Parallel Double-Swivel Isomers
Shift the Chain Axis

X = Oxygen		X = Sulfur	
Swivel	Shift (Å)	Swivel	Shift (Å)
PPP	4.5	MMP	0.8
OPP	7	MPM	4
MMO	9	MMO	6
OPO	9	PPP	7
		OPO	10.5

Similar sketches were made of the Ph-S-Ph-S-Ph swivel. No isomers giving collinearity were found, but the MMP isomer shown in Fig. 14 shifts the chain backbone by only approximately 1 Å. Seven isomers were found to have conformations giving nearly parallel continuation: OOP, PPP, OPO, MMO, MMP, MOM, and MPM. Of these, OOP and MOM appear to have excessive steric conflicts. The remaining five isomers are listed in Table 3 along with the extent to which the chain axis is shifted in the coplanar conformation. The absence of collinear isomers is related to the values of the various bond angles within the segment. Specifically, the similarity between the bond angles (120°) within the aromatic ring and the COC bond angle (123°) in the oxygen swivel increases the number of nearly collinear arrangements. This simplifying circumstance does not occur in the case of the sulfur swivels, since the CSC bond angle is 109° .

A number of similarities do exist between the Ph-O-Ph-O-Ph and Ph-S-Ph-S-Ph swivels, however, with respect to the isomers found to give collinear or parallel chain continuation. First, isomers giving either collinearity or parallelism with O generally give parallelism with S. Specifically, the two isomers MMP and MPM, which are collinear for oxygen, are parallel for sulfur (although MMP is almost collinear). (However, the third collinear isomer for the oxygen swivel, POP, is not even parallel in the sulfur case.) Second, the two isomers OOP and MOM involve very severe steric interferences in both the oxygen and sulfur cases.

Although the isomers which can give collinear continuation of the chain would be expected to cause the least disruption of the desired anisotropic phases, the isomers which can give a parallel continuation could also be useful. Nevertheless, in shifting the

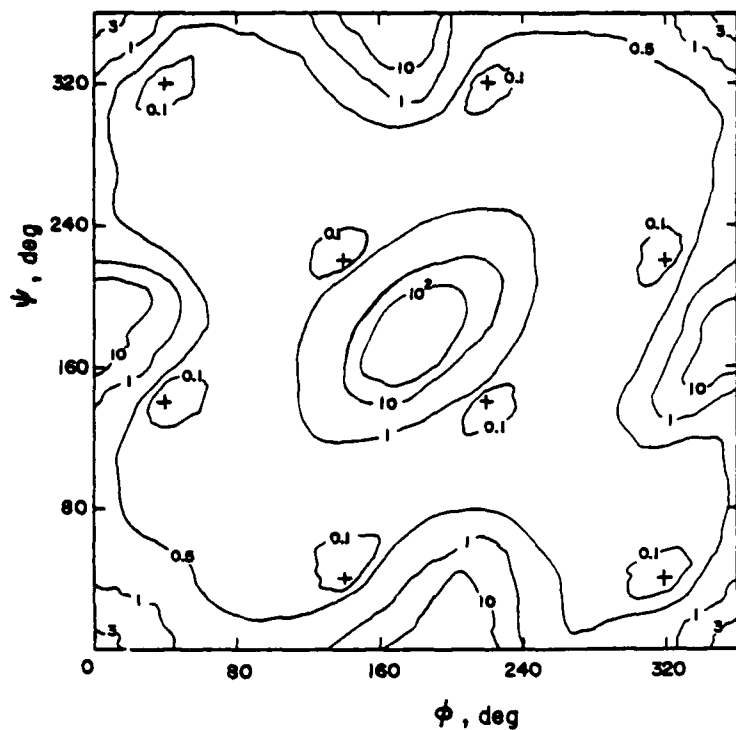


FIG. 11. Conformational energy map for the Pyr-S-Pyr swivel.

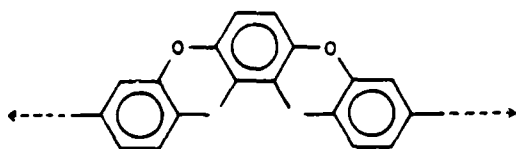


FIG. 12. A meta,para,meta double-oxygen swivel in a conformation which gives nearly collinear continuation of the chain.

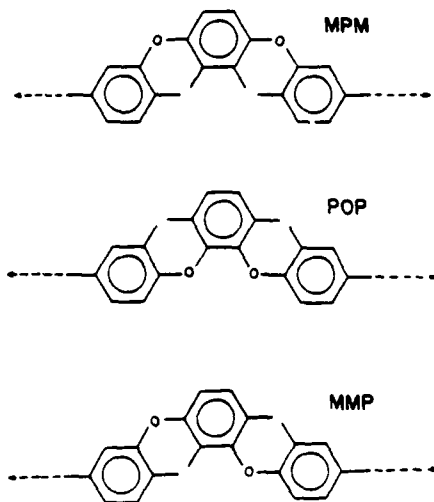


FIG. 13. The three isomers of the double-oxygen swivel which permit nearly collinear continuation of the chain.

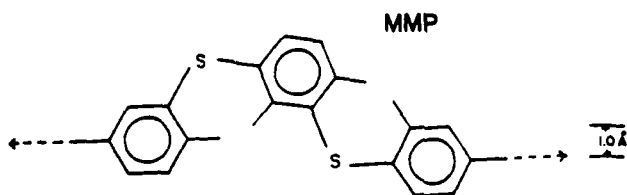


FIG. 14. A meta, meta, para, double-sulfur swivel which permits nearly collinear continuation of the chain.

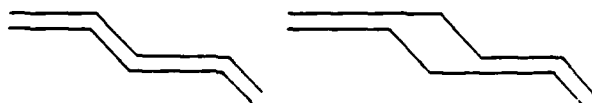


FIG. 15. Matched and unmatched shifts in chain axes.

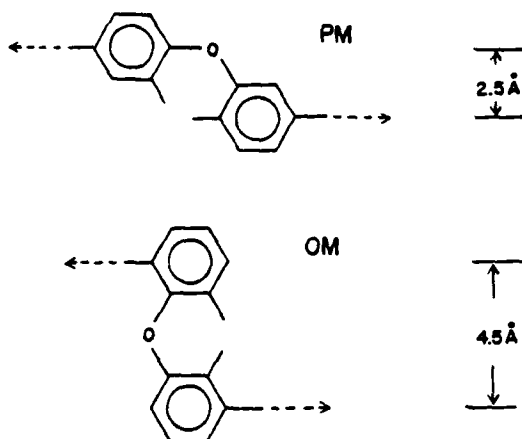


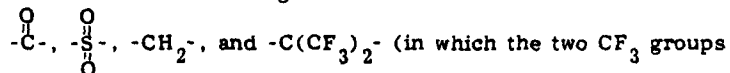
FIG. 16. Para,meta and ortho,meta single-oxygen swivels.

polymer's axis, the latter isomers may render a less-than-optimal overlap between neighboring polymer stretches in the anisotropic phase unless, perhaps, each of the stretches is "matched," as illustrated in Fig. 15, which is not likely. As shown in this sketch, "unmatched" stretches create imperfections, which could have a detrimental effect on the mechanical properties of the polymer.

With regard to the swivels giving parallel chain continuation, it should be noted that the PM and OM isomers of the single swivel Ph-O-Ph, shown in Fig. 16, may be advantageous over the double swivels, since a smaller nonaromatic segment is involved. This could improve the thermal stability of these polymers, since it has been reported that the thermal stability of an aromatic heterocyclic polymer decreases as the number of swivels in the chain increases [34]. Of course, swivels of the type Pyr-O-Pyr would be a further improvement by ensuring coplanarity. The PM isomer is particularly interesting in that the axis of the resulting polymer would be shifted by only approximately 2.5 Å. It should be noted, however, that the CSC bond angle (109°) in these swivels would preclude any "single" swivels of the type Ph-S-Ph or Pyr-S-Pyr from giving nearly parallel chain continuation.

Multiatom Swivels

A number of swivels somewhat more complicated than the O and S ones were also investigated in these calculations. These were



were held staggered with respect to the backbone bonds). All four were found to have overall bond flexibility equal to or better than the O and S links. If one or both of the R groups is phenylene, then the relative energy of the coplanar conformation is very high (but again is significantly decreased if bond angle deformation is permitted). In the case where both groups are pyridylene, these energies are reduced considerably, being approximately 0,

3, 8, 10, 16, and 19 kcal/mol for $\overset{\text{O}}{\parallel}\text{-C-}$, -S- , -O- , $\text{-C(CF}_3)_2\text{-}$, $\overset{\text{O}}{\parallel}\text{-S-}$, and $\text{-CH}_2\text{-}$, respectively. Results reported in the literature [19]

on the thermal stability of these various links in para-phenylene polymers of the type $[-\text{C}_6\text{H}_4\text{-X-}]$ suggest that they rank in sta-

bility in the order $\text{-C(CF}_3)_2\text{-} > \text{-O-} \approx \text{-S-} > \overset{\text{O}}{\parallel}\text{-C-} > \overset{\text{O}}{\parallel}\text{-S-} > \text{-CH}_2\text{-}$.

Therefore, on the basis of both thermal stability and conformational flexibility, it seems that the most promising swivels are -O- , -S- , $\text{-C(CF}_3)_2\text{-}$, and $\overset{\text{O}}{\parallel}\text{-C-}$.

Wholly Aromatic Swivels

Because of their aromatic nature, these diphenylene and 2,2'-dipyridylene swivels should have the greatest thermal stability. They can maintain parallel continuation of the chain if bonded to it either ortho,ortho or meta,meta as is illustrated in Fig. 17. (Although the para,para isomer provides collinearity, it does not of course give the "kink" needed for additional flexibility.) Since the desired parallelism occurs only when the two rings are coplanar, conformational energy calculations were conducted to determine both the overall flexibility of the swivel bond and the energetic accessibility of the desirable coplanar conformation.

Values of E for the diphenylene swivel were calculated at 5° intervals for various illustrative values of E_0 , including the values 4.0 [31] and 6.2 kcal/mol [32] used in previous studies. The value $E_0 = 4.6$ kcal/mol was found to reproduce the experimental value of 42° [46] for the minimum-energy, preferred rotation angle ϕ . The dependence of E on ϕ for this value of E_0 is presented in Fig. 13, and shows that rotations are quite unhindered over the range 40 to 140°. The energy at the coplanar conformation was found to be 3.5 kcal/mol, in good agreement with experiment [46]. It is relatively low, and could of course be diminished both by bond angle deformation and favorable interchain interactions.

For terphenylene or terpyridylene swivels, the MPM and PMM isomers were the only ones found to provide parallel chain

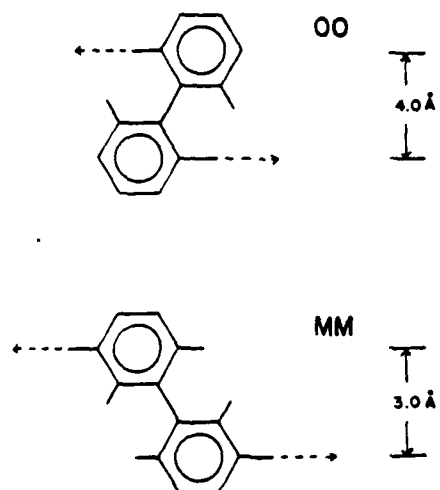


FIG. 17. Ortho,ortho and meta,meta diphenylene swivels.

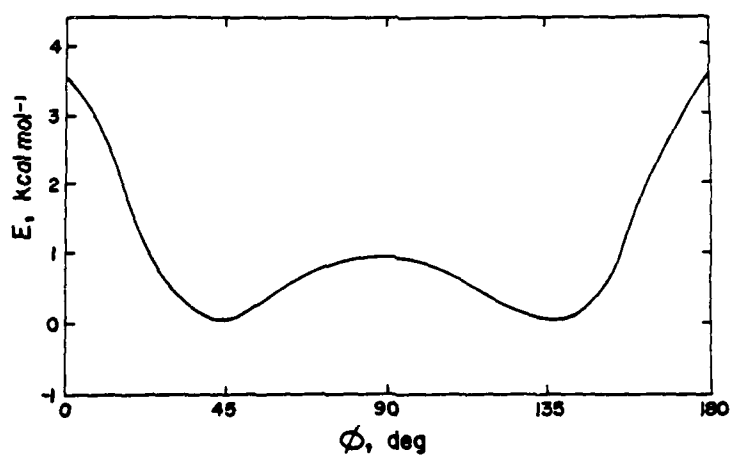


FIG. 18. The conformational energy of the diphenylene swivel shown as a function of rotation angle.

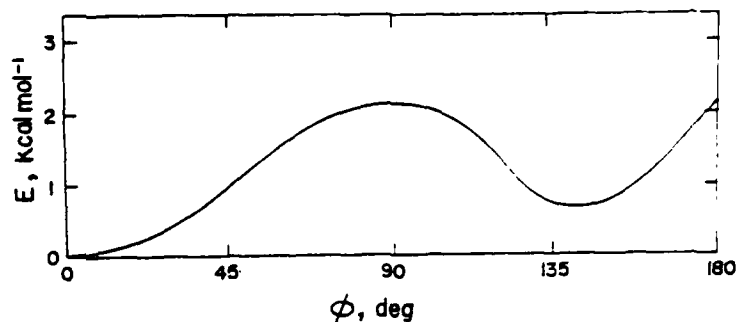


FIG. 19. The conformational energy of the dipyridylene swivel shown as a function of the rotation angle (with $\phi = 0^\circ$ corresponding to the two N atoms being located trans across the swivel bond).

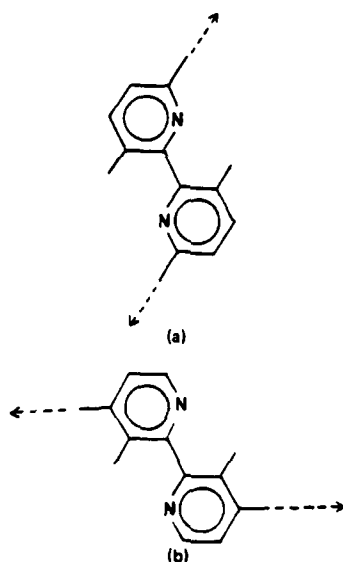


FIG. 20. The 2,2'-dipyridylene swivel with the two types of chain attachment which give parallel continuation of the chain, namely both ortho (a) or both para (b) with respect to the nitrogen atoms in the rings.

continuation in the coplanar conformation. For Ph-Ph-Ph, the MPM parallel conformation is made energetically accessible by rotation of the middle phenylene by approximately 20° [47]. This is impossible for the PMM isomer since its middle phenylene group is locked into place.

Replacement of one or both of the phenylenes by the 2-pyridylene group would be expected to relieve much of the interring congestion, thereby enhancing the flexibility of the swivel bond and facilitating the achievement of coplanarity. Results of conformational-energy calculations on the 2,2'-dipyridylene swivel are shown in Fig. 19, and are seen to be in agreement with this expectation. Specifically, all regions of configuration space for rotation about the swivel bond are within approximately 2 kcal/mol of the energy minimum, which is the coplanar conformation in which the two N atoms are trans to one another across this bond. With regard to the attachment of the chain segments to the 2,2'-dipyridylene swivel, it should be noted that the desired parallel continuation of the chain without excessive steric interferences requires that the points of attachment of the chain backbone to the swivel be either both ortho or both para with respect to the ring nitrogen, and that the swivel be in the trans conformation, as is shown in Fig. 20.

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Polarizabilities of Some Benzobisoxazole and Benzobisthiazole Rigid-Rod Polymers

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Introduction

The aromatic heterocyclic polymers considered in the present investigation are the *cis*-poly(benzobisoxazole) (PBO) shown in Figure 1, its *trans* modification, and the *trans* modification of the sulfur analogue, poly(benzobisthiazole) (*trans*-PBT). The electronic structures of these relatively rigid chain molecules are of considerable interest, for a variety of reasons. For example, charge distributions are relevant to both intramolecular^{1,2} and intermolecular^{1,3} energies of the chains, resonance stabilization is important with regard to conformational flexibility,² and energy band gap information is pertinent to electrical conductivity.⁴ Also of considerable importance are polarizabilities, since they are needed for the interpretation of solution property studies such as flow birefringence measurements. Experimental studies of this type are carried out to obtain rheological time constants and orientation parameters relevant to the processing of these materials.⁵ In this investigation, several theoretical approaches⁶⁻⁹ are used to calculate repeat unit polarizabilities of the three polymers mentioned above.

Theory

The bond lengths and bond angles in the three repeat units were obtained from the X-ray structural studies conducted on model compounds by Fratini and co-workers.^{10,11} The two PBO polymers have planar repeat units,

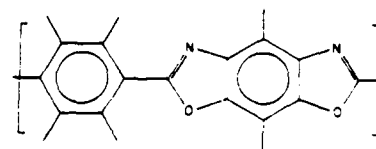


Figure 1. *cis*-PBO repeat unit.

but the *trans*-PBT repeat unit has the *p*-phenylene group rotated by 23.2°. ^{1,2,10,11} In this latter case, the plane of the phenylene ring was taken to be the plane of the molecule. For all three molecules, the plane of the molecule was in the *xz* plane, with the *z* axis coincident with the long molecular axis. The quantities of interest are the polarizability components α_{xx} , α_{yy} , and α_{zz} , their simple average $\bar{\alpha}$, and the anisotropic ratio defined by

$$\delta = \left[\frac{(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2}{(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})^2} \right]^{1/2} \quad (1)$$

The first method employed for all of these quantities was the quantum mechanical method of Marchese and Jaffé,⁶ in which second-order perturbation theory is combined with the CNDO/S CI formalism⁷ (complete neglect of differential overlap, configuration interactions). The second was the empirical scheme of Miller and Savchik,⁸ in which the average polarizability is obtained by summing atomic hybrid components τ_A

$$\bar{\alpha} = (N/4) \left[\sum_A \tau_A \right]^2 \quad (2)$$

in which *N* is the total number of electrons in the molecule. Pertinent values of τ_A for C, N, O, S, and H atoms are 1.428, 1.262, 1.290, 3.496, and 0.314 Å^{3/2}, respectively.⁸ The

Table I
Longitudinal and Transverse Bond Polarizabilities^a

bond	b_l	b_t
C-C ^b	1.88	0.020
C-C ^c	2.25	0.48
C-N	1.59	0.89
C=N	2.46	0.91
C-O	1.34	0.75
C-S	3.93	2.20
C-H	0.79	0.58

^a Reference 9; units are Å³ (10⁻²⁴ cm³). ^b Aliphatic carbon atoms. ^c Aromatic carbon atoms.

third is the bond polarizability method of Denbigh,⁹ in which both $\bar{\alpha}$ and the polarizability components are obtained by vectorial additions of longitudinal b_l and transverse b_t components of the polarizabilities of the bonds. The equations are

$$\alpha_{xx} = \sum_i (b_{li} \sin^2 \phi_i \cos^2 \theta_i + b_{ti} \sin^2 \theta_i + b_{ti} \cos^2 \phi_i \cos^2 \theta_i) \quad (3)$$

$$\alpha_{yy} = \sum_i (b_{li} \sin^2 \phi_i \sin^2 \theta_i + b_{ti} \cos^2 \theta_i + b_{ti} \cos^2 \phi_i \sin^2 \theta_i) \quad (4)$$

$$\alpha_{zz} = \sum_i (b_{li} \cos^2 \phi_i + b_{ti} \sin^2 \phi_i) \quad (5)$$

where ϕ_i is the angle between bond i and the z axis and θ_i is the angle between the x axis and the projection of bond i onto the xy plane.⁹ The polarizabilities for C-C and C-H bonds are already available in the literature,⁹ whereas for C-N, C=N, C-O, and C-S bonds, they were calculated from standard equations.⁹ For single bonds not involving H these are $b_l = 0.600 + 0.098r^3$ (where the bond length r is in Å) and $b_t/b_l = 0.56$. For double bonds $b_l = 0.600 + 0.385r^3$ and $b_t/b_l = 0.37$. These values are summarized in Table I.

The quantum mechanical method⁶ applied to the (H terminated) *cis*-PBO repeat unit gave $\alpha_{xx} = 4.69$, $\alpha_{yy} = 0.11$, and $\alpha_{zz} = 27.69$ and thus $\bar{\alpha} = 10.83$ Å³. This value of $\bar{\alpha}$ is almost the same as the experimental value of benzene,^{6,12} whereas the structure of the repeat unit suggests it should be 2-3 times this value. Similar studies¹³ of other, simpler molecules have also given serious underestimates of $\bar{\alpha}$, and this method was therefore not considered further.

The atomic additivity scheme⁸ gives the value of $\bar{\alpha}$ listed in the second column of Table II; the separate components are unfortunately beyond the scope of this method. The bond additivity scheme⁹ gave the values of $\bar{\alpha}$ listed in the following column, and these are seen to be in good agreement with those based on atomic additivities. The PBT chain is predicted to have a larger value of $\bar{\alpha}$ than the two PBO chains, since the C-S bond is much more

Table II
Calculated Average Polarizabilities, Polarizability Components, and Anisotropic Ratios for the Polymer Repeat Units^a

polymer	atomic additivity value ^b of $\bar{\alpha}$	bond additivity method ^c				δ
		$\bar{\alpha}$	α_{xx}	α_{yy}	α_{zz}	
<i>cis</i> -PBO	25.0	26.9	31.0	15.8	33.7	0.30
<i>trans</i> -PBO	25.0	26.9	31.2	15.8	33.6	0.30
<i>trans</i> -PBT	30.0	34.2	37.5	23.3	41.7	0.23

^a Units are Å³ (10⁻²⁴ cm³). ^b Reference 8. ^c Reference 9.

polarizable than the C-O bond (as is shown by the data in Table I). The corresponding values of the polarizability components are given in the next three columns. They were used to calculate values of the anisotropic ratio δ ; the results are given in the last column of the table and should be directly applicable to the interpretation of flow birefringence data.⁵ The only relevant experimental value of δ is that obtained from light scattering measurements carried out on some solutions of *trans*-PBT in methanesulfonic acid.⁵ Interpretation of these results in the very rough approximation that the chains have cylindrical symmetry gives $\delta = 0.5$.⁵ It is gratifying that the experimental and theoretical results are in at least qualitative agreement, particularly since the experimental situation is almost certainly complicated by significant protonation of the PBT chains.

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CALCULATED POLARIZABILITIES FOR SOME ALIPHATIC AND AROMATIC HYDROCARBONS

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ABSTRACT

Ground-state molecular polarizabilities of some aliphatic and aromatic hydrocarbons have been calculated using the method of Marchese and Jaffé. The polarizability components for the typical normal alkane *n*-heptane are found to be very nearly independent of conformation; those for biphenyl show a significant dependence but the average polarizability is approximately constant. The polarizabilities of the *n*-alkanes in general are seriously underestimated, but relatively good agreement with experiment is obtained for benzene and biphenyl.

INTRODUCTION

In a previous theoretical investigation [1], Marchese and Jaffé reported values for the static polarizabilities of a variety of small molecules, in both ground and excited states. The calculations were based on a coupling of simple perturbation theory with the semi-empirical CNDO/S CI formalism (complete neglect of differential overlap, configuration interactions), as developed by Del Bene and Jaffé [2]. The method has the advantage of computational simplicity and, at least in some cases, gives values of the polarizability which are in satisfactory agreement with experiment.

Static, ground-state polarizabilities are of considerable importance in several areas of polymer physical chemistry where, for example, they are needed in the interpretation of some types of light scattering data obtained on polymer solutions [3, 4]. The theoretical method under discussion could be of great interest in this regard, and the present investigation was carried out in order to test its possible applicability to long-chain molecules. It focuses on a series of normal (unbranched) alkanes of increasing length, and on benzene, biphenyl, and *p*-terphenyl, with attention being paid to possible effects of conformation on polarizability. Of these molecules, ethane and benzene were included in the previous study [1]; so also was *n*-butane, but only in the *trans* conformation. Comparisons between theory and experiment are used to gauge the utility of the method for these molecules and their polymeric analogues.

THEORY

The components α_{xx} , α_{yy} , and α_{zz} of the polarizability tensor were calculated for the molecules listed in Table 1*. In the first set of calculations, all rotatable carbon-carbon bonds were assigned to *trans* states (dihedral angle $\phi = 0^\circ$) [5], in which case the x axis was defined as the long axis of the molecule and the xy plane as the plane of the carbon atoms [1]. Calculations were also carried out to determine the effect of conformational changes on the polarizability of *n*-heptane and biphenyl. In the case of the irregular conformations of *n*-heptane, the x axis was placed along the long axis of the molecule with the y and z axes located so as to maximize the symmetry of the atomic coordinates. For the biphenyl, the x axis was placed along the molecular axis and the xy plane was placed intermediate to the planes of the two phenyl groups. The number of configurations in CI and consequently in the perturbation treatment was varied widely in order to minimize uncertainties from possibly protracted convergence of some of the calculated results. The values employed are given in the second column of Table 1.

RESULTS AND DISCUSSION

The results calculated for α_{xx} , α_{yy} , α_{zz} , and their simple mean $\bar{\alpha}$ are presented in columns three through six in Table 1.** Corresponding experimental values, where available [6-9], are given in the remaining columns; they pertain to the molecules in the gaseous phase, except for biphenyl, which was studied only in solution.

Ethane, propane and *n*-butane have only 49, 100, and 169 singly excited configurations, respectively, and CI could thus be extended to all these configurations [1]. For *n*-pentane and *n*-hexane the convergence seems protracted. For longer-chain alkanes, even 180 configurations appear grossly insufficient, since both $\bar{\alpha}$ and its components (which had increased with the number of carbon atoms from ethane to *n*-pentane) decrease for *n*-heptane and *n*-octane. In any case, these characteristics of the calculations obviously would not explain the fact that the calculated polarizabilities for the *n*-alkanes underestimate the experimental values by a factor of 2-3. Calculations carried out on *n*-heptane indicate that the discrepancy is also not due to the existence of the other conformational states *gauche* positive (g^+) and *gauche* negative (g^-) [5] in this molecule in the non-crystalline state.

*Since *n*-butane, *n*-hexane, and *n*-octane transform in point group C_{2h} , α_{xy} in the symmetry plane is non-vanishing; its values, however, were found to be sufficiently small ($<0.15 \text{ \AA}^3$) to be ignored.

**The earlier theoretical values reported for ethane, (*trans*) *n*-butane, and benzene [1] were generally somewhat higher because of a computational error; see F. Marchese and H. H. Jaffé, *J. Mol. Struct., Theochem*, in press.

TABLE 1
Ground-state polarizabilities^a of the molecules in their planar conformations^b

Molecule	Calculated results				Experimental results				Ref.	
	No. C ^c	α_{xx}	α_{yy}	α_{zz}	$\bar{\alpha}$	α_{xx}	α_{yy}	α_{zz}		$\bar{\alpha}$
Ethane	49 ^d	1.23	1.46	1.46	1.38	5.49	3.98	3.98	4.48	6
	60	1.70	1.72	1.99	1.80				6.29	7
Propane	90	1.95	2.04	2.19	2.06					
	100 ^d	1.97	2.05	2.19	2.07					
n-Butane	60	1.61	1.74	2.09	1.81				8.12	7
	90	2.14	2.35	2.39	2.29					
	120	2.54	2.69	2.81	2.68					
	169 ^d	2.62	2.75	2.92	2.76					
n-Pentane	60	1.67	0.77	1.28	1.24				9.95	7
	90	2.21	2.03	2.30	2.18					
	120	2.73	2.40	2.97	2.70					
	180	3.25	3.29	3.51	3.35					
n-Hexane	60	1.30	0.15	0.82	0.76				11.78	7
	90	1.84	1.64	2.12	1.87					
	120	2.57	2.45	2.45	2.49					
	180	3.46	3.32	3.48	3.42					
n-Heptane	60	1.38	0.11	0.16	0.55				13.61	7
	90	1.58	1.32	1.64	1.51					
	120	2.03	1.89	2.50	2.14					
	180	3.28	2.78	3.41	3.16					
n-Octane	120	1.64	0.88	1.19	1.24				16.44	7
	180	2.68	2.73	2.71	2.71					

TABLE 1 (continued)

Molecule	Calculated results				Experimental results				Ref.
	No. C ^c	α_{xx}	α_{yy}	α_{zz}	$\bar{\alpha}$	α_{xx}	α_{yy}	α_{zz}	
Benzene	60	8.10	8.10	0.69	5.63	11.10	11.10	7.4	8
	90	9.98	9.98	1.09	7.02				
	120	10.24	10.24	1.09	7.19				
	180	10.84	10.24	1.57	7.75				
Biphenyl	60	23.26	16.47	0.07	12.93	24.70	20.20	13.80	9
	90	23.50	15.58	0.40	13.16				
	120	23.51	15.63	0.95	13.36				
	180	24.24	16.19	1.18	13.87				
<i>p</i> -Terphenyl	90	41.73	22.82	0.02	21.52				
	180	41.73	22.85	0.05	21.54				
		42.04	22.97	0.43	21.81				

^aIn units of \AA^3 (10^{-24} cm³). ^bAll rotational states (*trans* ($\phi = 0^\circ$)). ^cNumber of electronic configurations included in the configuration interaction (CI) calculations. ^dCorresponds to the complete set of singly excited configurations.

Specifically, for the conformations tg^+g^-t , tg^+g^+t , ttg^+g^- , ttg^+g^+ , tg^+tg^+ , and tg^+tg^- , $\bar{\alpha}$ did not differ from that for the all-*trans* form by more than a few hundredths of an Å³. Thus, the method does not appear very promising for aliphatic hydrocarbon polymers such as polyethylene.

For the aromatic molecules benzene, biphenyl, and *p*-terphenyl, convergence is seen not to be a problem and the calculated polarizabilities for benzene and biphenyl are in satisfactory agreement with the available experimental results. It is of interest to note that in the case of these two molecules it is the out-of-plane (*zz*) components that are underestimated, presumably because of inadequacies of the basis set, as was pointed out previously [1]. In the case of the biphenyl, it is necessary to consider other conformations since this molecule is known to be non-planar in the non-crystalline state, with a rotational angle ϕ of approximately 20° in solution [10] and 42° in the gaseous phase [11]. The results calculated for various values of ϕ are given in Table 2. Decreases in α_{xx} and α_{yy} with increase in ϕ are partially offset by increases in α_{zz} and $\bar{\alpha}$ therefore remains approximately constant. Thus, the theoretical value of $\bar{\alpha}$ at $\phi \approx 20^\circ$ is also in satisfactory agreement with the experimental result obtained in solution [9]. The component α_{zz} remains small relative to α_{yy} up to rather large values of ϕ , which would cause uncertainty in the use [9] of experimental values of these components to estimate the degree of non-planarity of the biphenyl molecule.

The method thus seems to give satisfactory results for simple aromatic systems. It may work less well, however, for more complex aromatic molecules [1], particularly for polymer repeat units that are also heterocyclic [4]. The results are nonetheless encouraging in view of the well known difficulties [1] involved in calculating accurate values of the molecular polarizability.

TABLE 2

Calculated values of the polarizability of the biphenyl molecule in different conformations

$\phi(^{\circ})$	α_{xx}	α_{yy}	α_{zz}	$\bar{\alpha}$
0	24.24	16.19	1.18	13.87
10	24.12	16.09	1.30	13.84
20	23.56	15.79	1.70	13.68
30	23.04	15.12	2.27	13.48
40	22.33	14.46	3.05	13.28
50	21.56	13.62	4.01	13.06
60	20.81	12.62	5.12	12.85
70	20.19	11.50	6.35	12.68
80	19.77	10.26	7.65	12.56
89 ^a	19.63	9.10	8.83	12.52

^aAt exactly 90°, the symmetry of biphenyl (*D*_{1d}) interferes with execution of the desired calculation.

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The Flexibility of Biphenyl and Related Species Utilizable as Molecular Swivels in Rodlike Polymers. A CNDO/2 Analysis

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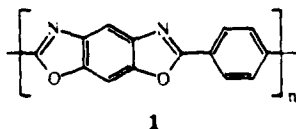
(Date of receipt: April 20, 1981)

SUMMARY:

Aromatic heterocyclic polymers are exceedingly attractive high performance materials because of their unusually high mechanical strength, chemical resistance and thermal stability, but are very difficult to process unless "swivel" atoms or groups are inserted along the chains to increase conformational flexibility. The present theoretical investigation employs the CNDO/2 method with direct geometry optimization to calculate such flexibility for the wholly aromatic swivels biphenyl, 2,2'-bipyridyl, 2-phenylpyridine, 2,2'-bipyrimidyl, and 2-phenylpyrimidine. The most important result is the prediction that both flexibility and accessibility of coplanar conformations should increase significantly with the number of *ortho*-CH groups replaced by N-atoms. The calculations also provide information on other conformation-dependent properties such as optimized geometries, charge distributions, and dipole moments, and these results are found to be in satisfactory agreement with the results of previous theoretical and experimental studies. Finally, since these chains are soluble only in strongly acidic media, the species mono- and diprotonated 2,2'-bipyridyl, 2,2'-bipyridyl · H₃O⁺, and 2,2'-bipyrimidyl · 2H₂O were also investigated with regard to some of these conformational characteristics.

Introduction

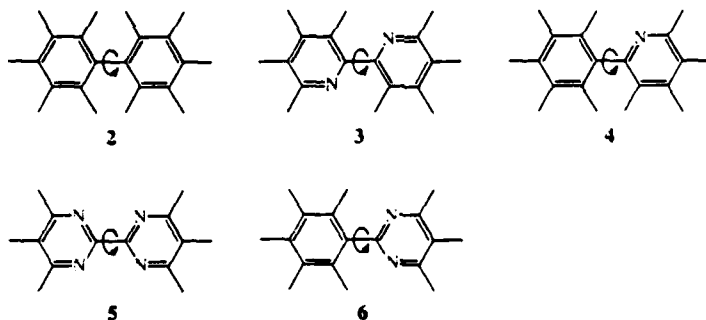
Solutions of rod-like polymers such as poly(1,3-oxazolo[4,5-*f*][1,3]-benzoxazole-2,6-diyl-1,4-phenylene) (1) undergo phase separation because of the high particle asymmetry¹⁻¹². Such polymers in the crystalline or liquid-crystalline state are of considerable interest and importance since they can be used to prepare films and fibers having very good mechanical strength, excellent thermal and thermo-oxidative stability, and resistance to most common solvents¹¹⁻¹⁶. These polymers should, therefore, prove suitable for applications requiring these high-performance characteristics. However, primarily because of their rigidity and relative insolubility in all but the strongest acids, these polymers pose serious processing problems¹¹⁻¹⁶.



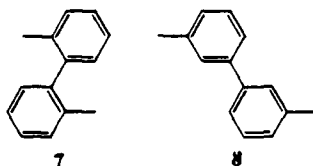
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The insertion of even a small number of flexible molecular fragments or "swivels" into such chains will increase their flexibility and tractability by allowing mutual rotation of adjacent chain elements about the swivels' rotatable bonds. This increased flexibility should improve the solubility and decrease the viscosity of the chain both in the bulk (undiluted) state and in solution. In practical terms, such structural modification will render the resulting polymer much more readily processable into useful forms.

In this paper, the relative conformational energies of several structurally related swivels were calculated using the semi-empirical CNDO/2 molecular orbital method¹⁷⁾ with direct geometry optimization. The conformational versatility of the swivels is of course of direct relevance to the induced flexibility of rigid-rod chains containing these swivels. The basic swivels considered in this study are biphenyl (2), 2,2'-bipyridyl (3), 2-phenylpyridine (4), 2,2'-bipyrimidyl (5), and 2-phenylpyrimidine (6). Such wholly aromatic swivels should exhibit good thermal and thermo-oxidative stability¹⁸⁾ and were found — in a previous preliminary study using highly empirical molecular-mechanics calculations¹⁹⁾ and in experimental studies²⁰⁾ — to merit a more detailed and more rigorous theoretical investigation.



The swivels 2–6 are all structurally similar but differ in the number and location of CH groups adjacent to the swivel bond that are replaced by nitrogen atoms. As reported earlier¹⁹⁾, such substitution by nitrogen atoms relieves the steric hindrance involving the hydrogens adjacent to the swivel bond and thus facilitates the achievement of coplanarity of the rings which, in turn, is conducive to good chain packing in molecularly ordered phases. In this connection, parallelism is obviously also of considerable importance. The swivels considered in the present work can maintain parallel continuation of the polymer-chain backbone (with only a 2–4 Å translation transverse to the chain axis) if the positions of attachment of the main chain to the swivel are both in ortho or both in meta positions (*o,o* and *m,m*, respectively) with respect to the swivel bond between the rings e.g. the units 2,2'-biphenylene (7) and 3,3'-biphenylene (8)¹⁹⁾. (Attachments at both *para* positions would preserve even collinear continuation of the polymer chain but would fail to provide a "kink" about which the polymer could assume multiple spatial configurations.)



Obviously, however, the desirable parallelism can occur only when the two rings in the swivel are coplanar. Hence, the features of the swivels addressed in this study that are of primary importance are their (i) preferred (lowest energy) conformations, (ii) overall flexibility (the extent and locations of those regions of configurational space of sufficiently low energy to be accessible), and (iii) energies in the desired coplanar conformations. In addition, other relevant conformation-dependent molecular properties, such as the geometry-optimized bond lengths and angles, partial charges, and dipole moments are obtained and compared with the results of previous theoretical and experimental studies.

It is likely, and indeed desirable in order to promote solubility, that the nitrogen-containing swivels are protonated in strongly acidic solvents (e.g., sulfuric acid, methane sulfonic acid, chlorosulfonic acid) usually required for these rodlike polymers¹¹⁻¹⁶. For this reason, the mono- and di-protonated forms of **3** were included in this study. In addition, dihydrated **5** and the hydronium-ion complex with **3** were also investigated to examine the conformational behavior of these swivels in an aqueous environment.

Computational Details

The basic technique employed consists of the CNDO/2 semi-empirical method developed by Pople et al.¹⁷ nested in an iterative scheme for achieving direct geometry optimization²¹. The CNDO/2 program used is part of the CNDO/S program, apart from conversion to double-precision arithmetic and inclusion of geometry optimization, that has been submitted to QCPE by one of the present authors (HHJ)²².

The direct geometry optimization of the molecule is based upon the gradient of the potential energy function, the computation of which is made more efficient in terms of computer time by exploiting symmetry aspects. Specifically, the number of coordinates defining the molecular geometry may be reduced by the use of symmetry coordinates, in which case non-totally symmetric coordinates may be ignored since the gradient, a totally symmetric function, vanishes for all such coordinates. Differentiation of the CNDO/2 total molecular energy expression with respect to each of the totally symmetric symmetry coordinates leads to the analytically defined elements of the gradient of the potential energy function. The optimization cycle is repeated until the absolute value of each gradient element becomes less than a specified threshold value. In practice, a convergence criterion of 0.1 eV/Å has been found to be acceptable²¹. The electronic energy calculated by CNDO/2 is very sensitive to changes in the nuclear coordinates of the molecule. Consequently, for the SCF-electronic-energy iteration the convergence criterion, taken as self-consistency between two successive calculations, was set to an extremely small value (10^{-9}) compared to that typically used (10^{-3}) in non-optimized CNDO/2 calculations²¹.

Results and Discussion

In all cases, geometry optimization was obtained after assuming an initial geometry, setting the torsional angle ϕ between the planes of the rings at a specified, desired value. Although the torsional angle was free to vary, in all calculations the initial and final (optimized) values differed by less than 5° because of the relative insensitivity of the total potential energy in these species to the magnitude of the torsional angle. Calculations were usually carried out with ϕ varied in intervals of 10° , followed by closer scans at 5° intervals in some cases, e.g. 2,2'-bipyridyl (3). Values of the calculated total energy E as a function of the torsional angle ϕ for each of the five basic swivels are given in Tab. 1. The corresponding values of the conformational energy, taken relative to that for the coplanar forms, are plotted versus ϕ in Fig. 1. In

Tab. 1. Calculated values of the total energy E as a function of torsional angle

ϕ in degrees	Total energy in eV per molecule ^{a)}				
	biphenyl	2,2'-bipyridyl ^{b)}	2-phenyl- pyridine	2,2'-bi- pyrimidyl	2-phenyl- pyrimidine
0 (180)	-2 544,418	-2 759,002 (-2 758,935)	-2 651,704	-2 973,912	-2 759,298
10 (170)	-2 544,431	-2 759,005 (-2 758,943)	-2 651,714	-2 973,913	-2 759,302
20 (160)	-2 544,464	-2 759,009 (-2 758,958)	-2 651,736	-2 973,917	-2 759,311
30 (150)	-2 544,503	-2 759,019 (-2 758,975)	-2 651,761	-2 973,923	-2 759,320
40 (140)	-2 544,531	-2 759,021 (-2 758,987)	-2 651,778	-2 973,926	-2 759,328
50 (130)	-2 544,545	-2 759,017 (-2 758,992)	-2 651,786	-2 973,927	-2 759,332
60 (120)	-2 544,551	-2 759,012 (-2 758,993)	-2 651,789	-2 973,927	-2 759,333
70 (110)	-2 544,553	-2 759,006 (-2 758,993)	-2 651,789	-2 973,925	-2 759,332
80 (100)	-2 544,553	-2 759,007 (-2 758,995)	-2 651,788	-2 973,924	-2 759,331
90	-2 544,553	-2 758,997	-2 651,788	-2 973,922	-2 759,330

^{a)} 1 electron-volt = $1.602 \cdot 10^{-19}$ J.

^{b)} Values in parentheses correspond to those for the supplement of ϕ .

the case of 3 conformational energies were calculated and displayed relative to that for the *trans*-coplanar form. Calculated values of the dipole moment as a function of ϕ are listed in Tab. 2. All of the results are discussed in detail in the following sections.

Biphenyl (2)

This molecule is planar or nearly so in the crystalline state²³⁻³³, but exhibits a torsional angle of approximately 42° between the planes of the rings in the vapor state^{26, 34-36}, and an angle of approximately 23° in the melt^{35, 36}. The coplanar conformation is hindered by steric interferences involving ortho-hydrogens, with a

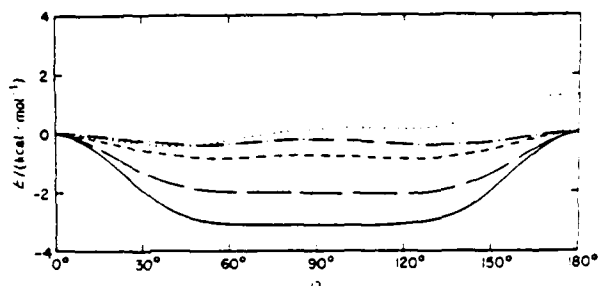


Fig. 1. Conformational energy shown as a function of torsional angle for biphenyl (—), 2,2'-bipyridyl (·····), 2-phenylpyridine (— — —), 2,2'-bipyrimidyl (- - - -), and 2-phenylpyrimidine (- · - ·). All energies are expressed relative to an assignment of zero for the $\phi = 0^\circ$ (*trans*) state

Tab. 2. Calculated values of the total dipole moments of the polar species

ϕ in degrees	Dipole moments in Debyes ^{a)}			
	2,2'-bipyridyl ^{b)}	2-phenylpyridine	2,2'-bipyrimidyl	2-phenylpyrimidine
0 (180)	0,00 (3,96)	2,20	0,00	1,57
10 (170)	0,50 (3,94)	2,21	0,12	1,58
20 (160)	0,67 (3,89)	2,22	0,16	1,60
30 (150)	0,85 (3,81)	2,23	0,20	1,63
40 (140)	1,58 (3,71)	2,25	0,23	1,65
50 (130)	1,71 (3,58)	2,27	0,26	1,69
60 (120)	2,03 (3,43)	2,28	0,29	1,73
70 (110)	2,32 (3,26)	2,31	0,32	1,75
80 (100)	2,60 (3,07)	2,32	0,33	1,77
90 (90)	2,85	2,32	0,35	1,78

^{a)} 1 Debye = $3,33564 \cdot 10^{-30}$ C · m.

^{b)} Values in parentheses correspond to those for the supplement of ϕ .

barrier height of approximately $8,4-12,6$ kJ · mol⁻¹ ($2-3$ kcal · mol⁻¹)³³. In the crystalline state *intermolecular* interactions favor the coplanar form by its more efficient packing and, in so doing, counteract the *intramolecular* steric hindrance, especially since the barriers to coplanarity are relatively low^{33, 37-42}.

Numerous calculations using both semi-empirical quantum-mechanical^{41, 43-47} and classical-mechanical^{19, 38, 40} techniques, separately and in combination^{37, 42, 48}, have also been performed in an attempt to describe the potential-energy curve, determine the preferred (minimum-energy) angle, and evaluate the energy barriers. Several^{37-42, 45, 47, 48} of these studies have been fairly successful in terms of agreement

with experiment, predicting a torsional angle in the range $32-40^\circ$ and a barrier to coplanarity of $5.0-18.8 \text{ kJ} \cdot \text{mol}^{-1}$ ($1.2-4.5 \text{ kcal} \cdot \text{mol}^{-1}$). However, the CNDO/2 studies done to date⁴³⁻⁴⁶⁾ uniformly predict a preferred (minimum-energy) angle of 90° instead of the experimental value of 42° found for the free molecule^{26, 34-36)}. In all of these CNDO/2 studies the molecular geometry (apart from the torsional angle) was taken from either experimental data or assumed idealized values and then held fixed. It was thus of special interest in the present study to determine if the implementation of complete geometry optimization corrects the erroneous result given in the aforementioned CNDO/2 studies⁴³⁻⁴⁶⁾.

As shown in Tab. 1 and in Fig. 1, the present calculations also give an absolute conformational-energy minimum at $\phi = 90^\circ$, in agreement with previous CNDO studies⁴³⁻⁴⁶⁾ but in disagreement with experiment^{26, 34-36)}. It appears from these results that, at least in the case of 2, geometry optimization cannot alone reconcile the differences between CNDO/2 and experiment. It is to be noted, however, that overall the conformational energy is very flat; in the range $\phi = 30-90^\circ$ E is within about $4.2 \text{ kJ} \cdot \text{mol}^{-1}$ ($1 \text{ kcal} \cdot \text{mol}^{-1}$) and in the entire configurational space ($\phi = 0-90^\circ$) within about $12.6 \text{ kJ} \cdot \text{mol}^{-1}$ ($3 \text{ kcal} \cdot \text{mol}^{-1}$) of the energy minimum. The barrier to coplanarity of $13.02 \text{ kJ} \cdot \text{mol}^{-1}$ ($3.11 \text{ kcal} \cdot \text{mol}^{-1}$) calculated here falls within the range of other estimates^{33, 37, 39, 41-46)}. For comparison, it is useful to cite an earlier molecular mechanics calculation carried out by two of the present authors¹⁹⁾. It also gave a very flat energy surface for $\phi = 40-90^\circ$ and a barrier to coplanarity of $14.7 \text{ kJ} \cdot \text{mol}^{-1}$ ($3.5 \text{ kcal} \cdot \text{mol}^{-1}$), when the intrinsic torsional barrier height was assigned the value $19.3 \text{ kJ} \cdot \text{mol}^{-1}$ ($4.6 \text{ kcal} \cdot \text{mol}^{-1}$) needed to reproduce the observed location (42°) of the energy minimum. Tajiri et al.⁴³⁾ have suggested that CNDO/2 overestimates the torsional angle in 2 because the method exaggerates the core repulsions, particularly those associated with interactions between the ortho-hydrogens. In view of the above comments, another contributing factor to the limitations of the CNDO/2 treatment in this regard may be that the torsional-potential well is too flat and too broad to permit an accurate determination of the preferred angle, especially considering that in practice the conformational-energy minimum is deduced by comparing small differences ($\approx 0.1 \text{ eV}$) in energy between large total-energy values ($\approx -2760 \text{ eV}$) which are in turn the sum of a large negative electronic energy term ($\approx -12000 \text{ eV}$) and a large positive core-repulsion term ($\approx 9240 \text{ eV}$).

Of special interest structurally is the variation in length of the swivel bond with increasing torsional angle. Experimental evidence indicates values of 1.50 \AA in the crystalline state^{24, 25, 28, 49)} and $1.48-1.50 \text{ \AA}$ in the gas phase^{26, 34-36)}. The present calculations give an average value of 1.46 \AA which is virtually invariant with changes in ϕ ; it was confirmed to be an equilibrium value by approaches from both larger and smaller starting lengths. This value is somewhat smaller than the experimental values, which is perhaps to be expected since the CNDO/2 method is known⁴⁹⁾ to underestimate equilibrium bond lengths. Several authors^{35, 38)} have suggested that the swivel bond should lengthen upon rotation away from $\phi = 0^\circ$ as a result of loss of resonance stabilization (decrease in double-bond character). Still others³⁹⁾ have noted that the swivel bond should lengthen as ϕ approaches 0° in an effort to relieve the steric hindrances between ortho-hydrogens. The present results showing near invari-

ance in the bond length suggest a compensatory effect throughout the rotational configurational space, because of the simultaneous decreases in resonance stabilization and steric repulsions³¹⁾ as ϕ departs from zero.

The bond angles and other bond lengths calculated are insensitive to ϕ and, furthermore, are in good agreement with experimental structural data^{25, 26, 32, 34, 52)}. The calculated values of the interatomic distance between ortho-hydrogens are found to be less than the sum (2.4 Å) of the van der Waals radii for H···H⁵³⁾ throughout the region $\phi = 0-40^\circ$. At $\phi = 40^\circ$ the interatomic H···H distance is nearly equal to the sum of the van der Waals radii, this distance normally corresponding to a minimum in the potential energy for a specific interaction. Since $\phi = 40^\circ$ is nearly that found experimentally (42°) for the free molecule^{26, 34, 36)}, it appears that the interaction between ortho-hydrogens plays a significant role in the determination of the preferred conformation.

2,2'-Bipyridyl (3) and its complexes

2,2'-Bipyridyl (3)

Replacement of one *ortho*-CH group on each ring in 2 by a nitrogen atom, as occurs in 3, should alleviate some of the steric hindrance involving the ortho-hydrogens that arises as ϕ approaches 0°. The desirable coplanar conformation is thus expected to be energetically more readily accessible for 3 (particularly with the nitrogens in *trans* position to the swivel bond) than for 2. Inasmuch as coplanarity is required for the maintenance of parallel polymer-chain continuation, the 2,2'-bipyridyl swivel would obviously have a significant advantage over the biphenyl one¹⁹⁾. However, the potential disadvantages may not be quite so apparent as the advantages but could prove significant. Specifically, the lone-pair electrons of the nitrogen are presumably less localized in space than the bonding-pair in the CH bond. The repulsion of two lone pairs (in the *cis*-form), or of the lone pair and an *ortho*-CH (in the *trans*-form) might conceivably increase rather than decrease a barrier to coplanarity. Moreover, the greater electronegativity of N relative to C and H leads to an increase in the magnitude of the atomic partial-charges throughout the species which in turn increases the significance of Coulombic interactions. Depending upon the precise partial-charge distribution (which must be assumed to vary with ϕ), these interactions could affect the energy of the coplanar conformations relative to other conformations.

The experimental dipole moment of 0.91 D found for the free molecule⁵⁴⁾ suggests a non-planar structure. Electron-diffraction studies²⁶⁾ reveal a rather flat potential-energy curve with no defined minima or maxima except for a maximum at the planar *cis*-conformation, indicating that the torsional angle is not limited in the same way as in 2. Also, calculations^{19, 48)} and more qualitative comparisons³⁶⁾ involving 2 and 3 have predicted the latter to be more flexible, in terms of both greater availability of configurational space and accessibility to coplanarity. On the basis of steric arguments, one would predict the *trans*-form of 3, while not necessarily the most stable conformation, to be preferred over the *cis*-form, in agreement with the finding that 3

exists in the *trans*-form in the solid state⁵⁵. In fact, an earlier study¹⁹ using analytical empirical potential-energy functions to represent the interactions found the *cis*-form to be about $8,4 \text{ kJ} \cdot \text{mol}^{-1}$ ($2 \text{ kcal} \cdot \text{mol}^{-1}$) above the minimum-energy, *trans*-form. However, the *cis*-conformation cannot be too difficult to achieve since it is readily adopted when **3** is either coordinated in solution with metal ions or exists in acidic media in the mono-protonated form⁵⁵⁻⁶¹.

The initial geometry for **3** in the present calculations was taken from X-ray crystallographic data⁵⁵. The torsional angle ϕ refers to the interplanar angle between the rings with the *trans*-conformation corresponding to $\phi = 0^\circ$. The most prominent features of the conformational energy curve, shown in Fig. 1, are (i) a very flat energy surface, with the region $\phi = 0 - 150^\circ$ within about $4,2 \text{ kJ} \cdot \text{mol}^{-1}$ ($1 \text{ kcal} \cdot \text{mol}^{-1}$) of the energy minimum, (ii) a shallow energy minimum located at $\phi \approx 40^\circ$, and (iii) barriers to coplanarity of approximately only $1,7 \text{ kJ} \cdot \text{mol}^{-1}$ ($0,4 \text{ kcal} \cdot \text{mol}^{-1}$) for the *trans*-conformation and $8 \text{ kJ} \cdot \text{mol}^{-1}$ ($1,9 \text{ kcal} \cdot \text{mol}^{-1}$) for the *cis*-conformation. These results are in good agreement with the CNDO/2 calculations of Borgen et al.⁶², assuming a fixed geometry. They also agree very well with the results of an earlier molecular mechanics calculation¹⁹ which found the *trans*-conformation to be of lowest energy, the *cis* to be $8,4 \text{ kJ} \cdot \text{mol}^{-1}$ ($2 \text{ kcal} \cdot \text{mol}^{-1}$) above it, and all regions of the conformational energy space to be within $8,4 \text{ kJ} \cdot \text{mol}^{-1}$ ($2 \text{ kcal} \cdot \text{mol}^{-1}$) of the calculated minimum. More importantly, the results are consistent with the experimental findings that the molecule is planar in the crystalline state⁵⁵ but non-planar as a free molecule^{26, 61}. The present results indicate that the molecule should exhibit nearly free rotation except for ϕ values near the *cis* coplanar conformation ($\phi = 180^\circ$). Nevertheless, it should be noted that even in **3** it appears that the steric repulsions (opposing coplanarity) are still sufficient relative to resonance effects (favoring coplanarity) to prevent the *trans* coplanar conformation from being the preferred one in the isolated molecule. This observation lends support to the contention mentioned earlier that the lone-pair electrons of the nitrogen of **3** may still pose an obstacle to achieving coplanarity similar to that posed by an *ortho*-CH group in **2**, although the calculated barrier to coplanarity for **3** ($1,97 \text{ kJ} \cdot \text{mol}^{-1}$ ($0,47 \text{ kcal} \cdot \text{mol}^{-1}$) for *trans*) is much less than ($13,0 \text{ kJ} \cdot \text{mol}^{-1}$ ($3,11 \text{ kcal} \cdot \text{mol}^{-1}$)) for **2**.

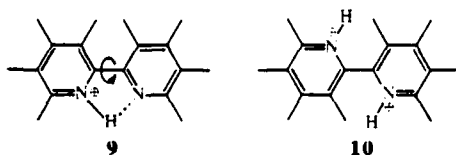
Coulombic interactions are of little importance in determining the preferred angle. The values of the partial charges on atoms C² and C^{2'} ($q = -0,05e$) and H³ and H^{3'} ($q = +0,017e$), which would experience the largest Coulombic interactions with nitrogen atoms N¹ and N^{1'} ($q = -0,23e$) as ϕ approaches 0° , are quite small. (Application of Coulomb's Law with a dielectric constant $\epsilon = 3$ to the entire partial charge distribution given by the present calculation yields a Coulombic energy difference of less than $0,84 \text{ kJ} \cdot \text{mol}^{-1}$ ($0,2 \text{ kcal} \cdot \text{mol}^{-1}$) between the conformations corresponding to $\phi = 0^\circ$ and 40° . This small value supports the assumption made in an earlier study that Coulombic effects in the 2,2'-bipyridyl swivel are insignificant¹⁹). From the calculated values of the dipole moment listed in Tab. 2 a mean value of 1,98 D at 25°C was calculated assuming a Boltzmann distribution weighted in the conformational energy. This value is larger than the observed value of 0,91 D⁵⁴). However, the calculated values are quite sensitive to changes in ϕ , ranging from $\mu = 0,0 \text{ D}$ at $\phi = 0^\circ$ (*trans*) to 3,96 D at 180° (*cis*).

As found for **2**, the length of the swivel bond is nearly invariant to changes in ϕ , with the average value being 1.46 Å. This is smaller than the experimental value of 1.49 Å²⁶⁾ but, as mentioned earlier, could be an artifact of the CNDO/2 technique⁴³⁾. The invariance in bond length may again be attributed to a balance between resonance effects favoring coplanarity and repulsive steric and Coulombic effects opposing coplanarity. Again, the calculated values of the bond angles and other bond lengths show little variation with ϕ and agree satisfactorily with values obtained from X-ray crystallography⁵⁵⁾.

These CNDO/2 calculations corroborate earlier molecular-mechanics calculations¹⁹⁾ that **3** is superior to **2** as a swivel in terms of (i) more energetically accessible conformations, i.e., greater equilibrium flexibility, (ii) smaller barriers between minima, and (iii) smaller barriers to coplanarity (hence increased probability of achieving the coplanar conformation required for parallel continuation of the polymer main chain)¹⁹⁾. Moreover, the basicity of the ring nitrogens should help to improve the solubility of the polymer in acidic media. The effects of protonation on the conformational characteristics of **3** are discussed in the next section.

Protonated forms of 2,2'-bipyridyl

The mono- and di-protonated forms **9** and **10** of **3** are of interest in this study particularly with regard to the extent to which protonation of the ring nitrogens⁶³⁾ affects the conformational characteristics of the parent species. Such an inquiry is particularly germane to the proposed use of these species as swivels in rodlike polymers since appreciable solubility of the latter is limited to strong acids, which certainly would result in protonation of the ring nitrogens within the swivels.



In considering the mono-protonated case **9**, one could envision the *cis*-coplanar conformation being stabilized relative to other conformations by the presence of the H⁺ straddled somewhere between the two nitrogens. So placed, the H⁺ would serve to reduce the Coulombic repulsions between the nitrogens. Experiments in fact do verify the presence of the *cis*-form under two pertinent solution conditions. First, the complexation of metal ions by **3** leads to the formation of a stable five-membered ring consisting of N—C—C—N' and the metal ion, which requires the *cis*-conformation⁵⁵⁻⁵⁸⁾. Second, the mono-protonated form of **3** is *cis*-coplanar or nearly so³⁶⁻⁴⁰⁾. At the same time, the present calculations have already indicated that Coulombic effects do not play an important role in the conformation of **3** so one would not expect the effect of neutralizing the Coulombic repulsions between the ring nitrogens to be very large. Moreover, the *cis*-conformation will still suffer from strong steric

repulsions between the ortho-hydrogens opposite the nitrogen atoms¹⁹). The *trans*-conformation, which for 3 itself was the more stable of the coplanar conformations, should experience strong steric repulsions involving the H⁺ and one of the ortho-hydrogens. It is expected, therefore, that the *trans*-conformation would be of high relative energy.

Results of the calculations summarized in Tab. 3 and in Fig. 2 confirm these qualitative projections. The *cis*-coplanar conformation ($\phi = 180^\circ$) for the mono-protonated form is the absolute energy minimum, approximately 21 kJ · mol⁻¹ (5.0 kcal · mol⁻¹) below the *trans*-coplanar conformation. In fact, from the *cis*-conformation the energy rises sharply with decreasing ϕ , goes through a maximum of about 25 kJ · mol⁻¹ (6 kcal · mol⁻¹) at $\phi = 90^\circ$ and then continues at ≈ 21 kJ · mol⁻¹

Tab. 3. Calculated values of the total energy for mono- and di-protonated 2,2'-bipyridyl (3)

ϕ in degrees	Total energy in eV per molecule	
	mono-protonated 3	di-protonated 3
0	-2 773,681	-2 783,989
30	-2 773,686	-2 784,013
60	-2 773,639	-2 784,006
90	-2 773,613	-2 783,980
120	-2 773,654	-2 783,962
150	-2 773,803	-2 783,920
180	-2 773,898	-2 783,857

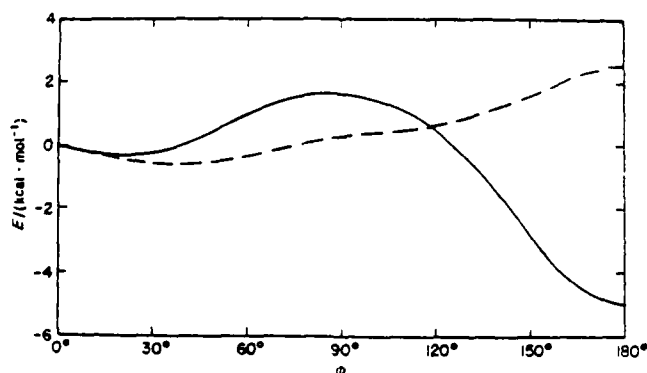


Fig. 2. The conformational energy profile for the mono-protonated (—) and di-protonated (---) forms of 2,2'-bipyridyl (3)

($\approx 5 \text{ kcal} \cdot \text{mol}^{-1}$) all the way to $\phi = 0^\circ$. This strong preference for the *cis*-conformation, despite the presence of strong steric repulsions between one pair of ortho-hydrogens, can be ascribed to the even stronger coplanar-favoring effects of resonance and the stabilization derived from the interaction between the proton and the more distant of the two nitrogen atoms. Whether or not this latter interaction qualifies as hydrogen bonding has been the subject of controversy⁵⁷⁻⁶¹. Regardless, it is apparently of sufficient strength to overcome the highly repulsive steric interactions arising in the *cis*-coplanar conformation. An estimate of the magnitude of this interaction is obtainable by comparing the relative energies of the *cis*-coplanar conformation for the mono-protonated case with that for the parent molecule **3**. Specifically, for **3** alone this conformation was calculated here to be about $8,4 \text{ kJ} \cdot \text{mol}^{-1}$ ($2,0 \text{ kcal} \cdot \text{mol}^{-1}$) above the energy minimum located at $\phi = 40^\circ$, while for the mono-protonated species this conformation is seen to be about $21 \text{ kJ} \cdot \text{mol}^{-1}$ ($5 \text{ kcal} \cdot \text{mol}^{-1}$) below the energy of this same value of ϕ . It follows then that the presence of the proton contributes about $29,3 \text{ kJ} \cdot \text{mol}^{-1}$ ($7 \text{ kcal} \cdot \text{mol}^{-1}$) toward stabilization of the *cis*-coplanar conformation. This value is precisely the order of that of typical H-bonds.

A prominent feature in these results is the dispersion of the proton's charge throughout the species. For example, in the *cis*-coplanar conformation the proton's nominal charge of $+1,0e$ has diminished to $+0,29e$. Further, comparison of the partial charges of all corresponding atoms for **3** and its mono-protonated ion reveals that the dispersion of the proton's charge extends essentially throughout the ion. Of course, this delocalization is most extensive for the *cis*-coplanar conformation since this conformation maximizes the interaction between both rings and the proton; this maximization of charge delocalization most certainly contributes to the preference for the *cis*-coplanar conformation.

Another prominent feature is the converged geometry for the *cis*-form, which was found to vary with the initial placement of the proton. If the proton is initially placed nearly equidistant (and radially outward) from each ring nitrogen, the converged geometry ($E = -2773,890 \text{ eV}$) in the vicinity of the proton is that shown in Fig. 3. The $\text{N} \cdots \text{H}^+$ distances of $1,14$ and $1,41 \text{ \AA}$ are quite reasonable for a $\text{N}-\text{H}^+ \cdots \text{N}$ hydrogen bonded structure. These relatively short $\text{N} \cdots \text{H}^+$ distances are achieved by contraction of the exo-ring bond angles about the swivel bond. If, on the other hand, the proton is initially placed in a position much further from the symmetrical one,

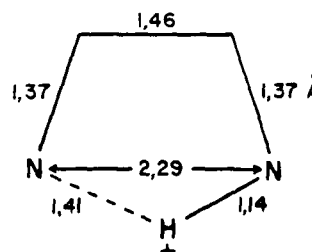


Fig. 3. The geometry of the lowest energy arrangement for the proton in the mono-protonated form of 2,2'-bipyridyl. The solid lines without arrowheads represent covalent bonds, and the dashed line a possible hydrogen bond

near one of the two N atoms, and accordingly much farther from the other, a quite different geometry is obtained. In this case, at an energy of $-2773,720$ eV or $16,8$ $\text{kJ} \cdot \text{mol}^{-1}$ (4 $\text{kcal} \cdot \text{mol}^{-1}$) above the previous structure, the converged geometry obtained is shown in Fig. 4. One of the $\text{N} \cdots \text{H}^+$ distances now is $2,33$ Å; although this is somewhat less than the van der Waals distance of $\approx 2,7$ Å, it is still long enough to preclude a hydrogen bond of any significant strength. The other $\text{N} \cdots \text{H}^+$ distance, on the other hand, at $1,07$ Å, is much more nearly that of a covalent NH bond. Consistent with these findings, the exo-ring angles at the swivel bond are not contracted. It appears extremely likely that the two "converged structures" of planar, mono-protonated **3** are separated by a potential barrier, although the flatness of the potential surfaces precludes the unambiguous demonstration of such a barrier.

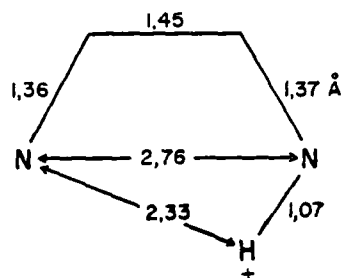


Fig. 4. An alternative arrangement for the mono-protonated form of 2,2'-bipyridyl; see legend to preceding Fig.

The di-protonated case should be and, as will be seen, is substantially different from the mono-protonated case in terms of conformational characteristics. Here, the stabilizing effect of charge delocalization operative in the *cis*-coplanar conformation for the mono-protonated case **9** are counteracted by severe steric and Coulombic repulsions owing to the presence of the two protons, each associated with a different nitrogen atom. The *trans*-coplanar conformation would be expected to experience steric repulsions similar to those found in **2**. The minimum-energy conformation is expected, therefore, to be non-planar.

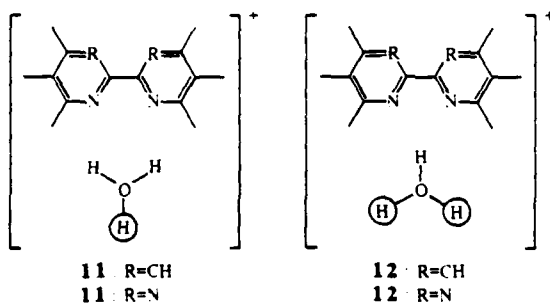
The results of the calculations are summarized in Tab. 3 and in Fig. 2. As expected, the preferred conformation is calculated as non-planar, with a minimum occurring at $\phi = 30^\circ$ and barriers to coplanarity of approximately $14,7$ $\text{kJ} \cdot \text{mol}^{-1}$ ($3,5$ $\text{kcal} \cdot \text{mol}^{-1}$) for *cis* and $2,1$ $\text{kJ} \cdot \text{mol}^{-1}$ ($0,5$ $\text{kcal} \cdot \text{mol}^{-1}$) for *trans*. These results disagree somewhat with the CNDO/2 calculations of Borgen et al.⁽²⁾, who found a minimum in the "binding energy" at $\phi = 0^\circ$.

In comparing the calculated conformational characteristics of **3** with its mono- and di-protonated forms, one finds similarities between the first and the last species. Specifically, both have a preferred angle of ϕ near $30-40^\circ$ with the more energetically accessible coplanar form being the *trans* at approximately $2,1$ $\text{kJ} \cdot \text{mol}^{-1}$ ($0,5$ $\text{kcal} \cdot \text{mol}^{-1}$) above the minimum. Also, for both species the *cis*-coplanar conformation is of relatively high energy (approximately $8,4$ $\text{kJ} \cdot \text{mol}^{-1}$ (2 $\text{kcal} \cdot \text{mol}^{-1}$) above the minimum value). The mono-protonated case, however, is in sharp contrast to both of these. Its preferred conformation is *cis*-coplanar, with the *trans*-form about

21 $\text{kJ} \cdot \text{mol}^{-1}$ (5,0 $\text{kcal} \cdot \text{mol}^{-1}$) above the *cis*. These calculations thus predict that the preferred coplanar conformation of 3 is a function of the acidity (i.e., protonating ability) of its medium. Specifically, conformations near or at *trans* are preferred in a neutral medium, moving to *cis* and then back again to or near *trans* with increasing acidity. This conclusion agrees with qualitative observations reported in a previous investigation⁵⁷.

2,2'-Bipyridyl-hydronium ion complex

This species is expected to exhibit intermolecular hydrogen bonding between the hydrogen atoms of the hydronium ion and the nitrogen atoms of the rings⁶⁰. The two distinct initial configurations of the hydronium ion relative to the bipyridyl in 11 and 12 were investigated. In 11 the hydronium ion is placed such that two of its O—H bonds point toward the nitrogen atoms with the rings in the *cis*-coplanar conformation. In 12, one of the O—H bonds is perpendicular to the C—C swivel bond connecting the two rings. In both cases, the H_3O^+ was given a pyramidal geometry in accordance with recent evidence⁶⁴. For the *cis*-coplanar conformation, this was achieved by setting the hydrogen(s) (specifically one in 11 and two in 12) of the H_3O^+ farthest from the bipyridyl moiety at an angle of 15° out of the plane of the rings. These out-of-plane hydrogens are circled in the illustration and Figures that follow. After geometry optimization the angle was found to have remained essentially at this value. Rotations about the C—C swivel bond were performed by rotating one of the pyridine rings about this bond by the angle ϕ , leaving all other atoms stationary.



The relative conformational energy as a function of ϕ is shown in Fig. 5. The preferred angle for 11 is about 150° (from *trans*), with barriers to coplanarity of 1,7 and 37,7 $\text{kJ} \cdot \text{mol}^{-1}$ (0,4 and 9,0 $\text{kcal} \cdot \text{mol}^{-1}$) for *cis* and *trans*, respectively. At approximately $\phi = 120^\circ$ the energy rises sharply and continues to be high ($\approx 42 - 50 \text{ kJ} \cdot \text{mol}^{-1}$ ($\approx 10 - 12 \text{ kcal} \cdot \text{mol}^{-1}$)) all the way to $\phi = 0^\circ$, principally due to the loss of one H-bond. While the *cis*-coplanar conformation is certainly of low relative energy, it is rather surprisingly not the preferred conformation. The $\approx 20^\circ$ deviation from planarity may be necessary to accommodate the H_3O^+ between the rings. The difficulty in accommodating the H_3O^+ in the *cis*-conformation is evidenced by the fact that the $\text{N} \cdots \text{N}$ interatomic distance is about 0,20 Å greater in the complex than it is

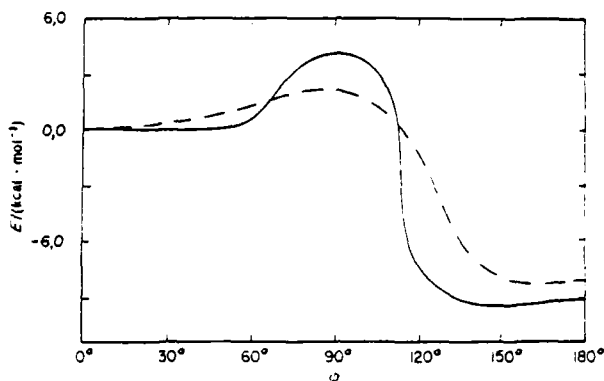


Fig. 5. The conformational energy profile for configurations 11 (—) and 12 (---) of the hydronium ion complex of 2,2'-bipyridyl

in the parent species. The preferred conformation for 12 is $\phi = 160^\circ$ with barriers to coplanarity of about 2.1 and 37.7 $\text{kJ} \cdot \text{mol}^{-1}$ (0.5 and 9.0 $\text{kcal} \cdot \text{mol}^{-1}$) for *cis* and *trans*, respectively. As seen for 11, the region $\phi = 0-90^\circ$ is of high relative energy (33.5 $\text{kJ} \cdot \text{mol}^{-1}$ ($\approx 8 \text{ kcal} \cdot \text{mol}^{-1}$)).

All conformations in 11 are about 42–50 $\text{kJ} \cdot \text{mol}^{-1}$ (10–12 $\text{kcal} \cdot \text{mol}^{-1}$) more stable than the corresponding ones in 12. This is because 11 permits the formation of two H-bonds, whereas in 12, at best, one 3-center H-bond is formed and, judging by the $\text{N} \cdots \text{H}^+$ distance (2.14 Å), it is weak. Thus, it is predicted that the observed arrangement should be 11 when 3 is near or at the *cis*-coplanar conformation. Since it is interesting to ask why optimization of 12 fails to converge to the more stable structure 11, calculations on intermediate structures were carried out to investigate this question. Starting from the converged geometry of *cis*-coplanar 12 the H_3O^+ moiety was turned about an axis through the oxygen atom and normal to the molecular plane by successive 20° increments until structure 11 was obtained. A small but significant barrier (8.4 $\text{kJ} \cdot \text{mol}^{-1}$ (2.0 $\text{kcal} \cdot \text{mol}^{-1}$)) was encountered between the two conformations, thus explaining why convergence from 12 to 11 was impossible.

Of special interest is the geometry of the H_3O^+ itself and its proximity to the 2,2'-bipyridyl moiety after these two parts of the complex have reached their minimum energy arrangements. This is illustrated for configuration 11 in Fig. 6. In it, the H_3O^+ remains symmetrically placed between the rings, resulting in two nearly linear $\text{N} \cdots \text{H}-\text{O}$ hydrogen bonds. It is apparent that the strong interaction between the ring nitrogens and nearby hydrogen atoms on H_3O^+ is instrumental in the stretching of two of the O—H bonds. The very different geometry obtained for configuration 12 is shown in Fig. 7. In this arrangement, the H_3O^+ has rotated to give one nearly linear $\text{N}-\text{H} \cdots \text{O}$ hydrogen bond; in this case, however, the N—H length is shorter than the $\text{H} \cdots \text{O}$ length, so 12 may be described more aptly as the hydrated conjugate acid of 3.

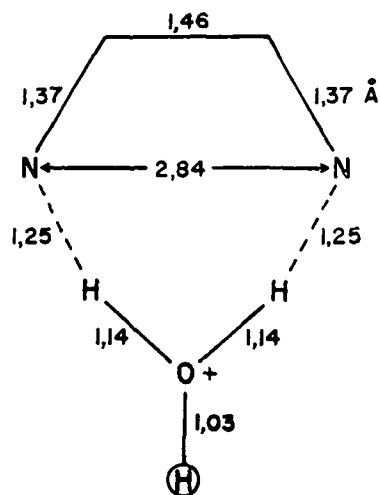


Fig. 6

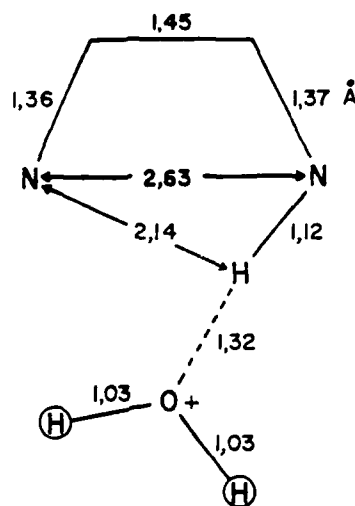


Fig. 7

Fig. 6. The geometry of the lowest energy arrangement obtained from configuration 11

Fig. 7. The geometry of the lowest energy arrangement obtained from configuration 12

2-Phenylpyridine (4)

This molecule can be thought of structurally as a cross between 2 and 3. As such, it is expected to exhibit conformational characteristics somewhat intermediate to these two species. The results in Tab. 1 and in Fig. 1 show that the energy minimum is broad ($\phi = 60 - 120^\circ$) with a barrier to coplanarity of about $8.4 \text{ kJ} \cdot \text{mol}^{-1}$ ($2.0 \text{ kcal} \cdot \text{mol}^{-1}$). As expected, this latter value falls between the corresponding values of $13 \text{ kJ} \cdot \text{mol}^{-1}$ ($3.1 \text{ kcal} \cdot \text{mol}^{-1}$) for 2 and $2.1 \text{ kJ} \cdot \text{mol}^{-1}$ ($0.5 \text{ kcal} \cdot \text{mol}^{-1}$) for 3. The value of ϕ predicted here is probably somewhat high owing to the tendency, already mentioned, of the CNDO/2 method to exaggerate the core repulsions⁴³. The swivel bond exhibits good overall flexibility in that the region $\phi = 25 - 90^\circ$ is within approximately $4.2 \text{ kJ} \cdot \text{mol}^{-1}$ ($1.0 \text{ kcal} \cdot \text{mol}^{-1}$) of the minimum and all ϕ values give energies within about $8.4 \text{ kJ} \cdot \text{mol}^{-1}$ ($2.0 \text{ kcal} \cdot \text{mol}^{-1}$). As was found for all the swivels investigated here, the length of the swivel bond is essentially invariant to changes in ϕ , with an average value of 1.46 \AA . Not surprisingly, the magnitude of the calculated dipole moment is essentially constant, as shown in Tab. 2.

2,2'-Bipyrimidyl and its dihydrated form

2,2'-Bipyrimidyl (5)

This species is of particular interest in that it represents the situation wherein all four of the *ortho*-CH groups of 2 are replaced by nitrogen atoms. This will of course

relieve all the steric hindrance involving the ortho-hydrogens and so should ensure easier accessibility of the coplanar conformations.

It is seen from Tab. 1 and Fig. 1 that all conformations are within about $1,7 \text{ kJ} \cdot \text{mol}^{-1}$ ($0,40 \text{ kcal} \cdot \text{mol}^{-1}$) of the shallow minimum at $\phi = 50^\circ$. These results thus substantiate the prediction of essentially unhindered, free rotation about the swivel bond. The calculated preferred angle of $\phi = 50^\circ$ is probably high for reasons mentioned earlier. As seen in Tab. 2, the dipole moment varies only slightly with conformation, ranging from a value of $0,0 \text{ D}$ at $\phi = 0^\circ$ to $0,35 \text{ D}$ at 90° .

Dihydrated bipyrimidyl

The dihydrate of **5** is expected to exhibit an intermolecular hydrogen bond between the hydrogen atoms of the water molecules and the nitrogen atoms of **5**. The two configurations **11'** and **12'** studied were analogous to **11** and **12** in the 2,2'-bipyridyl- H_3O^+ case. In a first study, coplanarity was imposed throughout the optimization. According to these calculations on the *cis*-conformation, configuration **11'** is more stable than **12'** by $43,1 \text{ kJ} \cdot \text{mol}^{-1}$ ($10,3 \text{ kcal} \cdot \text{mol}^{-1}$). Next, since the unhydrated **5** had been found to be non-planar, similar non-planar structures for both **11'** and **12'** were studied. Specifically, the C—C swivel bond was twisted by 40° . The two water molecules were rotated around the O—O axis by 20° in opposite directions for configuration **11'**, while they were held fixed for **12'**. For **11'**, the optimized structure gave a torsional angle of 72° (from *cis*) and a barrier to coplanarity of $26,8 \text{ kJ} \cdot \text{mol}^{-1}$ ($6,4 \text{ kcal} \cdot \text{mol}^{-1}$); for **12'** the optimized structure gave a torsional angle of 18° and a barrier to coplanarity of only $0,4 \text{ kJ} \cdot \text{mol}^{-1}$ ($0,1 \text{ kcal} \cdot \text{mol}^{-1}$). Thus, the CNDO/2 optimization predicts the most stable form of dihydrated **5** as a non-planar form of **11'**, similar to that found for the case of bipyridyl- H_3O^+ in the preceding section. In fact, many of the qualitative conclusions given for the latter case can be extended to the present case and thus are not reiterated here.

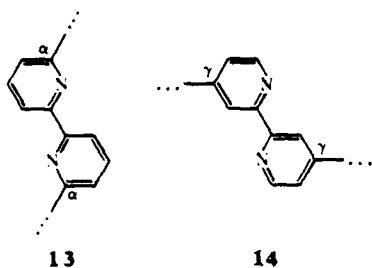
2-Phenylpyrimidine (6)

6 and **3** are similar in that both have two of the four ortho-positions occupied by nitrogen atoms but differ in that, in the former, both nitrogen atoms are in the same ring, while in the latter each ring contains one nitrogen atom. Because of these features, it is of particular interest to compare the conformational characteristics of the two molecules. While similarities in this regard are expected, **6** possesses the advantage of having no coplanar conformation exhibiting strong steric repulsions between ortho-hydrogens. In contrast, **3** exhibits these interferences of course in the *cis*-coplanar conformation. Hence, for **6** both (equivalent) coplanar conformations ($\phi = 0^\circ, 180^\circ$) should be of low relative energy while for **3**, as presented earlier, the *trans*-conformation is of low energy ($2,1 \text{ kJ} \cdot \text{mol}^{-1}$ ($0,5 \text{ kcal} \cdot \text{mol}^{-1}$)) but the *cis* is high ($8,4 \text{ kJ} \cdot \text{mol}^{-1}$ ($2,00 \text{ kcal} \cdot \text{mol}^{-1}$)).

As seen from Tab. 1 and Fig. 1, the swivel bond in **6** is overall less hindered than that in **3**. Specifically, for the former all conformations, including the coplanar conformation, are within about $3,4 \text{ kJ} \cdot \text{mol}^{-1}$ ($0,8 \text{ kcal} \cdot \text{mol}^{-1}$) of the shallow energy

minimum at $\phi = 60^\circ$. In contrast, for **3** the *cis*- and *trans*-coplanar conformations are 8,0 and 1,7 $\text{kJ} \cdot \text{mol}^{-1}$ (1,9 and 0,4 $\text{kcal} \cdot \text{mol}^{-1}$), respectively, above the minimum. Also, the calculated dipole moment of **6** varies only slightly with conformation, ranging from 1,57 D at $\phi = 0^\circ$ to 1,78 D at 90° (Tab. 2), in contrast to the more pronounced variation in **3**.

In summary, **3** has slightly greater accessibility of the *trans*- (but not the *cis*-) coplanar conformation, while **6** has greater overall flexibility. To the extent that better flexibility of the swivel leads to improved solubility for the rodlike polymer chain containing it, **6** should hold a slight advantage over **3**. The former swivel may be advantageous from a synthetic point of view too. It was pointed out earlier that the points of attachments of the main chain to each ring must be either both meta (*m,m*) or both ortho (*o,o*) with respect to the swivel bond in order to preserve parallel continuation of the main chain. The *o,o* isomer appears to involve a considerable amount of steric congestion so is not discussed further here. In **3** there are four possible *m,m*-geometrical isomers because of the fact that the meta positions on each ring are non-equivalent, i. e., one meta is α and the other is γ with respect to the ring nitrogen. Consideration of the units **13** and **14** shows that the *m,m*-isomer must be either both α - or both γ -types if the swivel is to preserve parallel chain continuation



while in the preferred, *trans*-coplanar conformation. Clearly, these specifications could pose some problems for the synthetic chemist attempting to incorporate such a swivel into a rodlike polymer chain. In contrast, the symmetry in **6** is such that both meta-positions (with respect to the swivel bond) on each ring are equivalent. Consequently, in terms of synthesis, attachment at either meta position on each ring is permissible. (Two conformations of the *m,m* isomers do not give parallel chain continuation but intermolecular interactions will favor rotation around the swivel bond by 180° to give the desired parallelism.)

Conclusions

The CNDO/2 method including a direct geometry optimization scheme was used to study the structural and conformational characteristics of several wholly aromatic molecules under consideration for use as possible swivels within rodlike polymer

chains. The basic molecules investigated here are biphenyl (2), 2,2'-bipyridyl (3), 2-phenylpyridine (4), 2,2'-bipyrimidyl (5), and 2-phenylpyrimidine (6). The molecules are structurally similar but differ in the number and location of ortho-CH groups replaced by nitrogen atoms. Such substitution is expected to improve the probability of achieving the desired coplanar conformations.

In terms of their potential for use as swivels, two features of primary importance are the barriers to coplanarity and overall flexibility. The barriers to coplanarity rank, as would be expected, in order of the number of such nitrogen substitutions, namely 5 ($1,7 \text{ kJ} \cdot \text{mol}^{-1}$ ($0,4 \text{ kcal} \cdot \text{mol}^{-1}$)) < 6 ($3,4 \text{ kJ} \cdot \text{mol}^{-1}$ ($0,8 \text{ kcal} \cdot \text{mol}^{-1}$)) < 3 ($cis = 8,4 \text{ kJ} \cdot \text{mol}^{-1}$ ($2,0 \text{ kcal} \cdot \text{mol}^{-1}$) $trans = 2,1 \text{ kJ} \cdot \text{mol}^{-1}$ ($0,5 \text{ kcal} \cdot \text{mol}^{-1}$)) < 4 ($8,4 \text{ kJ} \cdot \text{mol}^{-1}$ ($2,0 \text{ kcal} \cdot \text{mol}^{-1}$)) < 2 ($12,6 \text{ kJ} \cdot \text{mol}^{-1}$ ($3,0 \text{ kcal} \cdot \text{mol}^{-1}$)), where the numbers in parentheses represent the energy calculated for the particular barrier. In terms of overall flexibility about the swivel bond, as determined by the amount of configurational space of sufficiently low energy to be accessible, the species rank roughly in the same order as above, with 5 having the greatest overall flexibility. Consequently, on the basis of the above considerations, it is predicted that of the species studied here 5 would offer the greatest potential for use as a swivel, with the others following in the order listed above.

The effects of mono- and di-protonation on the conformational characteristics of 3 were studied and found to be significant. While the parent molecule and the diprotonated species both prefer *trans*- over the *cis*-coplanar conformation, just the opposite is true for the mono-protonated case. Hence, it is concluded that the coplanar conformation preferred by the species will be a function of the acidity of the medium, with *trans*-preferred in neutral media followed by a preference for *cis* (mono-protonated) and then back to *trans* (di-protonated) with increasing acidity. The results suggest the presence of hydrogen bonding for mono-protonated 3 in the *cis*-coplanar conformation, as evidenced by the strong preference for this conformation and by the bending of the exo-ring angles about the swivel atom in order to shorten the interatomic distances to reasonable values for the $\text{N} \cdots \text{H}^+ \cdots \text{N}$ hydrogen bond. The species 2,2'-bipyridyl- H_3O^+ and 2,2'-bipyrimidyl- $2\text{H}_2\text{O}$ were studied, each in two initial configurations, one with an O—H bond pointing to each N atom and the other with an O—H bond normal to the swivel bond. For each species, the former configuration is the preferred one.

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CNDO/2 Analyses of the Order of Protonation of Rodlike Polybenzobisoxazoles (PBO)

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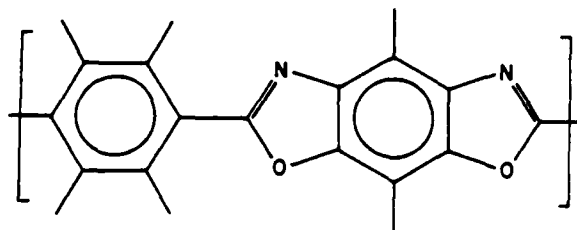
Summary

Protonation of the rodlike polybenzobisoxazoles (PBO) and polybenzobisthiazoles and their model compounds in acidic media will have significant effects on their solubility, solution behavior, geometry, and conformational characteristics. Experimental studies on the *cis*-PBO model compound suggest that the aromatic heterocyclic group can accept up to four acidic protons, first at each of the two nitrogen atoms then at the two oxygen atoms. In this study geometry-optimized CNDO/2 calculations were carried out on the *cis*-PBO model compound to determine the order of successive protonation, estimate differences in proton binding energies, and provide information on the effects of successive protonation on the geometry and charge distribution. The results indicate that protonation occurs in the order nitrogen, nitrogen, oxygen, oxygen, which is consistent with the greater basicity of nitrogen relative to oxygen. The difference in energy between initial protonation at nitrogen versus oxygen is ca. 60.7 kcal mol⁻¹. Second protonation is preferred at the other nitrogen rather than at the more distant oxygen by nearly the same amount, suggesting that energetically the initial protonation at the nitrogen has a negligible effect on subsequent protonation and that the two oxazole moieties are highly insulated from each other. Repulsive Coulombic interactions between the acidic protons have a negligible influence on whether the second protonation occurs at the nitrogen or the oxygen considered. Coulombic effects will in fact slightly favor at the nitrogen since, despite its closer proximity to the nitrogen first protonated, protonation there yields a more delocalized and hence less repulsive charge distribution than at the oxygen.

Introduction

The rodlike polybenzobisoxazoles (PBO) and polybenzobisthiazoles are high-performance polymers since films and fibers processed from these materials exhibit high strength, good thermo-oxidative stability, and resistance to most common solvents (ARNOLD, 1979; HELMINIAK, 1979; WELSH, et al., 1981, 1982; WOLFE, et al., 1979; WONG, et al., 1977). The only materials found suitable as solvents for these materials are very strong acids such as chlorosulfonic acid, methanesulfonic acid, and polyphosphoric acid. Recent experimental and theoretical studies have focused on the behavior of these polymers in acidic media in order to provide information regarding their solubility characteristics and solution properties. In most cases the studies have been applied to small model compounds such as

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for the cis-PBO. (In the trans isomer a nitrogen and oxygen within the same oxazole ring switch places.) Some of these studies (BERRY, 1981; THOMAS, et al., 1980) have indicated that with increasing acidity the cis-PBO model compound can exist in the $2H^+$ -form, with one acidic proton binding to each nitrogen atom, or in the $4H^+$ -form, with the two additional protons binding to the two oxygen atoms. Both spectroscopic (THOMAS, et al., 1980) and theoretical (WELSH, et al., 1982) evidence have provided details as to the extent to which successive protonation alters the geometry and conformational characteristics of these species.

A more fundamental question to be addressed is the precise order of successive protonation of the basic atoms in these species. While in general nitrogen atoms are more basic than oxygen atoms and hence should protonate first, the proximity of the atoms involved gives rise to Coulombic effects which could alter the expected sequence. This has pertinence to the cis isomer in particular since the two nitrogen atoms lie on the same side of the molecular axis and therefore are closer to each other than they are in the trans isomer. The presence of significant Coulombic effects could result in a different sequence of protonation for the cis and trans isomers. Coulombic considerations also arise in considering the site of second protonation.

In the present study, geometry-optimized CNDO/2 (complete neglect of differential overlap) calculations were carried out to predict the order of protonation within the cis-PBO model compound. Also obtained are differences in proton binding energies between $N-H^+$ and $O-H^+$ in these species, as well as information regarding charge distributions and Coulombic effects. The results indicate that protonation occurs in the order nitrogen, nitrogen, oxygen, oxygen, which is consistent with the greater basicity of nitrogen relative to oxygen. Thus, repulsive Coulombic effects between the acidic protons have a negligible influence on the precise sequence of protonation. In fact, following initial protonation of a nitrogen atom, Coulombic energies alone favor protonation at the other nitrogen rather than at the more distant oxygen by ca. $0.7 \text{ kcal mol}^{-1}$. Both initial and second protonation is favored at the nitrogen rather than at the oxygen by ca. $60. \text{ kcal mol}^{-1}$, obtained by comparing the total CNDO/2 energies calculated for the resulting species.

Methodology

The technique employed consists of the CNDO/2 semi-empirical molecular orbital method (POPLE and BEVERIDGE, 1970) nested in an iterative scheme for achieving direct geometry optimization (KONDO, 1978). The initial geometry for the flat cis-PBO model compound was taken from a similar calculation on the unprotonated molecule (WELSH, et al., 1982) which in turn was nearly identical to that observed by X-ray analysis (WELLMAN, et al., 1979). The order of successive protonation was

determined by comparing the geometry-optimized CNDO/2 total energy for the following different species: (1) one H^+ on a nitrogen atom, (2) one H^+ on an oxygen atom, (3) one H^+ on each nitrogen atom, (4) one H^+ on each oxygen atom, and (5) one H^+ on a nitrogen atom and another H^+ on an oxygen atom. In each case, the H^+ was initially placed in the same plane as the heterocyclic group at the typical bond distance (1.05 Å) away from the basic atom and bisecting the exo-ring angle. All calculations were applied to the model compound in the flat, coplanar form, which is the conformation observed in the crystalline state (WELLMAN, et al., 1979).

Results and Discussion

Comparison between the first two species mentioned above yields information regarding the initial site of protonation. The results indicate that the $N-H^+$ bond formation is preferred over that of $O-H^+$ by ca. 60.7 kcal mol⁻¹. Placing the acidic proton in a more tetrahedral arrangement relative to the oxygen atom (at various angles ranging from 30° to 60° out the plane of the heterocyclic ring) reduced the preference for protonation at N only to ca. 56 kcal mol⁻¹. This preference is qualitatively in agreement with, but quantitatively considerably larger than, values obtained by ab initio calculations on simple non-aromatic bases, such as H_2NOH and HNO which prefer protonation at N rather than at O by ca. 24.3 and 15.5 kcal mol⁻¹, respectively (DELBENE, 1982; DELBENE, et al., 1982). For these two species, the present methods yield preferences for N of ca. 33.0 and 14.2 kcal mol⁻¹, respectively. The agreement between the two methods is acceptable, suggesting that the value of 60.7 kcal mol⁻¹ obtained in the present study may be realistic and not merely an artifact of the CNDO/2 technique itself.

A further indicator of the relative stability of the two bonds is obtained by comparison of the delocalization of the acidic proton's formal charge. Specifically, the proton retains a partial charge of 0.215e in the $N-H^+$ form compared with 0.330e in the $O-H^+$ form, demonstrating that the former case is superior in terms of charge delocalization. In terms of the alteration of the charge of the basic atom before and after it is protonated, however, there is little difference between the nitrogen and the oxygen. Specifically, the partial charge changes from $q = -0.301e$ to $q = -0.200e$ ($\Delta q = +0.10e$) for the nitrogen atom and from $q = -0.293e$ to $q = -0.205e$ ($\Delta q = +0.09e$) for the oxygen atom. Hence, an advantage in protonating at nitrogen rather than at oxygen lies more in its superiority in dispersing the proton's formal charge throughout the species and not primarily in the electron withdrawing ability of the basic atom per se. Calculated bond lengths are nearly the same, being 1.04 Å for $O-H^+$ and 1.06 Å for $N-H^+$.

Having established that initial protonation at one of the nitrogen atoms is preferred, comparison of the 3rd, 4th and 5th species considered provides information regarding the second site of protonation. The results indicate that protonation at the other nitrogen atom rather than at the more distant oxygen atom is preferred by ca. 63.6 kcal mol⁻¹, approximately the same value obtained for initial protonation. This preference is not immediately obvious since in this case the effects of possible Coulombic repulsions must be considered. Specifically, a second proton placed at the other nitrogen will be much closer (5.72 Å) to the initial proton than a second proton at the more distant oxygen atom (7.05 Å). This difference in proximity could result in more repulsive Coulombic interactions and hence a less preferred situation for the former case. However, comparisons of the two cases in this respect indicate that Coulombic energy differences are negligible relative to the differences in binding energies and actually

favor second protonation at nitrogen. Application of Coulomb's Law $E_{\text{coul}} = \frac{q_1 q_2}{\epsilon d}$ with $\epsilon = 1$ yields $E_{\text{coul}} = 3.2 \text{ kcal mol}^{-1}$ and $E_{\text{coul}} = 3.9 \text{ kcal mol}^{-1}$ for the $\text{H}^+ \cdots \text{H}^+$ interaction energy for the case of N,N and N,O protonation, respectively. The slight Coulombic preference (less repulsion) for nitrogen protonation is a consequence of the protons having a smaller partial charge in this case, which offsets their closer proximity. Interestingly, in either case the second protonation again results in substantial delocalization of the proton's formal charge. Specifically, a second proton located at a nitrogen atom has $q = +0.237e$ while one at an oxygen atom has $q = +0.350e$. Both of these values are nearly identical to those occurring with initial protonation, so it appears that the middle benzene ring in the benzobisoxazole group acts as a charge buffer, thus preventing significant charge dispersal through it. In terms of the energetics and charge effects involved in protonation, each of the oxazole rings within a benzobisoxazole group appears to behave nearly independently of one another.

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Abstract 1

CNDO studies on nonplanar conformations in some cis and trans polybenzo-
bisoxazoles and polybenzobisthiazoles

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While essentially rigid in the axial direction, the rodlike polymers cis and trans polybenzobisoxazole (PBO) and polybenzobisthiazole (PBT) do exhibit conformational flexibility with respect to rotations about the bonds between alternating phenylenes and heterocyclic groups. Since preparation of high-strength materials from these polymers requires a high degree of alignment, this flexibility should be important in this regard. CNDO/2 calculations were therefore carried out to obtain the conformational-energy profiles of related model compounds. The cis- and trans-PBO models prefer the coplanar conformation while the barrier to the perpendicular conformation is ca. 8.4 kJ mol^{-1} . The trans-PBT model prefers $\phi = 20^\circ$ with barriers to the coplanar and perpendicular conformations of about 2.1 and 25.0 kJ mol^{-1} , respectively.

Model compounds of cis-PBT are bowed in the crystalline state. The bond-strain energies apparently responsible for bowing are estimated by comparing

Abstract 1

the CNDO/2 energy of the observed "bowed" molecule to that of a fictitious planar form. The "bowed" form is more stable by a large amount, indicating that in-plane bond-angle and bond-length distortions are not sufficient to relieve bond strain. Bowing hence appears to be a necessary alternative to these mechanisms for relieving the considerable strain within the planar form.

* UC affiliation only.

Effects of Protonation on the Conformational Characteristics
and Geometry of the Rodlike Benzobisoxazole (PBO)

Polymers: A CNDO/2 Study

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Effects of Protonation on the Conformational Characteristics and Geometry of the Rodlike Benzobisoxazole (PBO) Polymers: A CNDO/2 Study. W. J. Welsh, Department of Chemistry and Polymer Research Center, The University of Cincinnati, Cincinnati, OH 45221 and College of Mount St. Joseph, Mount St. Joseph, OH 45051, and J. E. Mark, Department of Chemistry and the Polymer Research Center, The University of Cincinnati, Cincinnati, OH 45221.

SUMMARY

Recent experiments on model compounds suggest that rodlike polybenzobisoxazole (PBO) and polybenzobisthiazole (PBT) chains are protonated when dissolved in highly acidic solvents. The PBO model compound can exist as a $2H^+$ ion, with one proton on each nitrogen atom, or (depending on the acidity of the medium) as a $4H^+$ ion, with two additional protons on the oxygen atoms. The PBT model compounds generally form $2H^+$ ions, owing to the lower basicity of sulfur atoms relative to oxygen atoms. In the present study geometry-optimized CNDO/2 calculations have been carried out in an attempt to predict the effect of protonation on the conformational characteristics and geometry of PBO model compounds. Values of the conformational energy versus rotation of the end-phenylenes about the heterocyclic group are calculated for cis-PBO model compounds in the unprotonated form and as $2H^+$ and $4H^+$ ions. All three species prefer the coplanar conformation with maximum barriers, occurring at the perpendicular conformation, of ca. 8.4, 33.6, and 84.0 kJ mol⁻¹ for the unprotonated form, the $2H^+$ ion, and the $4H^+$ ion, respectively. Steric arguments would suggest that repulsions between the acidic protons and the ortho-hydrogens on the phenylenes would render the coplanar conformation more repulsive than other orientations. However, detailed analysis of the optimized geometries reveals that the rotatable bond shortens with protonation, indicating an increased bond strength and hence increased conjugation energy.

Calculations of Electronic Band Structures for Some Rigid
Benzobisoxazole and Benzobisthiazole Polymers

D. BHAUMIK and J. E. MARK, Department of Chemistry and Polymer Research Center,
The University of Cincinnati, Cincinnati, Ohio 45221

Synopsis

Quantum-mechanical methods were employed to calculate electronic band structures for the poly(benzobisoxazole)(PBO) and poly(benzobisthiazole)(PBT) chains originally synthesized and much studied because of their utility as high-performance fibers and films. For cis-PBO, trans-PBO, and trans-PBT chains in their coplanar conformations, the band gaps in the axial direction were found to be 1.72, 1.62, and 1.73 e.V., respectively. Since trans-PBT is nonplanar, calculations on it were also carried out as a function of the rotation angle ϕ about the C-C bond joining the two ring systems in the repeat unit. The band gap was found to increase markedly with increase in nonplanarity, as would be expected from the decrease in charge delocalization. The calculations suggest the most likely value of ϕ to be $\sim 30^\circ$, in good agreement with the experimental value 23° obtained by X-ray analysis of a crystalline trans-PBT model compound. At this value of ϕ , the calculated value of the band gap is 1.98 e.V. All of these values are very close to the corresponding values 1.4 - 1.8 e.V. reported for trans-polyacetylene, which should encourage further theoretical and experimental investigations of their electronic properties.

Abstract 4

Polymer Chemistry

A THEORETICAL INVESTIGATION OF CHAIN PACKING AND ELECTRONIC BAND STRUCTURE OF THE RIGID-ROD POLYMER TRANS-POLY(p-PHENYLENE BENZOBISTHIAZOLE) IN THE CRYSTALLINE STATE

Poster Presentation

Am. Phys.

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J. E. Mark	Same; 475-2453	Yes	Yes	Am. Chem.

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University of Cincinnati

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A THEORETICAL INVESTIGATION OF CHAIN PACKING AND ELECTRONIC BAND STRUCTURE OF THE RIGID-ROD POLYMER TRANS-POLY(p-PHENYLENE BENZOBISTHIAZOLE) IN THE CRYSTALLINE STATE. D. Bhaumik and J. E. Mark, Department of Chemistry and the Polymer Research Center, The University of Cincinnati, Cincinnati, Ohio 45221.

The extended Huckel method was employed to calculate electronic band structures in trans-poly(p-phenylene benzobisthiazole) (trans-PBT) in an attempt to elucidate the packing and electronic properties of these chains in the crystalline state. The unit cell energies thus calculated indicate that the most stable arrangement for trans-PBT corresponds to the chains in planar configurations, at an inter-planar spacing of 3.5 Å, and shifted axially by 3.0 Å relative to one another. These calculated results are in good agreement with experimental results obtained on the polymer and on relevant model compounds. No discernible dispersion of the energy bands perpendicular to the planes is observed, indicating that the neighboring chains are electronically non-interactive, as was found earlier for trans-polyacetylene and polyethylene. Similarly, the band gap of 1.69 e.V. in the axial direction for one of a pair of chains was nearly the same as that, 1.73 e.V., calculated previously for an isolated trans-PBT chain. These values are in the range 1.4 - 1.9 e.V. reported for trans-polyacetylene, which has been extensively studied because of its promise as a semi-conductor.

It is a pleasure to acknowledge financial support from the Air Force Office of Scientific Research, and to thank Professors R. Hoffmann and M.-H. Whangbo for providing some of their computational programs.

Abstract 4

A THEORETICAL INVESTIGATION OF CHAIN PACKING AND ELECTRONIC BAND STRUCTURE OF THE RIGID-ROD POLYMER TRANS-POLY(p-PHENYLENE BENZOBISTHIAZOLE) IN THE CRYSTALLINE STATE

BY

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Introduction

The rigid-rod polymer trans-poly(p-phenylene benzo-bisthiazole) (trans-PBT) (1), shown schematically in Figure 1, has been studied

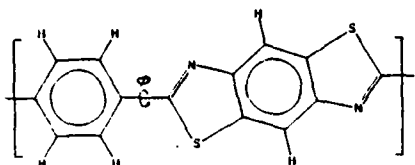


Fig. 1.

with regard to its electronic band structure in a preliminary way (2). This first attempt (2) at characterizing the electrical properties of this interesting class of polymers was very useful, but focused exclusively on the axial direction of the chains. Since the molecules form highly ordered fibers (1), however, it is possible to carry out experimental measurements perpendicular as well as parallel to the chain direction, and it thus becomes important to calculate the effect of inter-chain interactions on electronic properties. Obtaining such information on trans-PBT in the crystalline state was the goal of the present investigation. Specific aspects of particular interest were the use of band structures to elucidate chain packing arrangements, calculating the energy band gap perpendicular to the chains, and estimating the effect of inter-chain interactions on the band gap in the axial direction.

Theory

The delocalized crystalline orbitals required in the quantum mechanical approach employed were obtained using the tight-binding scheme based on the extended Hückel approximation (2-6). All valence atomic orbitals of the H, C, N, and O atoms were included; for S atoms, only s and p orbitals could be considered because of space limitations in the computer program.

In the present calculations lattice sums were carried out to second-nearest neighbors. The geometrical parameters (bond lengths and bond angles) (7-9) of the repeat unit of trans-PBT were obtained from the x-ray structural studies conducted on model compounds by Fratini and coworkers (7,8). Also relevant here is the fact that both experimental investigations (10) and molecular mechanics calculations (11) indicate that trans-PBT chains in the crystalline state are planar and at an inter-planar spacing of approximately 3.5 Å.

The unit cell for trans-PBT was taken to be two repeat units stacked one above the other and separated by 3.5 Å. To determine the relative axial shift between two chains, one chain was gradually shifted along its axis, in steps of 0.5 Å, to a maximum shift of 5.0 Å. In doing so, a portion of the repeat unit falls outside the unit cell boundary; therefore, the corresponding part of the repeat unit was introduced from the opposite side, within the unit cell boundary, keeping the number of atoms within the cell the same. The chain was shifted by a maximum value of only 5.0 Å (repeat unit length ~ 12.0 Å) because of the symmetry of the chains. In each step Δx of the shift, the dihedral angle ϕ around the C-C bond between the phenylene ring and thiazole part of the chain was varied in increments of 10° from 0° to 90° to determine the most probable configuration of the individual chains in the crystalline form. For each configuration and arrangement, the total energy per unit cell $\langle E_T \rangle$ is calculated (5,6) from its band structure as a function of the relative axial shift Δx and dihedral angle ϕ , respectively. The unit cell structure which corresponds to the minimum total energy is identified as the most stable packing arrangement.

Results and Discussion

The band structures of the trans-PBT unit cell along the perpendicular (inter-planar) direction are computed for different values of relative axial shift Δx and dihedral angle ϕ , and the total energy $E_T(\vec{k})$ plotted against the wave vector \vec{k} . The energy $\langle E_T \rangle$ per unit cell will be minimum when the corresponding $E_T(\vec{k})$ vs. \vec{k} curve encloses maximum area (because the $E_T(\vec{k})$'s are all negative). As is illustrated in Figure 2, the minimum

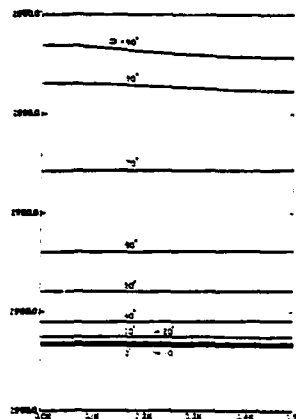


Fig. 2.

energy of the unit cell for any Δx corresponds to the $\phi = 0^\circ$ configuration of the individual chains, i.e., the chains favor the planar form in the crystalline phase, in agreement with experiment (10) and with the results of molecular mechanics calculations (11).

Abstract 4

The plots of $E_p(\vec{k})$ against \vec{k} for different values of the relative shift, with a fixed dihedral angle $\phi = 0^\circ$, are shown in Figure 3. It is clear from this figure that

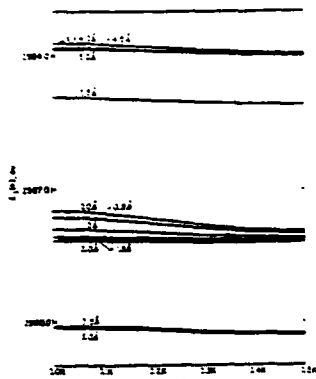


Fig. 3.

a relative shift of $\Delta x = 3.0 \text{ \AA}$ will be the most favourable arrangement of the chains. This value is somewhat smaller than the experimental value 4.5 \AA (7,8) obtained for a trans-PBT model compound, but the agreement between theory and experiment could, of course, be considerably better for Δx for the polymeric chains, which have not yet been studied experimentally in this regard.

The band structures calculated for trans-PBT in the perpendicular (inter-planar) direction show no detectable dispersion of the energy bands, which indicates that the neighboring chains are electronically non-interactive. Similar effects have been observed (12) in the band structures of trans-polyacetylene and polyethylene in the perpendicular direction. This weak chain-chain interaction should perhaps be expected at the large inter-chain separation (3.5 \AA) in trans-PBT chains. Although the sulfur d-orbitals had to be neglected, their inclusion probably would not change the band structure significantly because of this large spacing.

The band structure of the trans-PBT unit cell along the axial direction with $\Delta x = 3.0 \text{ \AA}$ and $\phi = 0^\circ$ is shown in Figure 4. The computed band gap along this direction is

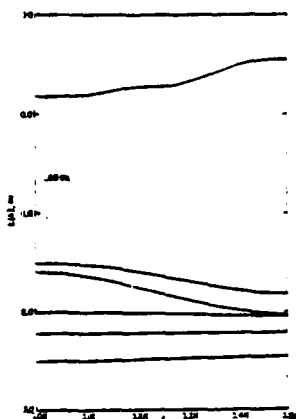


Fig. 4.

1.69 e.V., which is almost equal to the band gap 1.73 e.V. similarly calculated (2) but with neglect of interchain interactions. This is in agreement with the conclusion that neighboring trans-PBT chains interact only very

weakly. Most important, the band gap values are in the range 1.4 - 1.9 e.V. reported for trans-polyacetylene, which has been extensively studied because of its promise as a semi-conductor.

Acknowledgements

It is a pleasure to acknowledge financial support from the Air Force Office of Scientific Research (Chemical Structures Program, Division of Chemical Sciences), and to thank Professors R. Hoffmann and M.-H. Whangbo for providing some of their computational programs and some very helpful advice.

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10. Calculations of the Electronic Band Structures for Some Rigid Benzobisoxazole and Benzobisthiazole Polymers, D. Bhaumik and J. E. Mark, submitted to J. Polym. Sci., Polym. Phys. Ed.
11. A Theoretical Investigation of Chain Packing and Electronic Band Structure of the Rigid-Rod Polymer Trans-Poly(p-Phenylene Benzobisthiazole) in the Crystalline State, D. Bhaumik and J. E. Mark, in preparation.
12. Theoretical Investigations of Rigid-Rod Polymers, W. J. Welsh, D. Bhaumik, and J. E. Mark, in preparation.
13. Random-Coil Configurations of the Polyformals $[\text{CH}_2\text{O}(\text{CH}_2)_y]$. V. Dipole Moments, Unperturbed Dimensions, Optical Anisotropies, and Molar Kerr Constants for 1,3-Dioxolane Polymers Containing Structural Irregularities, E. Riande, E. Saiz, and J. E. Mark, Macromolecules, 13, 448 (1980).
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22. CNDO/2 Molecular Orbital Calculations on the Antifolate DAMP and Some of its Analogues, W. J. Welsh, J. E. Mark, V. Cody, and S. F. Zakrzewski, submitted to "Proceedings of the Seventh International Symposium on Pteridines and Folic Acid Derivatives", W. de Gruyter Pub. Co., Berlin, 1983.
23. Theoretical Investigation of Conformational Isomerism in the Alicyclic-Aromatic Molecule 2-(4-Morpholiniothio)Benzothiazole, D. Bhaumik and J. E. Mark, in preparation.

Preprints and reprints of all papers are sent to the Air Force of Scientific Research as they become available. Preprints of the papers dealing directly with the rigid-rod polymers are also sent to other investigators in the Air Force Ordered Polymers Program.

PROFESSIONAL PERSONNEL

1. Dr. J. E. Mark, Senior Investigator; Professor of Chemistry and Director of the Polymer Research Center, The University of Cincinnati.
2. Dr. W. J. Welsh, Postdoctoral Fellow and Adjunct Professor, The University of Cincinnati, and Assistant Professor, College of Mount St. Joseph.
3. Dr. D. Bhaumik, Postdoctoral Fellow, The University of Cincinnati.
4. Dr. J. L. Thiele, Postdoctoral Fellow, The University of Cincinnati.
5. Mr. K. Nayak, Graduate Student, The University of Cincinnati.
6. Dr. H. H. Jaffé, Professor of Chemistry, The University of Cincinnati.
7. Dr. J. L. Ackerman, Assistant Professor of Chemistry, The University of Cincinnati.

INTERACTIONS

1. Some of the above material has been presented as part of a general lecture on "Statistical Properties of Chain Molecules" at the University of Minnesota, Bell Telephone Laboratories, The University of Cincinnati, Istanbul Technical University, the Weizmann Institute of Science, Ball Corporation Laboratories, Du Pont Experimental Station, Batelle Columbus Laboratory, Drexel University, University of

Maine, University of Tennessee, Procter & Gamble Laboratories, Sandia National Laboratories, University of New Mexico, and Virginia Polytechnic Institute.

2. Paper #14 was presented at a meeting of the International Union of Pure and Applied Chemistry, Florence, Italy, September, 1980.
3. Papers #1-4 were presented at a National Meeting of the American Chemical Society held in Atlanta in March, 1981.
4. Papers #5 and 16 were presented at a National Meeting of the American Physical Society held in Phoenix in March, 1981.
5. Paper #17 was presented at a National Meeting of the American Chemical Society held in New York in August, 1981.
6. Papers #8-10, 21, and 23 were presented at a National Meeting of the American Chemical Society held in Las Vegas in March, 1982.
7. Papers #7, and 18-20 were presented at a National Meeting of the American Chemical Society held in Kansas City in September, 1982.
8. Paper #22 was presented at the Seventh International Symposium on Pteridines and Folic Acid Derivatives held in St. Andrews, Scotland in September, 1982.
9. Paper #11 will be presented at a National Meeting of the American Chemical Society to be held in Seattle in March, 1983.

10. Essentially all of the work on the rigid-rod polymers has been presented and discussed in detail at various Reviews of the Air Force Ordered Polymers Program, organized by Dr. T. E. Helminiak and held approximately annually at the Wright-Patterson Air Force Base in Ohio.



J. E. Mark

December 3, 1982

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