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Polarizabilities of Trans and Cis Polyacetylene and Interactions Among Chains in Crystalline Polyacetylene

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In this paper, we use the semi-empirical Hartree-Fock method, introduced within the finite electric field perturbation approach, to calculate the molecular and pi-system polarizabilities of trans and cis polyene $H(-CH=CH-)_n H$ (n = 3,4,5,...,18). The result is that for a given n, the order of both molecular and pi-system polarizabilities of polyene is trans > cis. This result is consistent with the order of experimental values of trans and cis hexatriene. When the n increases from 3 to 18, the contribution of pi-system polarizability to the molecular polarizability increases from 45% to 70%. Using these results, we have extrapolated the polarizabilities of both trans and cis polyacetylene. The order is trans > cis. These results and crystal parameters lead to an estimate of the dispersion energies among polyacetylene chains. The result is also E_{disp}(trans) > E_{disp}(cis).

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Polarizabilities of Trans and Cis Polyacetylene and Interactions Among Chains in Crystalline Polyacetylene

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ABSTRACT

In this paper, we use the semi-empirical Hartree-Fock method introduced within the finite electric field perturbation approach, to calculate the molecular and pi-system polarizabilities of trans and cis polyene $H(-CH=CH-)_nH$ (n = 3,4,5,...,18). The result is that for a given n, the order of both molecular and pi-system polarizabilities of polyene is trans > cis. This result is consistent with the order of experimental values of trans and cis hexatriene. When the n increases from 3 to 18, the contribution of pi-system polarizability to the molecular polarizability increases from 45% to 70%. Using these results, we have extrapolated the polarizabilities of both trans and cis polyacetylene. The order is trans > cis. These results and crystal parameters lead to an estimate of the dispersion energies among polyacetylene chains. The result is also $E_{disp}(trans) > E_{disp}(cis)$.

KEY WORDS: polarizability; polyacetylene; cis/trans; CNDO; dispersion energy

I. INTRODUCTION

Polyacetylene (PA) is an important conductive polymer which has two isomers - trans and cis (see Fig. 1). Since PA was synthesized[1,2] and it was found that the conductivity of doped PA rapidly increases from 10^{-6} $(\Omega cm)^{-1}$ to as high as 10^3 $(\Omega cm)^{-1}$ with increasing dopant concentration,[3] much experimental and theoretical research[4,5] has been reported, including differences between trans and cis PA.[6-8] Polarizability is an important property of a material and closely related to interactions among molecules and the dielectric coefficient of the material. Because PA is relatively insoluble and decomposes before melting,[9] these experimental difficulties have so far precluded the measurement of the polarizability of either trans and cis PA.

Davies[10] has studied the pi-system polarizabilities of the trans polyene series, using the perturbed HMO method. He found that the α_{xx}^{π}, which is the component of pi-system polarizability along the carbon chain, is proportional to the L^3, where L is the length of carbon chain. Recently, Hurst et al[11] have calculated the polarizabilities of trans polyene series, $H(-CH=CH-)_n H$ (n = 2,3,...,11), using the *ab initio* coupled-perturbed Hartree-Fock method, and the extrapolated polarizability of trans PA is 60.3 a.u./C2H2. To our knowledge, no study of the polarizability of cis-PA and the contribution of the pi-system polarizability to molecular polarizability has yet been reported. It is therefore interesting to calculate and compare the pi-system and the molecular polarizabilities of both cis and trans PA, and to discuss their differences, which is the purpose of this article.

II. THE METHOD

Because PA can be considered an infinite polyene and given the difficulty of directly calculating the polarizability of an infinite polymer, the best method available is to calculate the polarizabilities of a series of polyenes with finite chain length, and then extrapolate to the infinite limit, i.e., PA. Hence the longer the polyene chain, the more reliable the extrapolated result for PA may be expected to be. We therefore choose a method for which chain length is not a severe limitation.

Zyss et al[12,13] have calculated the polarizabilities of many conjugated molecules using the semi-empirical Hartree-Fock method introducing a finite electric field perturbation, obtaining good results. This method can be briefly described as follows. If $\hat{H}_o$ is the single-electron Hamiltonian operator of an unperturbed system and $\vec{F}$ is a finite external electric field, the single-electron Hamiltonian of the perturbed system is

$$\hat{H} = \hat{H}_o + \vec{r}\cdot\vec{F} \tag{1}$$

where $\vec{r}$ is the coordinate vector of the electron, and where we have used $F = 10^{-4}$ a.u.[13]. Substituting eq. (1) into the Hamiltonian operator in the Roothaan equations,[14] one obtains the molecular polarizability as

$$\alpha_{ii} = [\mu_i(F=F_i) - \mu_i(F=0)]/F_i \tag{2}$$

$$\alpha = \frac{1}{3}\sum_i \alpha_{ii} \qquad (i = x,y,z) \quad , \tag{3}$$

where μ_i is the component of the molecular dipole moment along the i-axis.

Given the desirability of performing the calculation on as large a polyene molecule as possible, we choose a semi-empirical method (CNDO/2)[15] instead of an *ab initio* technique. Considering the importance of the pi-system in polyene and PA, we are especially interested in the contributions of the $2p_z$ (pi) electron to the molecular polarizability, and these are reported separately as α^{π}.

In Table 1, we list the relative experimental values[16] and our calculated results for the polarizabilities of trans and cis hexatriene. The structure parameters of hexatriene come from experimental values.[17,18] Our results are consistent with experiment and demonstrate the reliability of this method.

Only a few structure parameters of polyene molecules have been determined, and these all approach the standard values: L(C=C) = 1.35 A, L(C-C) = 1.45 A, ∢CCC = 120°, the same as the case for the determined and optimized PA parameters.[19,20] Therefore we take the standard parameters as the structure parameters of both trans

and cis polyene. The coordinate system is as shown in Fig. 1. It is possible to distinguish between trans and cis forms only for n ≥ 3, and hence our calculation starts with n = 3.

III. RESULTS

In Table 2 we list pi-system and molecular polarizabilities and the contributions of pi-system to molecular polarizability. Some of this data is illustrated in Fig. 2. From these results, we derive the following conclusions:

[1] When n is the same, the order of both molecular and pi-system polarizabilities of trans and cis polyene is: trans > cis, also shown in Fig. 2. This order is consistent with the order of experimental polarizabilities of trans and cis hexatriene.

[2] The molecular polarizability of polyene mainly comes from the contribution of the pi-system. The longer the carbon chain, the larger the contribution of pi-system. When n increases from 3 to 18, the contribution of pi-system increases from 45% to 70%.

[3] A value for $\alpha^\sigma/n = \alpha/n - \alpha^\pi/n$ is easily calculated. This difference is nearly constant over the entire range of n, as shown in Fig. 2. This means that the polarizability of the sigma-system in a -CH=CH- unit for various polyenes is the same, which obviously differs from the pi-system. The σ polarizability is essentially independent of chain length. This differs from the π polarizability because of the delocalized nature of the π system.

To generalize the polyene results to PA, we require a function which accounts for the fact that $d[\frac{\alpha}{n}]/dn \rightarrow 0$ for large n. The proposed function[11] is

$$\log(\alpha/n) = a + b/n + c/n^2 \quad . \tag{4}$$

This implies that $\lim_{n\rightarrow\infty} \alpha/n = 10^a$ for PA. Our values and Hurst's are compared in Table 3. The relative polarizabilities of the cis and trans PA are in the same order as for the polyene series. However, the pi-electron contribution for PA is larger than for polyene, as shown in Table 3.

IV. DISCUSSION

We begin by considering the reasons why the trans isomer polarizability is larger than for the cis. First are geometric considerations. If L is the length of the carbon chain, $L = n \times \ell$, then ℓ is the length of the projection of a unit cell [-CH=CH-] (including both a C=C and C-C bond) on the x-axis. In our calculation, ℓ is equal to 2.425 A and 2.125 A for trans and cis polyene, respectively. The projection of trans is larger than cis by 0.3 A. This makes the conjugation length of the trans polyene pi-system longer than cis polyene's by n x 0.3 A, when n is the same. This is the main reason that both pi-system and molecular polarizabilities of trans polyene are larger than cis polyene.

Besides the difference in x-axis projection length between the trans and cis unit structures, we consider another factor affecting polarizability magnitude. The unit cell of trans PA consists only of one -CH=CH- segment, whereas a unit cell of cis PA consists of two -CH=CH- segments, as shown in Fig. 1. This demonstrates that the translational symmetry of trans PA is higher than cis PA. Clearly, the higher the translational symmetry, the larger the delocalizability, and the larger the polarizability. Thus one would expect the trans and cis isomers to differ is subtle chemical respects in addition to geometrical effects. We expect similar effects for finite polyenes as well.

Two functional forms to describe the polarizability of trans-polyene have been given in the literature. Hurst et al[11] suggest that $\alpha \approx N^\gamma$, where they find $\gamma \approx 1.6$ for small polymers. However, if the delocalization length is finite, then γ must also be a function of n and must eventually tend toward 1, i.e., the polarizability is proportional to n. We specify the proportionality constant as

$$\alpha = Cn^\gamma \tag{5}$$

where two parameters, C and γ, are to be fitted to the data. Equation (5) will provide some significant physical insight in what follows.

Hurst et al[11] have proposed yet another function, given by eq. (4). Parameter a has clear physical significance already mentioned. Parameters b and c only influence the behavior at small n, and from physical arguments (i.e., a less conjugated system), we know that $b < 0$. We have fitted our data to the Hurst

function for *trans* PA, with the results are shown in Table 3. It is seen that our value for *a* corresponds with that of Hurst very closely, and thus our value for the PA polarizability is close to that obtained by Hurst. This implies that as the chain becomes longer, the values obtained for the polarizability will more closely match the *ab initio* results. Since Hurst used polyenes with n - 2, 3,...,11, and we use n - 3, 4, ...,18 from which to extrapolate the polarizability of PA, this implies that the semi-empirical method with minimal Slater type basis can closely match the *ab initio* result. However, parameters *b* and *c*, which affect short-chain behavior, are less reliable.

The physical significance of the power law (eq. 5) depends on how C is defined. If C is defined as C_∞, the limiting value of α/n as $n \to \infty$, then $C_\infty - 10^a$, identical to the limiting value in eq. (4), and eq. (5) is valid for large n when γ - 1. On the other hand, if C is defined as C_0, the polarizability of the $-C2H2-$, i.e., α for n - 1, so that the form can be fitted to small n but will be incorrect in the large n limit if γ is assumed to be constant. Further, in this case it is apparent that γ cannot converge to unity since then the polarizability of the infinite chain would equal that for n - 1. Finally, C_0 must be equal for both cis and trans polymers, and therefore has a very definite physical meaning. It is clear that γ has a different physical interpretation depending on how C is chosen.

A least squares fit to determine C_0 in the trans and cis cases reveals 17 a.u. ± 1 a.u. Given C_0 - 17, it is then possible to plot the necessary value of γ from the CNDO and Hurst data. This is shown in Fig. 3, and several points can be made. First, we note that values for γ are larger in the trans case than for the cis. This is consistent with the value of *a*, and with the notion that the trans form has a larger polarizability. Secondly, it is apparent that γ goes through a maximum at approximately n - 9 for the cis isomer, and n - 10-11 for the trans isomer. This probably reflects a distance related to the delocalization effect in polyene, indicating that electrons are delocalized over a larger region in the trans isomer than the cis.

Figure 4 illustrates the α_{xx}^π/n and the α_{xx}^π/n^2 for trans polyene. Using HMO theory (infinite delocalization length), Davies[10] showed that this ratio should increase proportionally to n^2 for trans-PA. If the delocalization length were

infinite, then one would expect the HMO theory to be accurate, but Fig. 4 indicates that it is not valid. Therefore, the existence of a typical delocalization length is further indicated.

V.   THE DISPERSION ENERGY OF CRYSTALLINE PA

The crystal structure parameters of both trans and cis PA have been determined[20,21] and are similar to each other (see Fig. 5 and Table 4). Because PA is a nonpolar material, we can estimate the dispersion energy among PA chains in crystals as

$$E_{disp} = - \frac{3}{4} \times \frac{\alpha^2 I}{R^6} \quad , \tag{6}$$

where I is the ionization energy of PA,[22] and R is the distance between centers of two chains. The calculated results and relevant parameters are listed in Table 4, and E_{disp} is the sum of the dispersion energies between chain 1 and chains 2, 3, 4, 5, 6, 7, 8 & 9, respectively. We use the extrapolated α/n for PA, as calculated above, and the all centers of nine PA units are on the same plane. Consistent with our previous results, E_{disp} for the trans PA is larger than for cis. These are shown in Table 4.

VI.   CONCLUSION

We have calculated the polarizability of a series of trans and cis polyene molecules. Our results compare favorably with those of Hurst.[10] The data have been fitted to an appropriate function, and it is found that our data and Hurst's have the same limiting behavior. We therefore conclude that the polyene data may be extrapolated to provide information about polyacetylene.

Further, we have considered the relative polarizability of trans and cis polyene, and we show that trans has a larger polarizability than cis. An inquiry into the reasons for this phenomena indicate that it is a function of geometry and of symmetry.

Finally, we have presented data on the crystal dispersion energy. We find dramat. differences between the trans and cis forms, which should in principle be measurable, thereby allowing experimental confirmation of our results.

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Table 1. Polarizabilities of Trans and Cis Hexatriene

(unit: a.u.)

| | Present Work | Experimental Data [16] | | |
	α	Refractivity	Density (g/cm^3)	α
Trans	73.1920	1.5135	0.7369	87.4565
Cis	71.1604	1.4577	0.7175	81.4466

Table 2. Polarizabilities of Trans and Cis Polyene

$H(-CH-CH-)_n H$ (unit: a.u.)
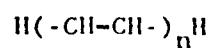
n	Trans			Cis		
	α_π	α	$\alpha_\pi/\alpha(\%)$	α_π	α	$\alpha_\pi/\alpha(\%)$
3	33.03	73.20	45.13	31.62	71.62	44.16
4	55.37	109.01	50.80	51.45	104.71	49.14
5	82.24	149.22	55.11	74.59	141.05	52.88
6	112.84	193.06	58.45	100.40	180.02	55.77
7	146.54	239.94	61.07	128.37	221.10	58.06
8	182.39	289.13	63.17	157.94	263.76	59.88
9	221.13	340.31	64.98	188.91	307.78	61.37
10	260.65	393.11	66.30	220.64	352.54	62.59
11	302.33	447.67	67.53	253.61	398.50	63.64
12	344.77	502.97	68.55	287.06	444.98	64.51
13	388.20	559.97	69.40	321.05	491.95	65.26
14	432.54	616.34	70.18	355.52	539.39	65.91
15	477.17	673.86	70.81	390.16	586.98	66.47
16	522.56	731.85	71.40	425.08	634.87	66.95
17	568.11	790.25	71.89	460.35	683.11	67.39
18	614.15	848.86	72.35	495.77	731.47	67.78

Table 3. Polarizabilities per -C2H2- of Trans and Cis PA

(unit: a.u.)

	a	α_π	a	b	c	α	α^π/α
Present Work							
Trans PA	1.6903	49.012	1.7782	-2.0830	2.7304	60.007	81.67%
Cis PA	1.5710	37.239	1.6918	-1.6389	2.0907	49.181	75.72%
ab initio (6-31G)[11]							
Trans PA			1.7803	-1.8398	1.8920	60.298	

Table 4. The E_{disp} Among Chains and Relevant Parameters of Trans and Cis PA

	Trans PA	Cis
Cell Parameter (unit: A, degree)[20,21]		
A	4.24	7.61
B	7.32	4.39
C*	2.46	4.47
α	90.	90.
β	91.5	90.
γ	90.	90.
Ionization Energy (a.u.)	0.243	0.246[22]
E_{disp}(kc/mol)	9.873	5.194

* The C-axis is along the carbon chain, and the repeat unit along the C-axis is -C2H2- for trans PA and -C4H4- for cis PA.
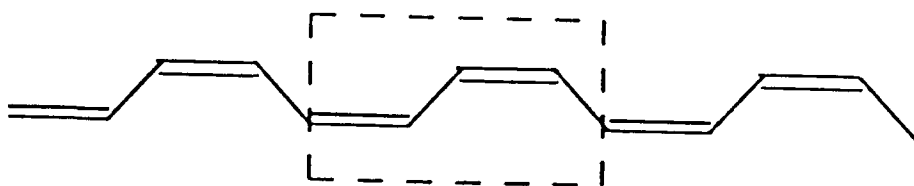
FIGURE CAPTIONS

Fig. 1   Diagram of the geometry of trans (a) and cis (b) polyacetylene.   The polyacetylene unit cell is indicated by the dashed lines.   The coordinates used in this calculation are illustrated, with the z-axis taken as perpendicular to the page.   The origin is chosen as the center of mass for each member of the polyene series.

Fig. 2   Polarizability of polyene as a function of chain length, comparing the trans and cis isomers.   Also shown are the *ab initio*[11] results and the sigma-electron polarizability for the trans species.   The sigma-electron polarizability for the cis isomer is almost identical.

Fig. 3   Parameter γ versus polyene length.

Fig. 4 α^{π}_{xx}/n and α^{π}_{xx}/n^2 for trans-polyene.

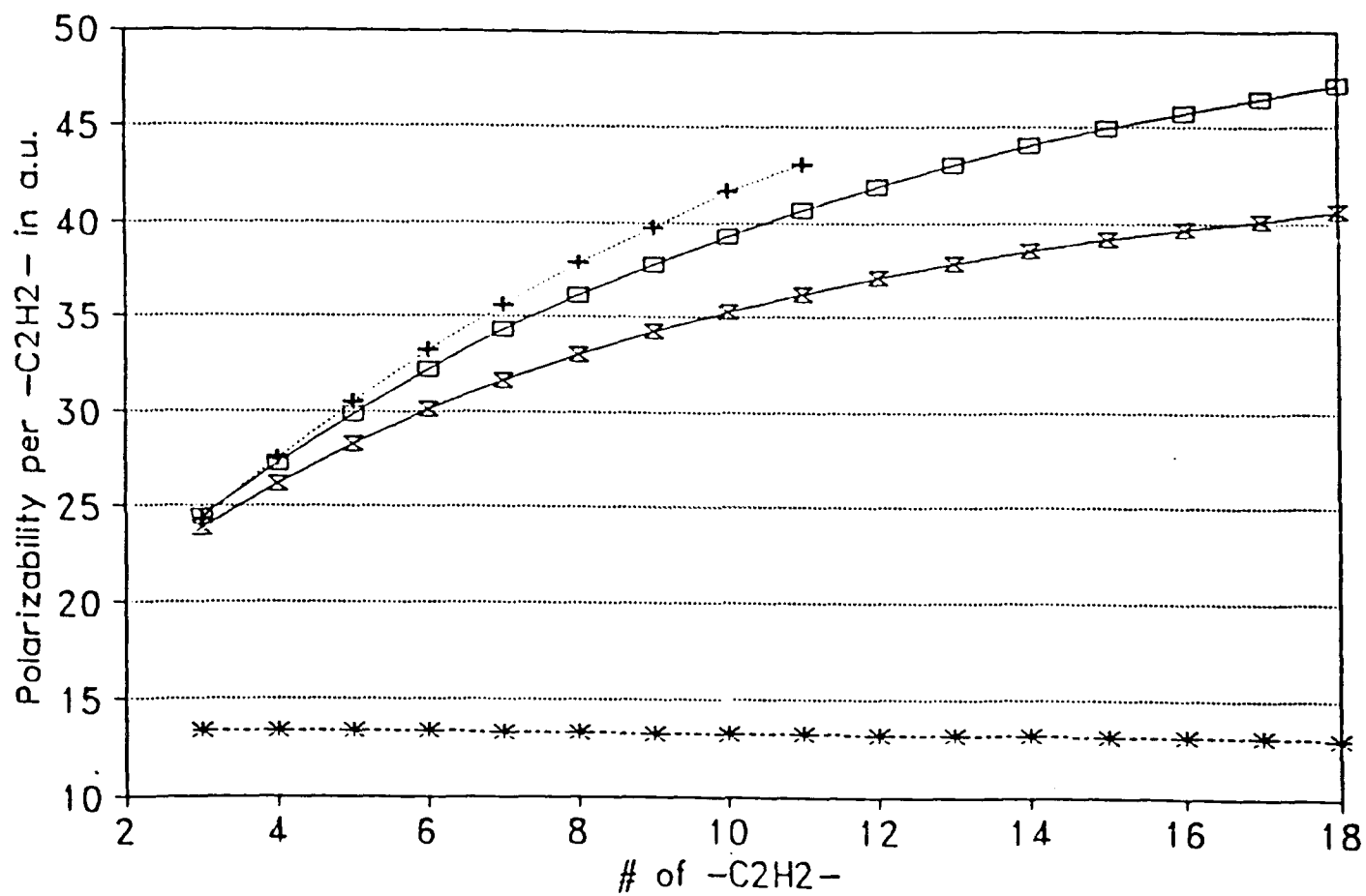Fig. 5   The (001)-plane for the crystal unit cell of trans and cis polyacetylene.

Fig. 1.

(a)

(b)

Fig. 2

Fig. 3

Fig 4

Fig 4

Fig. 5.