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X-Ray Diffraction by Thermotropic Main-Chain Polymers Having Side Groups: Part B. Rigid Polyesters

by

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X-Ray Diffraction by Thermotropic Main-chain Polymers Having Side Groups: Part B. Rigid Polyesters

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Synopsis

Thermotropic poly(sulfonyl hydroquinone terephthalate) with either H or CH_3 in the lateral substituent, was aligned by drawing from nematic melts. Virtually identical x-ray intensity distributions were recorded consisting of 'disks' of intensity periodically spaced along the meridian and concentric rings of intensity lying in the equatorial plane of reciprocal space. They correspond to what is expected for the hexagonal packing of parallel periodic chains that are randomly displaced along the chain axes. Using interactive graphics, appropriate molecular models were deduced in conformity with the observed diffraction intensities.

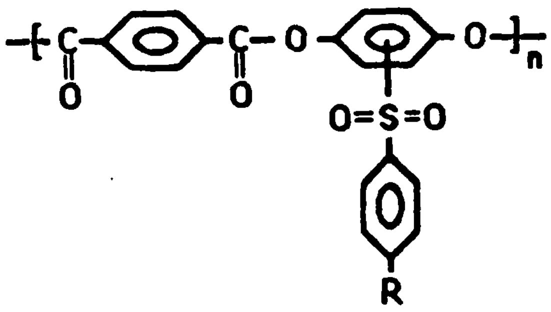
INTRODUCTION

Improvements in tensile strength that accompany increased rigidity (tighter bonding) in long-chain molecules composed of anisometric monomers must be weighed against the consequent increase in the melting point -- often to unattainable temperatures below which the polymer decomposes. The factors that control the relative rigidity of polymers exhibiting thermotropic properties at functional temperatures have been studied for some time.[1,2] Thus it is known that both the melting and isotropization temperatures can be lowered in four ways: (1) the introduction of flexible spacers between the anisometric monomers (discussed further in Part C);(2) the placement of lateral substituents (side groups) on the repeating units; (3) the introduction of bends or kinks in the repeating monomer; or (4) by random copolymerization of two or more comonomers. The molecular structures of copolymers have been studied effectively using x-ray diffraction[3,4] whereas only limited attempts have been made so far to characterize the molecular arrays in more rigid liquid-crystalline polymers[3,5] (LCPs).

The present study was undertaken to establish the molecular structure of rigid thermotropic chains having lateral substituents that lower the melting points sufficiently to make the mesophase accessible to study before the sample decomposes. The particular polymers selected have the same chemical structure as do the semiflexible polymers discussed in Part C. Thus it is possible to compare the packing of the 'same' kinds of chains in a rigid and semiflexible form.

EXPERIMENTAL

Two thermotropic polyesters based on a diad ester mesogenic unit containing an arylsulfonyl substituted hydroquinone group were selected for this study. The resulting poly(sulfonyl hydroquinone terephthalate), abbreviated PSHQ-TPA, has the following structure:



where R is H or CH_3, respectively.

The thermal properties of both polymers were examined first using differential scanning calorimetry. The melting points are indicated in Table I but the clearing temperatures could not be reached before the samples decomposed. Next, the density of both polymers was measured by flotation in an aqueous solution of potassium carbonate at 25°C and found to have the values shown to the right in Table I. These values can be compared to the lower packing density (1.17 ± 0.01 g/cc) of like semi-flexible chains having the same two lateral substituents.

TABLE I

Thermal transition points and densities

Substituent at R	T_m(°C)	T_i(°C)	Density(g/cc)
H	265	>390	1.31
CH_3	201	>390	1.33

Cylindrical samples for x-ray diffraction were prepared by drawing fibers directly from the nematic melts. All of these samples were examined in a Buerger precession camera, using Cu Kα radiation from an 18 KW rotating-anode generator monochromatized by a bent graphite crystal, before and after further annealing for several hours at temperatures just below the melting points. The subsequent structural interpretations were carried out using a Quantimet 900 to measure the recorded intensity distributions and Evans and Sutherland PS300 interactive graphics to model the molecular structures.

RESULTS AND DISCUSSION

Figure 1 typifies the x-ray diffraction photographs recorded. No significant differences were noted between mechanically aligned samples and those subsequently annealed. The intensity distribution recorded is exactly what is expected from a close-packed array of rigid-rod-like chain molecules.[6] The reciprocal-lattice coordinates transposed to direct space yield the values listed in Table II where the $hk0$ indices were assigned assuming a hexagonal net [expression (5) in Part A] with $a = 1.44_4$ and 1.56_7 nm, respectively, for H-PSHQ-TPA and CH_3-PSHQ-TPA. The length of the repeat unit deduced from the 00ℓ spacing of 1.22 ± 0.01 nm can be compared with that for the extended PSHQ-TPA unit, 1.27 ± 0.01 nm calculated using known bond distances.

TABLE II

Spacing values corresponding to x-ray maxima (nm)

$hki\ell$ / Polymer	$10\bar{1}0$	$11\bar{2}0$	$30\bar{3}0$	0001	0002	0003	0004
H-PSHQ-TPA	1.26_3	0.71_6	0.41_7	1.19_3	0.60_4	0.40_7	0.30_8
CH_3-PSHQ-TPA	1.36_5	0.78_0	0.45_2	1.20_3	0.60_3	0.40_7	0.30_6

The molecular structure corresponding to the observed intensity maxima was modeled with the aid of interactive graphics which permit the depiction of a molecule either in skeletal (outline) form or with the constituent atoms represented by spheres of appropriate (van der Waals) radii. Because it is easier to examine a structure in three dimensions while looking 'through' individual molecules as they are moved about relative to each other, the skeletal display is preferred. The effective volume 'belonging' to each monomer, resulting from its rotational freedom about the chain axis, can be represented by a prism (since a cylinder cannot be depicted by the available instrument). For present purposes, an octagonal prism was selected to represent the monomer with the attached hydroquinone group portrayed in skeletal outline. A side view of such rigid chain molecules is shown in Fig. 2. The relative displacement of the chains are random and the lateral groups are shown in one of many possible dispositions, the only restriction placed on them being that they not impinge on each other.

A view of this array along the chain direction is shown in Fig. 3. As can be seen therein, the most efficient packing of parallel chains (octahedra in cross section) occurs when they fall upon the nodes of a hexagonal net. To accommodate the lateral hydroquinone groups, alternate nodes (surrounded by six chains forming a hexagon) were left unoccupied. Note that these nodes, in turn, constitute a hexagonal net whose unit cell is outlined in solid lines in Fig. 3. The dimensions of such cells, however, do not conform with the values deduced by x-ray diffraction (Table II) and the calculated density exceeds the measured value. By removing an additional chain, it is possible to produce the array depicted in Fig. 4. The side groups are shown displaced (arbitrarily) in such a way that two side groups fall in the site vacated by the removed chain. The calculated density of this array is reduced to 1.43 and 1.27 g/cc for the H and CH_3 substituted side groups, respectively. The resulting larger unit cell is indicated by solid lines in Fig. 4 and agrees well with the measured x-ray values in Table II when the appropriate dimensions of the side groups are inserted in the model. It is readily apparent in Fig. 4 that the densely populated ($hk0$) planes have indices $(10\bar{1}0)$, $(11\bar{2}0)$ and $(30\bar{3}0)$ so that their diffraction intensities should be and are considerably larger than those of the unobserved $20\bar{2}0$, $21\bar{3}0$, and $22\bar{4}0$ reflections.

Although the idealized packing shown in Fig. 4 epitomizes the molecular array giving rise to the observed x-ray intensity distribution (Fig. 1), the molecules in the nematic state of an LCP have considerable freedom of motion. Even in the quenched-in array, the chains may not occupy the lattice nodes in Fig. 4 exactly so that observed $hk0$ reflections are not sharp. If the relative mean-square displacements $\bar{u}^2$ of a chain from the mth lattice node are small and random but interdependent on the like displacements of the nth chain, it is possible to posit an interchain coefficient α_{mn} such that $\alpha = 1.0$ when $m=n$ (i.e., chains m and n occupy the same node) and $\alpha \rightarrow 0$ as the interchain separation increases. It is readily shown[7] that this leads to an intensity dependence

$$I \propto \exp(-2M) \sum_{m} \sum_{n} 2M\alpha_{mn} \exp(2\pi i/\lambda)(S-S_o) \cdot (R_m-R_n) \qquad (1)$$

where $2M = (4\pi \sin\theta/\lambda)^2 \bar{u}^2$ has the same form as the familar Debye-Waller factor. The intensity distribution in (1) has maxima when the Laue conditions are satisfied and increases in breadth with increasing diffraction angle θ, i.e., as $hk\ell$ increases. Thus the broadening due to random displacements of the chains reinforces the broadening due to temperature induced vibrations of the molecules.[8]

CONCLUSIONS

Making use of the entire intensity distribution in reciprocal space, it is possible to deduce a molecular packing model for the rigid thermotropic main-chain polyester that corresponds directly to the observed intensity values, shapes, and locations. The availability of interactive graphics to examine various possible models rapidly and from all angles in three dimensions greatly facilitates such an analysis. It is shown that the two polyesters examined represent 'textbook examples' of the hexagonal packing of rigid-rod-like chains with no correlations between the relative displacements of the homopolymers along the chain directions.

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Figure Legends

Fig. 1. Zero-level precession photograph of hydrogen-substituted PSHQ-TPA ($\bar{\mu} = 1°$, F = 60 mm).

Fig. 2. Side view of a single layer of extended PSHQ-TPA chains randomly displaced along the chain direction.

Fig. 3. End view of hexagonal packing of PSHQ-TPA chains with unit cell outlined and $(11\bar{2}0)$ and $(\bar{1}2\bar{1}0)$ planes indicated by dotted lines.

Fig. 4. End view of correct packing of PSHQ-TPA chains with the unit cell outlined in solid lines.

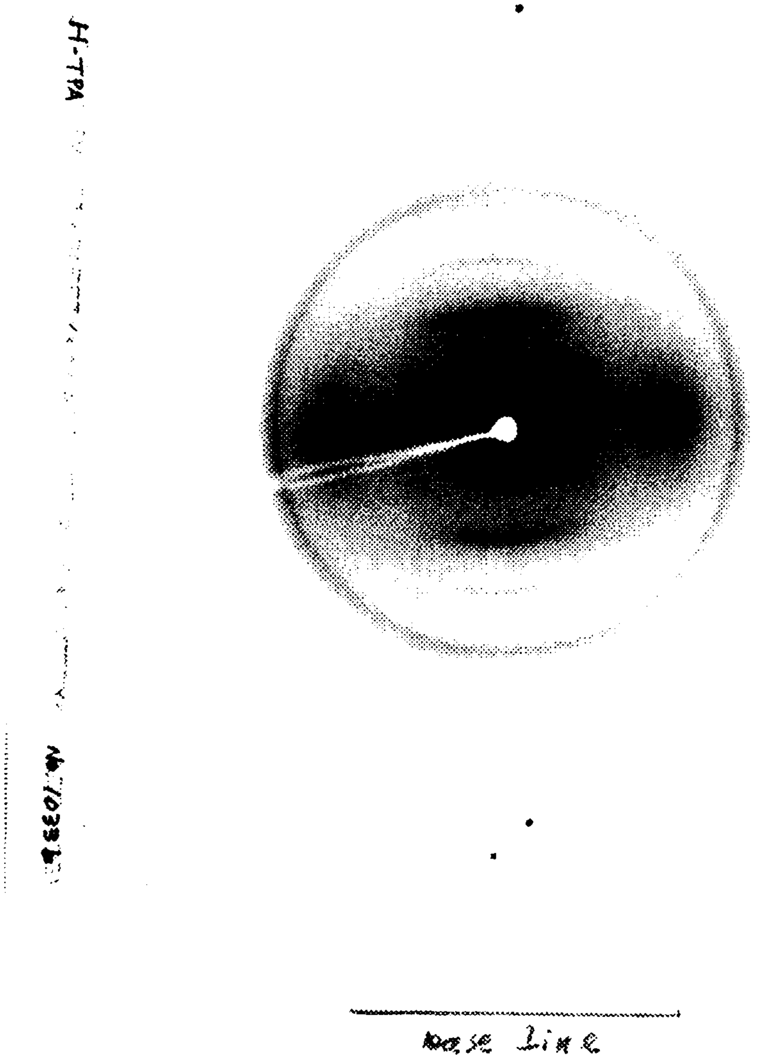

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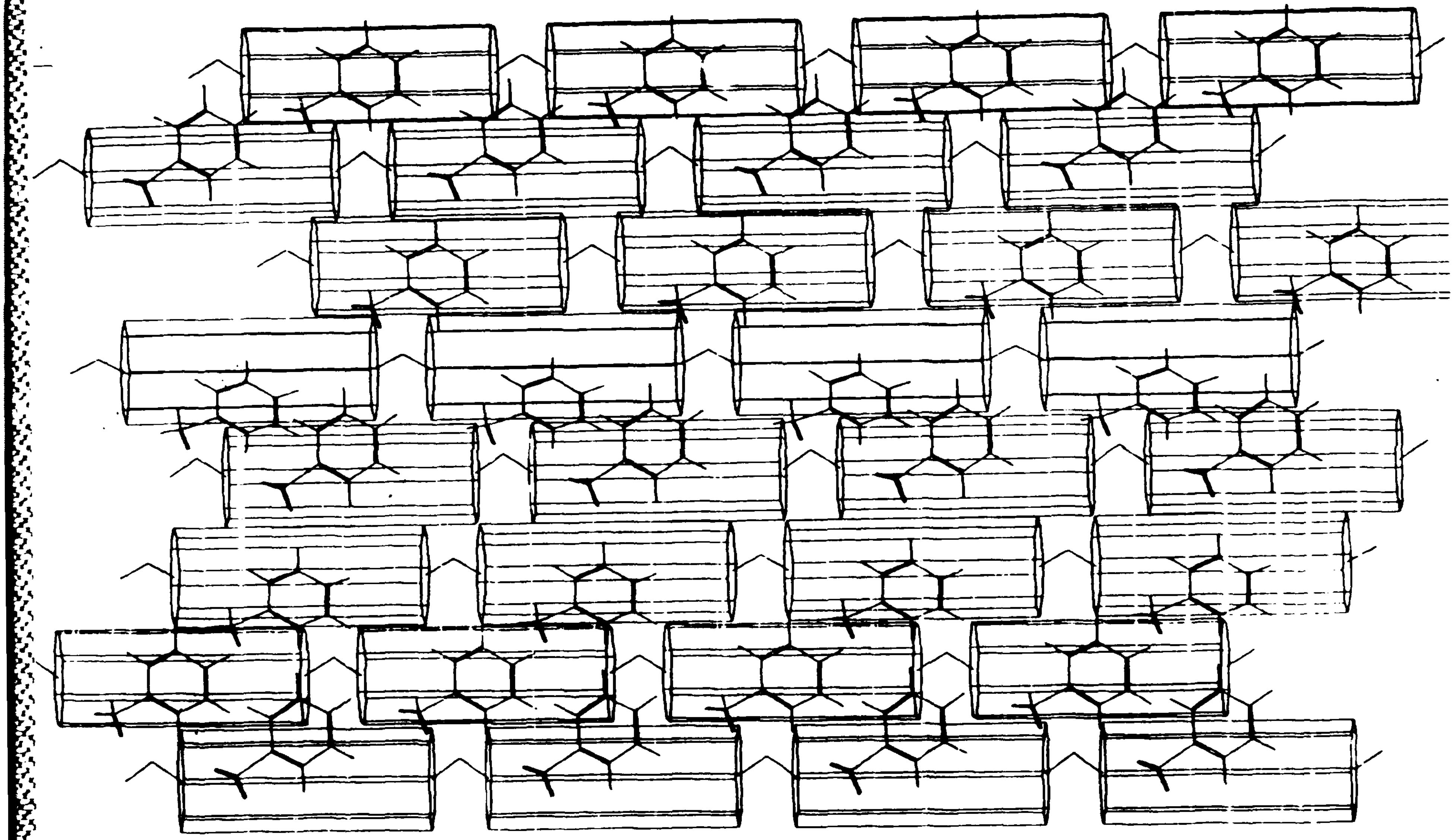
Fig. 2



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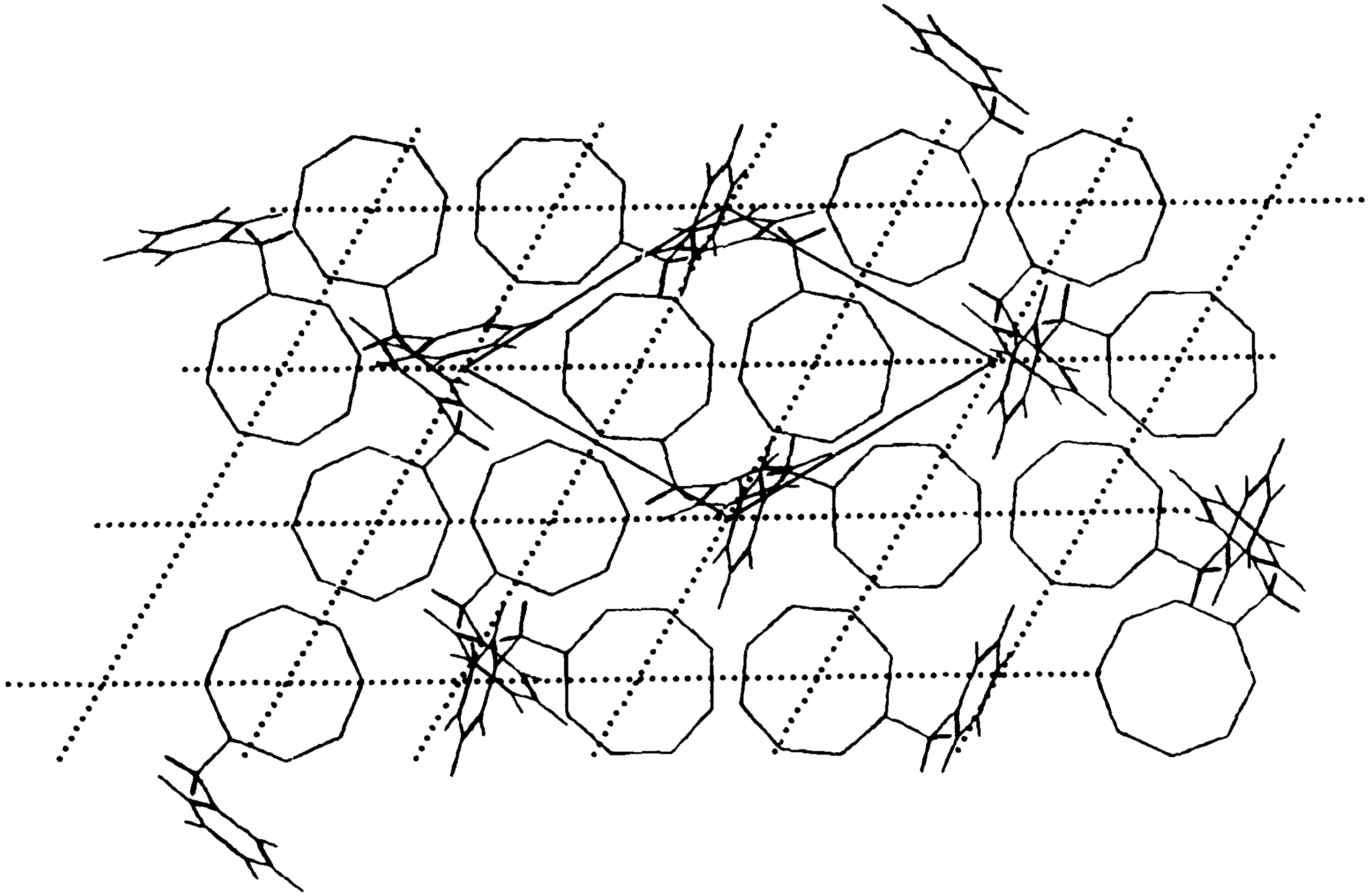

Fig. 3

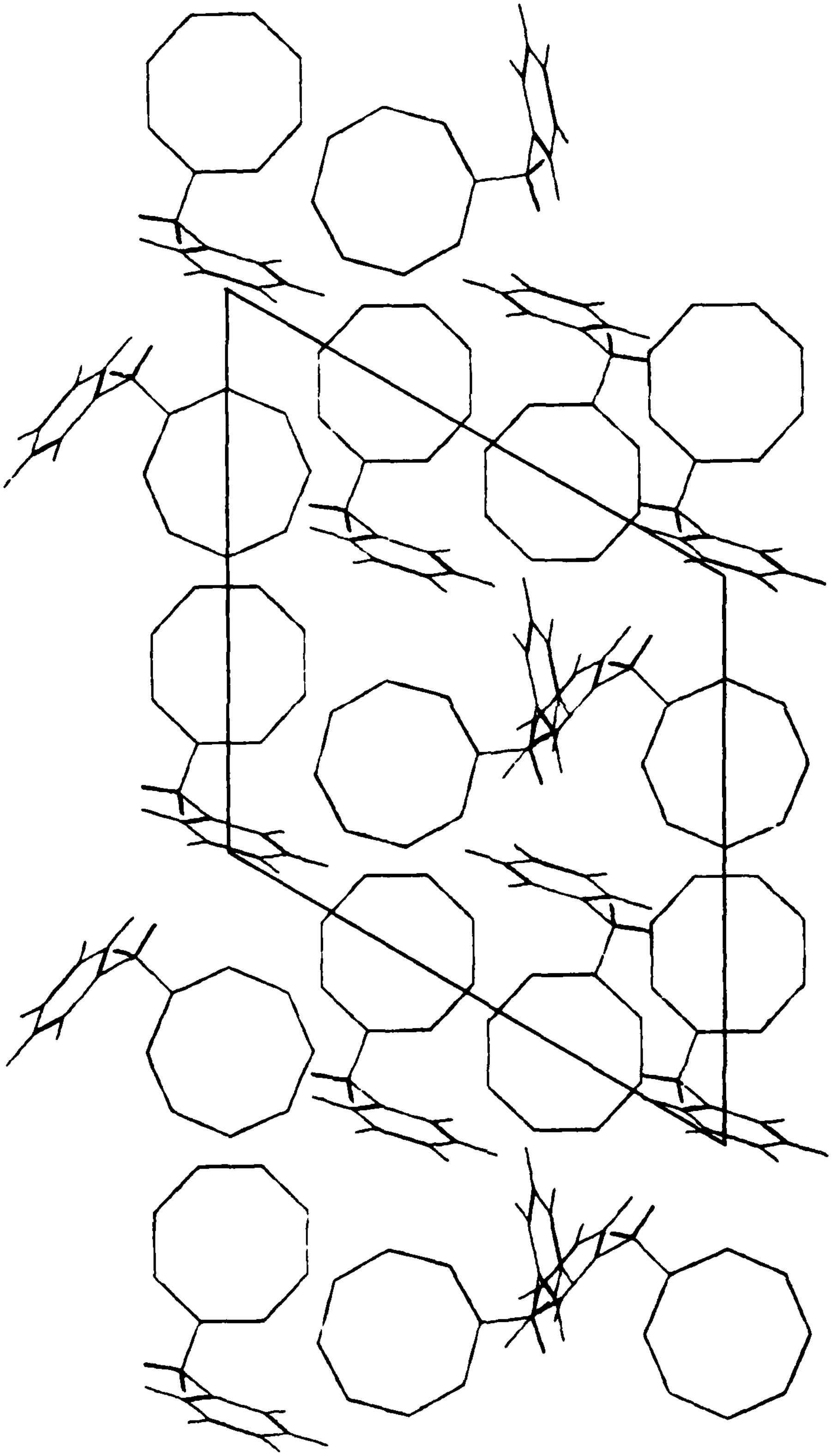

Fig. 4

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