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Melting and crystal structure: the melting parameters of some polyphenyls

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[Plate 4]

Melting mechanisms have been studied for diphenyl, and *o*-, *m*- and *p*-terphenyl.

The *volume increase on melting* is largest for the linear polyphenyls and smallest for branched molecules which can interlock in the melt. In no case will the volume increase permit the 'onset of rotation' on melting.

Viscosity measurements give marked indications of the growth of cybotactic groups in the melts on approaching the freezing-points, especially in the case of *o*-terphenyl, where the ratio $H_{\text{vap.}}/E_\eta$ reaches exceptionally low values near the freezing-point. Plots of *fluidity against specific volume* and the marked tendency of the melt of *o*-terphenyl to supercool give further indications of the presence of interlocked groups of molecules in the melt.

Introduction

In studying mechanisms of melting of crystals, one line of attack is to use units of structure which are extremely simple, such as atoms of the inert gases, or molecules which are effectively spherically symmetrical. For such cases theoretical descriptions of the solid and liquid state, though still not fully adequate, are beginning to permit calculation of important melting parameters, such as the volume and entropy changes on fusion, and thermodynamic and transport properties of the melts. On the other hand, for more complex units of structure more than one mechanism of melting may contribute to the transformation from solid to liquid. To make progress in the experimental study of melting of crystals containing these less simple units of structure it is helpful to compare the behaviour of molecules of closely related structure, where small variations can be introduced by chemical synthesis.

One unit of structure which is of extremely widespread importance is the six-membered aromatic ring of carbon atoms. Studies of melting of molecules consisting of fused aromatic nuclei have shown (Al-Mahdi & Ubbelohde 1953) that in many cases any randomization of orientation of the molecules on melting is far from 'complete rotation'. Studies of transport processes such as viscous flow in the melts show that clusters of roughly co-operative molecules increase in importance as the temperature approaches and traverses the freezing-point (Al-Mahdi & Ubbelohde 1955). The present research deals with the melting parameters of polyphenyls in which the groups are linked with each other by a single C—C bond. Though restricted oscillations of the phenyl groups with these C—C bonds as axes may play some part in the melting process, in such molecules conjugation and intramolecular repulsions prevent any extensive crumpling of the carbon skeleton.

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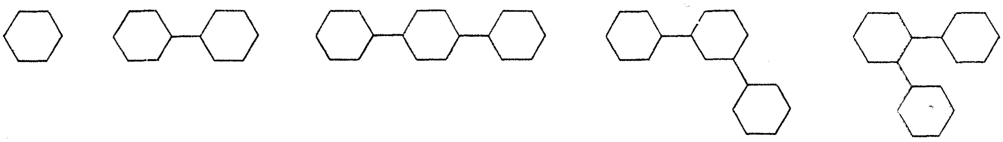
Because of the stiffness of the carbon skeletons, it is possible to compare experimentally the behaviour of 'model melts' containing units of structure which may be symbolized as



In no case is the volume increase on melting found to be sufficient to permit 'rotation' in the melt. Furthermore, on cooling the melts, as the melting-point is approached, transport properties such as the viscosity show marked signs of the formation of interlocked clusters of molecules or 'cybotactic' groups. This behaviour is particularly marked for *o*-terphenyl melts. Since these also show the most pronounced tendency to supercool, the clusters formed on melting appear to differ in average structure and properties from the more ordered molecular aggregates which can act as 'crystal nuclei'. The cybotactic clusters are also too small to exhibit optical anisotropy in the melts; in fact, using ordinary wave-lengths of visible light, the first polyphenyl to show 'liquid crystal' behaviour is *p*-quinquephenyl (Vorländer 1927). Further evidence for the extensive interlocking of molecules in melts such as *o*-terphenyl is obtained from comparisons of the activation energy for viscous flow, E_η, with the latent heat of vaporization $H_{\text{vap.}}$. The ratio $H_{\text{vap.}}/E_\eta$ reaches exceptionally low values for *o*-terphenyl near the freezing-point, as if this liquid were highly associated.

Experimental details and results

Published results were used for benzene (*International critical tables*). Diphenyl was obtained from May and Baker Ltd, and all three terphenyls were obtained from Monsanto Chemicals. All these substances were freed from polar impurities by chromatography on a column of activated alumina (Peter Spence, type H), using benzene as elutrient in the case of diphenyl, hot benzene in the case of *p*-terphenyl, and low-boiling petroleum ether fractions as elutrients for the branched terphenyls. Middle fractions from the chromatographic purification were then sublimed *in vacuo* at 10^{-3} to 10^{-4} Hg, and the middle cuts from the sublimations had the following freezing-points:

diphenyl	70·0 ± 0·1° C,
p-terphenyl	213·0 ± 0·1° C,
m-terphenyl	87·0 ± 0·1° C,
o-terphenyl	55·5 ± 0·1° C.

These freezing-points were determined from the breaks on the dilatometric curves described below.

Vapour pressures of the liquids were determined by evaluating the boiling-points under different pressures of oxygen-free nitrogen, using standard precautions to ensure true vapour-liquid equilibrium independent of the rate of boiling and the rate of supply of heat. Temperatures were determined by means of shielded

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standardized mercury thermometers. The present purpose was to evaluate mean heats and entropies of vaporization. Mean values are summarized in table 1. The constants in the vapour-pressure equation refer to the formula

$$2{\cdot}303 \log_{10} p = A - H_{\text{vap.}}/RT,$$

where p is in mm Hg, with T in ° K, and $H_{\text{vap.}}$ in cal/mole.

TABLE 1. VAPOUR PRESSURE PARAMETERS OF POLYPHENYLS

substance	temp. range (° C)	A	$H_{\text{vap.}}$ (kcal)	$S_{\text{vap.}}$ (e.u.)
benzene*	—	—	7·35	20·8
diphenyl	220 to 260	18·015	11·915	22·0
	150 to 220	18·975	12·855	—
p-terphenyl	330 to 390	19·15	16·34	24·8
	270 to 330	20·115	17·495	—
m-terphenyl	330 to 380	19·03	15·965	24·5
	260 to 330	19·76	16·835	—
o-terphenyl	280 to 340	18·895	14·835	24·3
	220 to 280	19·75	15·765	—

* Data from Rossini *et al.* 1947.

Viscosity measurements

Viscometers used were of the Ubbelohde type with an overflow device for easy adjustment of the volume in the viscometer as the temperature is raised. The viscometer capillaries were of Veridia precision-bore capillary tubing with the capillary ends ground flat to minimize the need to correct for kinetic energy of flow. The liquid could be driven through the capillary in either direction by the application of pressure to either arm of the viscometer. Pressures of from 0 to 20 cm Hg could be applied to the liquid in the viscometer, the pressure being held constant to ± 0·1 mm Hg by a manostatic device. Times of flow were determined with a stopwatch to ± 0·1 s and with a reproducibility of 0·2 % or better. The viscometers were immersed in liquid thermostats controlled by toluene or mercury expansion regulators to ± 0·025°. In order to test for Newtonian behaviour, reciprocals of times of flow were plotted against the driving pressures, at various temperatures. No departures from linearity could be detected greater than experimental error, showing that the melts could be treated as Newtonian at linear flow rates not exceeding 240 cm/s even near the freezing-points.

The most compact representation of the results of viscosity measurements is to record plots of $\log \eta$ against I/T. For benzene, diphenyl and *p*-terphenyl, the plots (not shown) are practically straight lines. Marked departures from linearity are observed for *m*-terphenyl (figure 1) and especially for *o*-terphenyl (figure 2). Further details of the transport parameters are given in table 4.

Determination of volume changes on melting

Volume changes on melting were determined by a dilatometric method. The substance was introduced into a Pyrex bulb of about 3 to 4 ml. capacity, and after repeated melting and freezing *in vacuo*, to remove dissolved gases, the bulb

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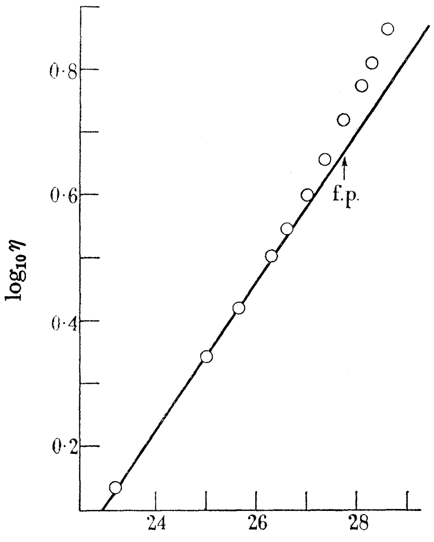

Figure 1. Plot of $\log_{10}\eta$ against $1/T$° K for *m*-terphenyl.

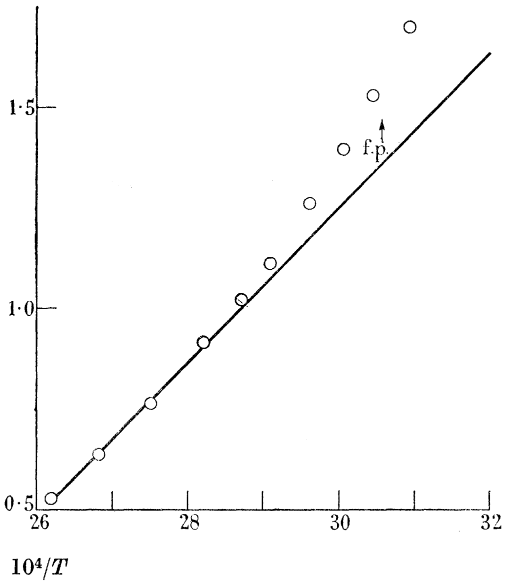

Figure 2. Plot of $\log_{10}\eta$ against $1/T$° K for *o*-terphenyl.

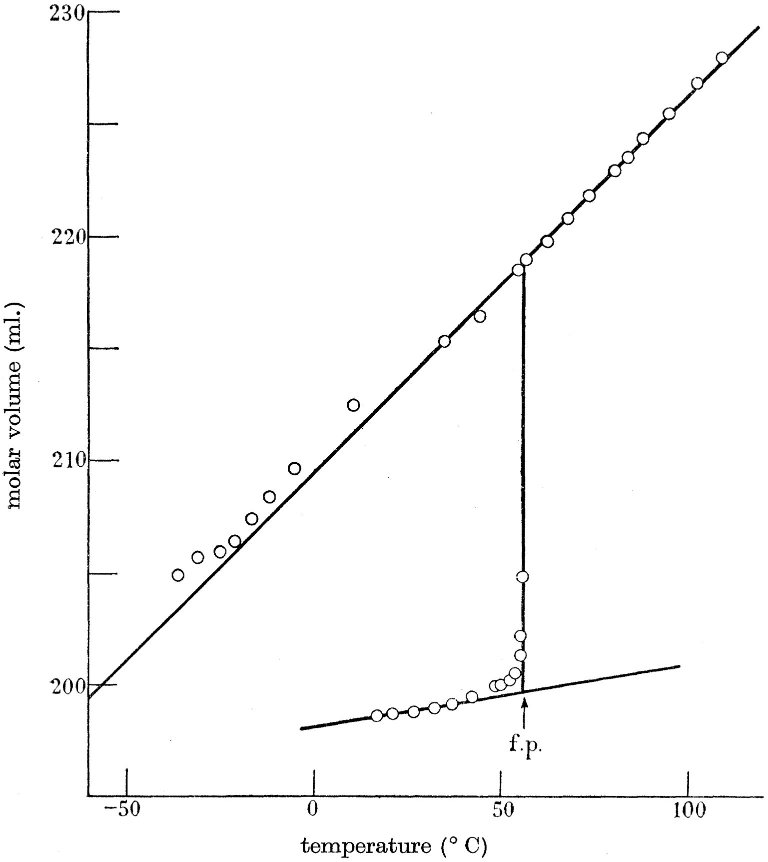

Figure 3. Dilatometry of *o*-terphenyl.

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was sealed to a stem of 2·5 mm bore capillary. The dilatometer was then filled with mercury as an indicator liquid, and the level of the mercury was determined at various temperatures to ± 0·005 cm with a travelling microscope. The dilatometer was finally emptied and its volume determined by filling to a reference mark with mercury. This enabled the specific volumes to be determined from the dilatometric readings at various temperatures.

As in all dilatometric experiments, the molar volume of the melt can be determined with very considerable accuracy. The molar volume of the solid at the freezing-point is measured on the polycrystalline mass obtained on freezing, and may be too large if precautions to prevent vacuoles in the mass are inadequate. This can be tested to some extent by repeated freezings and measurements of the reproducibility of the observations. If vacuoles are present in the solid, their presence will become evident by collapse processes as the temperature is raised. There may be a fall in the slope of the plot of specific volume of solid against temperature and perhaps also a sharp drop in the specific volume just as the solid begins to melt. For the present series of hydrocarbons the freezing/melting cycle was repeated until vacuoles in the solid were absent as determined by the above criteria. Values of the molar volumes for the solids were then reproducible to within ± 0·25 % and for the liquid to within ± 0·05 %.

Results for *o*-terphenyl are illustrated in figure 3 and other values are summarized in table 2. Whenever possible supercooled melts were included. The tendency to supercooling is very marked for *o*-terphenyl and decreases in the sequence *o*-terphenyl > *m*-terphenyl > *p*-terphenyl < diphenyl.

DISCUSSION

Space requirements for rotation in the melt

For convenience, dilatometric parameters which may throw light on the melting process are summarized in table 2.

TABLE 2. OBSERVED DILATOMETRIC PARAMETERS OF MELTING FOR THE POLYPHENYLS

parameter	benzene	diphenyl	*p*-terphenyl	*m*-terphenyl	*o*-terphenyl
V_1	87·3	155·2	237·05	221·0	218·6
V_1 per aromatic ring	87·3	77·6	79·0	73·7	72·9
V_s	77·0	133·8	199·8	200·4	199·7
$\Delta V_f/V_s$ (%)	13·4	16·0	18·7	10·6	9·45
$\Delta V_f/V_s$ (%) per aromatic ring	13·4	8·0	6·2	3·5	3·15
$10^4\alpha_s$	—	3·0	3·67	1·8	1·33
α_s per aromatic ring	—	1·5	1·22	0·6	0·44
$10^4\alpha_1$	13·6	8·25	9·2	6·3	7·25
α_1 per aromatic ring	13·6	4·12	3·1	2·1	2·4

Symbols: V_1 = molar volume of liquid at freezing-point in ml.
V_s = molar volume of solid at freezing-point in ml.
ΔV_f = change of molar volume on melting in ml.
α_1 = coefficient of expansion of liquid.
α_s = coefficient of expansion of solid.

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The structure of the polyphenyls

For interpreting the present findings, it is necessary to use other information about the space configuration of the polyphenyls. One important feature in these molecules is that conjugation across the C—C bonds joining the phenyl groups contributes energy terms of about the same order of magnitude as the repulsion energies between *o*-hydrogen atoms on proximate phenyl groups. For the present purpose the molecules may be treated as practically rigid, except for the possibility (depending on the environment) of rotations about the bonds joining the phenyl groups.

A detailed study of bond orders of the bonds joining the phenyl groups in the polyphenyls shows that the conjugation increases only slightly as the length of the polyphenyl chain is increased (Coulson & Jacobs 1949). In *m*-polyphenyls the conjugation does not increase at all; each ring is effectively conjugated only with its nearest neighbours. These findings are confirmed by the ultra-violet adsorption spectra of the polyphenyls (Gillam & Hey 1939). The resonance energy of a phenyl—phenyl bond in such a molecule, which must be overcome in order to twist the aromatic rings out of coplanarity, is therefore fairly constant and has a value of about 8 kcal/bond (Pauling & Sherman 1933). In an isolated molecule, the steric interaction of the hydrogen atoms *ortho* to the phenyl—phenyl bond (they are 1·8 Å apart as compared to 2·34 Å in intermolecular contact, Kitaĭgorodskii 1946) may well be able to overcome this resonance energy and so pull the benzene rings out of coplanarity. How far this occurs for the molecules under investigation depends on their structure, and on the environment.

Linear polyphenyls

Theoretical calculations (Samoĭlov & Dyatkina 1948) indicate that in isolated molecules of *p*-polyphenyls the planes of the aromatic rings should make angles of about 30° with the neighbouring rings. Electron diffraction by diphenyl (Bastiensen 1949, 1950) indicates that in the gaseous state there is an angle of 45° between the planes of the aromatic rings with possible oscillations by these planes of 10° about this average position. Other electron-diffraction patterns (Karle & Brockway 1944) do not distinguish between a coplanar or non-coplanar structure in the vapour phase. In the crystalline state X-ray investigations indicate coplanar structures for diphenyl (Dhar 1932) and *p*-terphenyl (Pickett 1933; Hertel & Romer 1933). This is confirmed for diphenyl by studies of magnetic anisotropy (Pacault 1949). Ultra-violet absorption spectra indicate that diphenyl assumes a coplanar structure in the crystal but is non-coplanar in solution (therefore presumably also in the melt) and in the vapour (Merkel & Wiegand 1947, 1948).

Branched polyphenyls

From X-ray studies (Lonsdale 1937, cf. Farag 1954) 1.3.5-triphenylbenzene is non-coplanar in the crystals and *m*-terphenyl is probably similar. Similarly, *o*-terphenyl (Clews & Lonsdale 1937) is non-coplanar in the crystals with the end rings at an angle of 50° to the middle ring (see figure 7*c*, *d*, plate 4). Electron-

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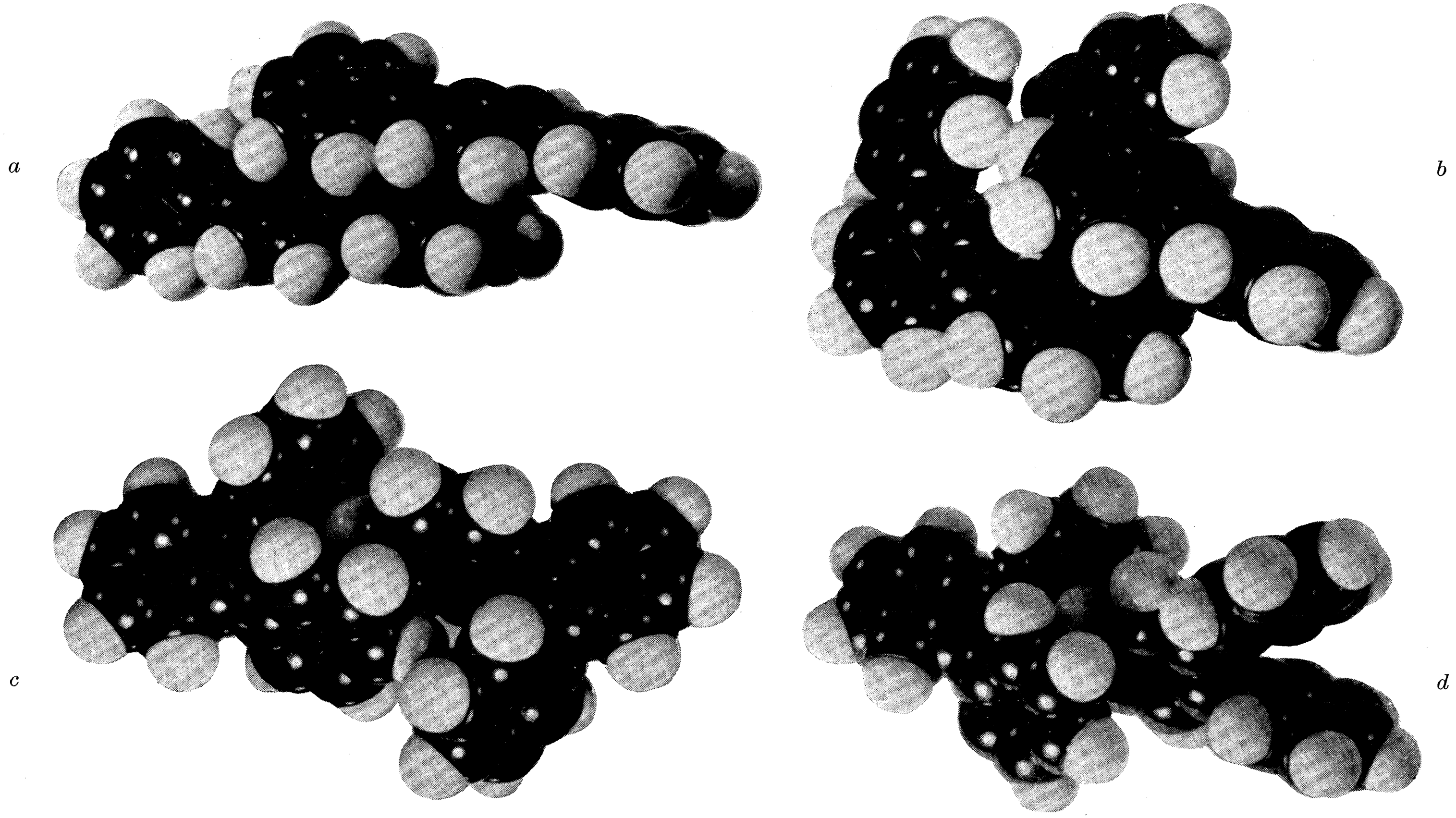

FIGURE 7. Preferred relative positions of the phenyl rings are shown in each molecular model. Pairs of models illustrate the possibilities of interlocking for (*a*) *p*-terphenyl (little or no interlocking), (*b*) *m*-terphenyl (moderate interlocking), (*c*) and (*d*) *o*-terphenyl (strong interlocking).

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diffraction studies (Karle & Brockway 1944) show that *o*-terphenyl in the vapour phase has the two end rings orthogonal to the middle ring. Independent oscillations of the end rings may range to ± 15° from the normal position, but oscillations of greater angle would have to be in phase.

It must thus be inferred that in polyphenyls the mutual orientation of the planes of the phenyl groups depends upon the state of aggregation. In the crystals, intermolecular repulsions keep the aromatic rings of linear polyphenyls coplanar. When packing requires more space the molecule may be non-coplanar even in the crystals of 1.3.5-triphenylbenzene and *o*-terphenyl. In the liquid state, and still more in the gaseous state, the greater free volume will probably allow many of the molecules to be non-coplanar.

Figure 7*a*, *b*, plate 4, shows the relative positions of the aromatic rings of *p*- and *m*-terphenyl in configurations of minimum potential energy for the isolated molecules. Figure 7*c* shows the relative positions of the aromatic rings of *o*-terphenyl as reported for the crystalline state. These are also structures likely to be adopted by these molecules in the melt.

Though the freedom of orientation of the planes of the phenyl groups somewhat modifies minimum space requirements in the melts, there is no evidence for any extensive deformation of the angles between the planes of the aromatic groups. The rigidity of the molecular skeletons in this respect has a predominant influence on packing in the melt, and on flow characteristics described below.

Volume changes on melting

Minimum volumes required for 'rotation' of the molecules in the melt have been calculated on the basis that diphenyl and *p*- and *m*-terphenyl molecules have their aromatic rings coplanar. Volumes have been computed for rotation about three mutually perpendicular axes through the centroid of the van der Waals envelopes. Essential details are shown in figure 4*a*, *b*. For *o*-terphenyl, the planes of the two end rings were assumed to make an angle of 50° with the middle ring (see figure 7*c*, *d*). Volumes were calculated for rotation about three mutually perpendicular axes through the centroid of the projection shown in figure 4*c*, *d* which represents the van der Waals envelopes of the end rings projected on to that of the parent ring. The position of the 'long axis' is indicated for each case in figure 4 by arrows. The other axes are mutually perpendicular to this one, through the centroid of the area shown.

Table 3 compares the results of these computations with the actual molar volume of the melts. Where the assumptions made in the computations do not give the smallest possible space requirements, for example when the preferred structure is one with the rings at small angles to each other (see figure 7*a*, *b*), this is indicated by an asterisk. Where the assumptions give a value which is certainly too small, this is indicated by a prime. However, any such discrepancies are small and do not affect the conclusion that there is no molecular 'rotation' in the melts of any of these molecules, except benzene.

Comparison of the minimum volumes required for 'rotation' with the volumes of the liquids shows that none of these polyphenyl molecules will 'rotate' in the

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melts near the freezing-points. Coefficients of expansion of the liquids (table 2) suggest that 'rotation' will not be feasible even up to the boiling-point of the liquids, unless there are further anomalous volume increases at higher temperatures.

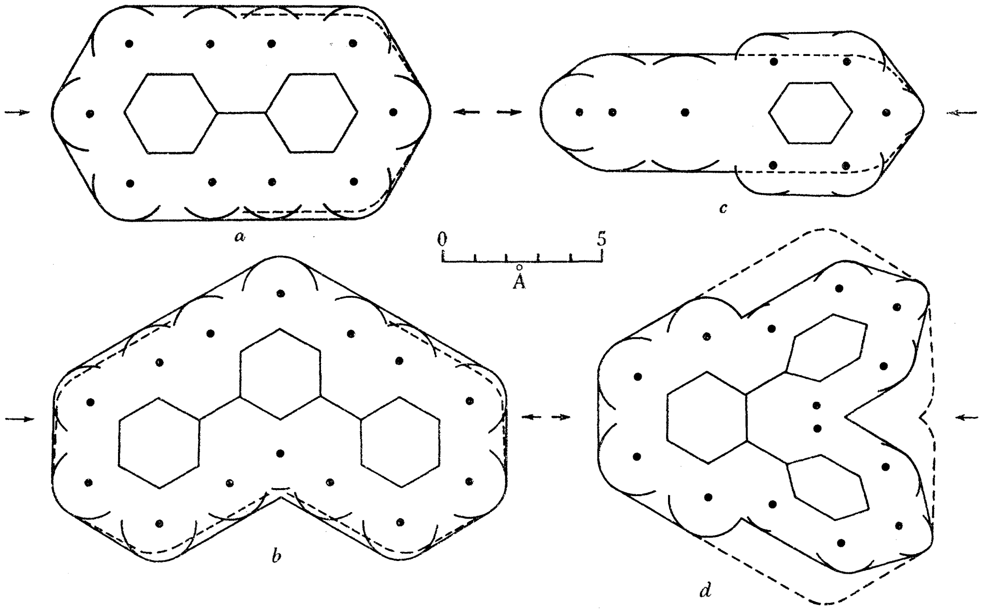

FIGURE 4. Van der Waals repulsion envelopes of (*a*) diphenyl, (*b*) *m*-terphenyl, (*c*) *o*-terphenyl viewed in the plane of the middle ring, (*d*) *o*-terphenyl viewed from above the plane of the middle ring. In (*a*), (*b*), the broken lines indicate the effect on these envelopes of rotating the rings with respect to each other to the most preferred position. In (*c*), (*d*), the dotted lines show the repulsion envelopes for a planar *o*-terphenyl molecule and indicate the serious steric interaction which would occur if planarity were attained.

TABLE 3. SPACE REQUIREMENTS FOR 'ROTATION' OF THE POLYPHENYLS

		volume required per mole for rotation about		
	molar vol. of melt at f.p. (ml.)	long axis (ml.)	short axis (ml.)	vertical axis (ml.)
benzene*	87·3	111	120	76
diphenyl	155·2	210	345*	207′
p-terphenyl	237·5	301	695*	399′
m-terphenyl	221	475*	595*	315′
o-terphenyl	218·6	295	447	310

* Al-Mahdi & Ubbelohde (1953).

Inspection of table 3 also shows that the long axis becomes the easiest for rotation as the length of the aromatic chain increases. Space requirements for rotation of branched molecules are more nearly spherically symmetrical.

Inspection of table 2 shows that on melting the volume change per aromatic nucleus falls in the series of molecules:

$$\text{benzene} > \text{diphenyl} > p\text{-terphenyl},$$

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and that it falls markedly on branching of the chain of aromatic nuclei

$$p\text{-terphenyl} \gg m\text{-terphenyl} > o\text{-terphenyl}.$$

The degree of interlocking of the molecules must increase markedly in the inverse order. This is further brought out by the results for the fluidities discussed in the following section.

Transport processes in the melt

Benzene and its linear homologues diphenyl and *p*-terphenyl give practically straight-line plots of log η against $1/T°$ K. Table 4 records the constants in the equation $\eta = A \exp (E_\eta/RT)$ which give the best fit to the experimental results. Inspection of table 4 shows that on approaching the freezing-point an increased activation energy required for flow is perceptible for benzene and for diphenyl. A similar increase is much more marked for *m*-terphenyl, and is extremely striking for *o*-terphenyl. Neither of these compounds gives a straight line plot at all.

TABLE 4. TRANSPORT PARAMETERS IN MELTS OF POLYPHENYLS

	benzene	diphenyl	*p*-terphenyl	*m*-terphenyl	*o*-terphenyl
			above m.p.		
E_η	2·42	3·41	3·76	5·34	7·93
A	$1{\cdot}01 \times 10^{-2}$	$9{\cdot}59 \times 10^{-3}$	$1{\cdot}64 \times 10^{-2}$	$2{\cdot}70 \times 10^{-3}$	$9{\cdot}95 \times 10^{-5}$
			around m.p.		
E_η	2·63	3·80	same	7·40	16·04
A	$7{\cdot}19 \times 10^{-3}$	$5{\cdot}43 \times 10^{-3}$	same	$1{\cdot}73 \times 10^{-4}$	$7{\cdot}41 \times 10^{-10}$

The units of E_η are kcal/mole, and of A centipoises.

Structure of melts of linear polyphenyls

For benzene and its linear homologues, it is noteworthy that the resistance to viscous flow *per benzene ring* becomes smaller as the molecule lengthens. Considerable adlineation of the molecules is indicated in these melts. This is further borne out by the ratio $H_{\text{vap.}}/E_\eta$ which rises as the chain of phenyl groups lengthens (table 5), and also by the changes in magnitude the entropy ΔS_η of flow, as the phenyl chain increases (see below).

TABLE 5. VALUES OF THE RATIO $H_{\text{vap.}}/E_\eta$ AND ΔS_η FOR MELTS OF POLYPHENYLS

	benzene	diphenyl	*p*-terphenyl	*m*-terphenyl	*o*-terphenyl
		$H_{\text{vap.}}/E_\eta$			
above m.p.	3·06	3·50	4·47	2·99	1·87
near m.p.	2·81	3·13	same	2·16	0·93
		ΔS_η (e.u.)			
above m.p.	−1·71	−2·70	−4·59	−0·84	5·71
near m.p.	−0·91	−1·50	same	4·65	29·3

Technically, it has not yet proved possible to extend the vapour pressure curves of these melts down to near the freezing-points. Results given in table 1 suggest that

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$H_{\text{vap.}}$ increases somewhat on lowering the temperature, but not enough to invalidate the comparisons in table 5, which use the $H_{\text{vap.}}$ at the boiling-point under normal pressure.

It has not yet been possible to extend these experiments to *p*-quaterphenyl and *p*-quinquephenyl. Provisionally, however, for the linear polyphenyls it seems reasonable to postulate cybotactic groups with roughly parallel long axes. For any one molecule the groups grow in size as the freezing-point is approached and traversed. At corresponding temperatures for the different molecules, the cybotactic groups grow in size as the number of phenyl groups increases. For *p*-quinquephenyl the liquid crystalline character of the melt is stated to be perceptible at ordinary wave-lengths of light. A transition to a more disordered arrangement in the melt has been briefly reported at about 44° above the melting-point (Vorländer 1927). Optical studies on melts with a suitable range of wave-lengths are planned to investigate these phenomena more fully.

The entropies of activation for viscous flow may be briefly discussed in the light of the analysis proposed by Ewell (1938) and by Bondi (1946). Actual experimental results may be recalculated in terms of the expression derived from the theory of absolute reaction rates (Glasstone, Laidler & Eyring 1941).

$$\eta = \frac{hN}{V}\exp\left(-\frac{\Delta S_\eta}{R}\right)\exp\left(\frac{E_\eta}{RT}\right). \tag{1}$$

If values of E_η are taken to be the same as the semi-empirical values recorded in table 4 (see, however, Van Velden 1947), from the observed viscosities values of ΔS_η can be calculated by means of equation (1). Even if all the theoretical considerations advanced by various workers are not adopted, transport parameters calculated in this way are quite clearly defined, and may be compared with other liquids. Benzene and the linear polyphenyls give more or less normal values of the ratios $H_{\text{vap.}}/E_\eta$, showing that the structure of these melts is not exceptionally interlocked into clusters. Some increase of clustering on approaching the freezing-point is indicated for benzene and diphenyl, but the change is small. Similarly, the values of ΔS_η are small and negative, as is the case for many hydrocarbons (Bondi 1946).

Structure of melts of branched polyphenyls

Quite a different structure of the melt is indicated by the transport parameters of *m*- and *o*-terphenyl. For these melts, *interlocked* cybotactic groups of molecules may be postulated in the melt. Changes in A and E_η as the temperature rises (table 4) suggest that these groups diminish in size quite steeply above the freezing-point. At the same time, marked super-cooling is observed for the melts before spontaneous crystallization occurs. This indicates that any such groups must be distinct in structure from the more ordered arrangement required before a group can act as a nucleus for crystallization. For these molecules, the smaller values of the ratio of $H_{\text{vap.}}/E_\eta$ (table 5) indicates that larger holes must be formed in the melt for movement to occur.

The magnitude of the ratio $H_{\text{vap.}}/E_\eta$ indicates that energy to be supplied to permit viscous flow approximates to that for a full Schottky hole in the liquid

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structure. The high positive entropies of activation for these interlocked molecules are noteworthy. Presumably the number of ways in which a full Schottky hole can be supplied is large and so the entropy of activation is positive. Differences in the rotational and vibrational energies of the activated state may also contribute to these large positive entropies of activation, which appear to be characteristic of liquids with a very pronounced interlocking structure.

Figure 7 illustrates the relative possibility for interlocking of the molecules of the terphenyls. It is evident that the *o*-terphenyl molecule has a structure which facilitates interlocking with neighbours much more than that of molecules of the other two isomers.

Because of the high viscosity and extensive super-cooling of *o*-terphenyl, it can be chilled to a glass when Pyrex tubes of 2 mm diameter containing the melt are plunged into a bath of acetone cooled by solid carbon dioxide. This is of interest since the number of glasses known to be formed from non-polar molecules is not large.

Fluidity-specific volume relationships

On any theory of the structure of melts, the fluidity must depend on the 'free volume' left unoccupied by the molecules. According to semi-empirical arguments developed by Batschinski (1913) and by Herzog & Kudar (1933), plots of the fluidity $1/\eta$ against the specific volume of a liquid should give straight line relationships for 'normal' liquids. These plots can be used as a diagnostic for any exceptionally marked change of structure as the freezing-point is approached. The Batschinski relationship states that

$$1/\eta = (v-w)/C,$$

where C and w are constants. As the volume contracts, benzene, diphenyl and *p*-terphenyl are indeed found to decrease linearly in fluidity and show only slight departures from the straight line, as the freezing-point is approached. With *m*- and especially with *o*-terphenyl, on the other hand, very marked departures from the straight line relationship are found, pointing to a marked change in mechanism of transport as the temperature of the melt approaches the freezing-point. The broken line in figures 5 and 6 shows the fluidity/volume relationship for melts of *m*- and *o*-terphenyls close to the freezing-point. The fluidities of these melts at higher temperatures (where they will begin to approximate to 'normal' liquids) are significantly greater than would be indicated by the fluidities close to the freezing-point. This can be attributed to 'breaking up' of the cybotactic groups of these melts as the temperature is raised. Values of the 'constants' C and w are of interest for comparisons with liquids of less anomalous structure, and are recorded in table 6. The Batschinski plots are shown only for instances where the curvature is marked, in figures 5 and 6.

The marked trend with *m*-terphenyl and especially with *o*-terphenyl is noteworthy.

According to the interpretation of the Batschinski relationship given by Herzog & Kudar (1933) this marked rise in C indicates more and more interlocking and

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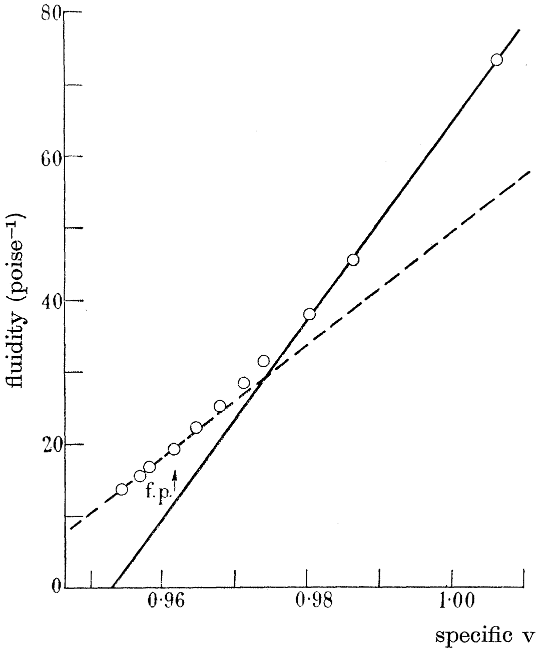
inhibition of molecular rotations in the melts. In view of these findings, it is perhaps noteworthy that *o*-terphenyl still behaves as a Newtonian melt, so far as the shear rates investigated are concerned.



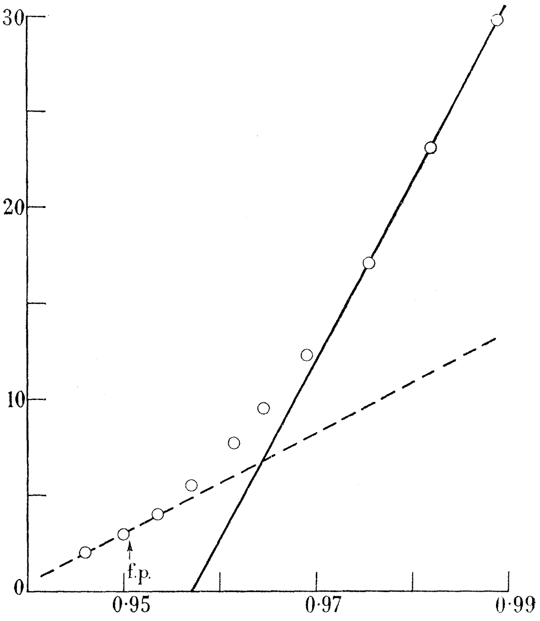


FIGURE 5. Batschinsky plot for *m*-terphenyl. FIGURE 6. Batschinsky plot for *o*-terphenyl.

TABLE 6. BATSCHINSKI FLUIDITY PARAMETERS FOR MELTS OF POLYPHENYLS

	benzene	diphenyl	*p*-terphenyl	*m*-terphenyl	*o*-terphenyl
			well above f.p.		
w	1·05	0·959	0·932	0·952	0·958
C	$5{\cdot}75\times10^{-4}$	$6{\cdot}82\times10^{-4}$	$8{\cdot}01\times10^{-4}$	$7{\cdot}40\times10^{-4}$	$10{\cdot}5\times10^{-4}$
			close to f.p.		
w	1·04	same	same	0·938	0·934
C	$6{\cdot}21\times10^{-4}$	same	same	$12{\cdot}15\times10^{-4}$	$37{\cdot}0\times10^{-4}$

Mechanism of melting of the polyphenyls

At present, only contributory statements can be made, since a complete theory of melting covering all the processes involved requires more experimental information. For reasons stated in Al-Mahdi & Ubbelohde (1953) the entropy of fusion and especially the increment in molar specific heats $\Delta\,(C_{\text{melt}}-C_{\text{solid}})$ are required to decide how far the increase in vibrational entropy of a (disordered) liquid structure can account for melting. These measurements are in hand for the polyphenyls. In the meantime, the findings recorded above extend the working model previously proposed for the melting of stiff anisotropic molecules. It is interesting

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to find that the departure from a linear log η against I/T relationship previously reported for melts of various polar molecules by Jenckel (1939) and by Dodd & Mi (1949) as the melting point is traversed is now found, in much more marked degree, for these non-polar hydrocarbons. Some form of structural association into groups or clusters of molecules in the melt seems to explain this effect. Though group formation in the melts may become more important as the freezing-point is approached, any 'break' in the properties of these fluids would seem to be gradual, and not exactly at the freezing-point as suggested by Dodd & Mi (1949) for the molecules studied by these workers. The present findings make it clear that any such cybotactic groups are not to be identified with crystal nuclei, for which the geometrical requirements are likely to be much more stringent. This conclusion helps to explain how certain properties of melts such as viscosity can foreshadow freezing without involving spontaneous crystallization on traversing the freezing-point.

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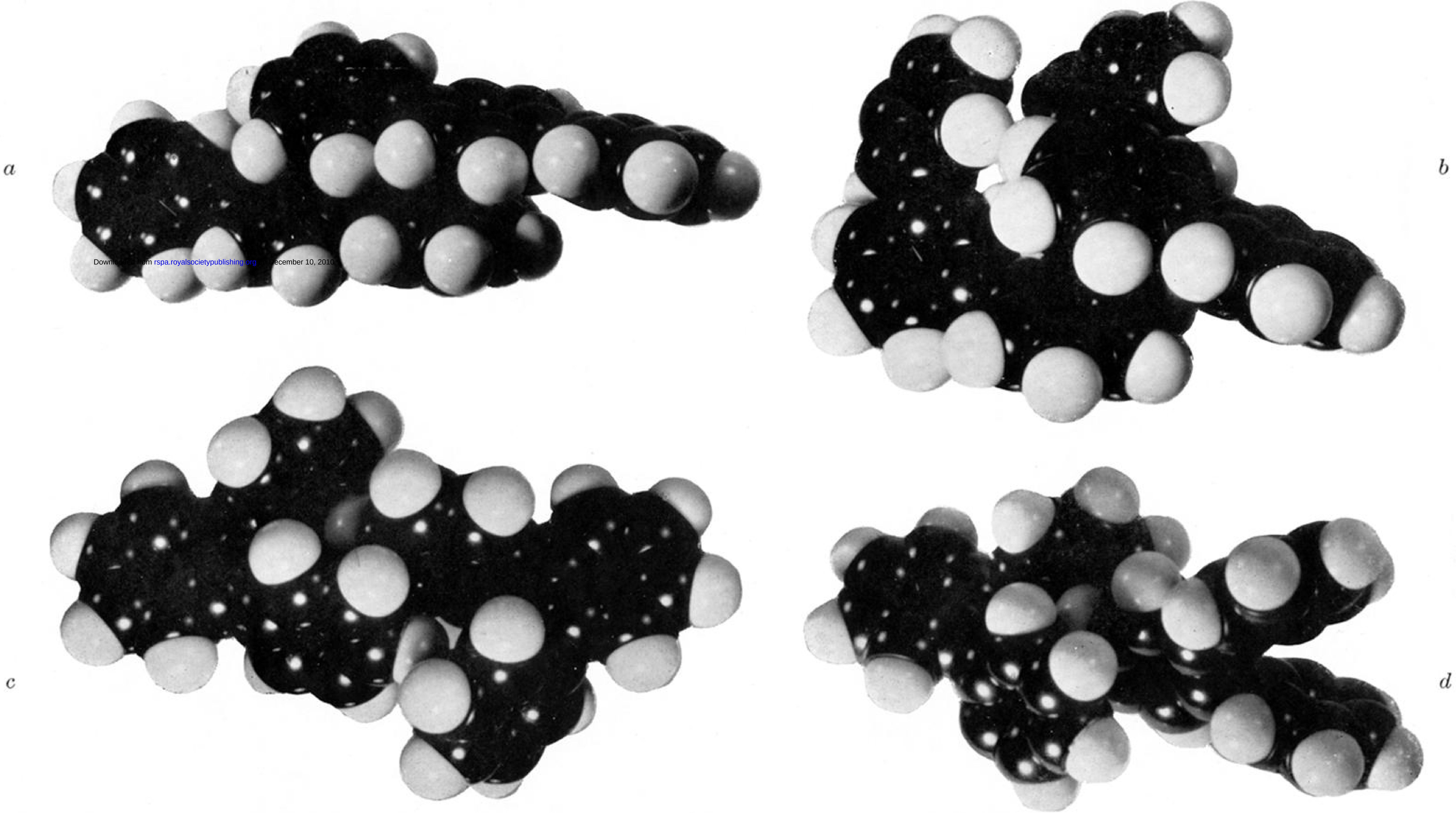

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FIGURE 7. Preferred relative positions of the phenyl rings are shown in each molecular model. Pairs of models illustrate the possibilities of interlocking for (*a*) *p*-terphenyl (little or no interlocking), (*b*) *m*-terphenyl (moderate interlocking), (*c*) and (*d*) *o*-terphenyl (strong interlocking).