The Crystal and Molecular Structure of *p*-Phenylenediacrylic Acid Diethyl Ester

By Hachiro Nakanishi and Katsuhiko Ueno

Research Institute for Polymers and Textiles, Sawatari, Kanagawa-ku, Yokohama 221, Japan

and Yoshio Sasada

Faculty of Science, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan

Photopolymerizable crystals of *p*-phenylenediacrylic acid diethyl ester are monoclinic, $P2_1/a$, with $a = 7.399$ (2), $b = 9.894$ (4), $c = 10.167$ (4) Å, $\beta = 99.74$ (4)°, and $Z = 2$. The structure was solved by the direct method and refined by a block-diagonal least-squares calculation to $R = 0.050$ for 1219 observed reflexions. Closer examination reveals some common features among this and other similar photopolymerizable crystals: small but definite internal rotation in a conjugated system with lone-pair electrons, constancy of lengths and angles about the single bond between benzene and the ethylenic double bond, and a parallel plane-to-plane stack which is quite favourable for the reaction.

Introduction

A group of diolefinic compounds are photopolymerized in the crystalline state to give linear polymers containing a cyclobutane ring in the main chain (for a review see Hasegawa, Suzuki, Nakanishi & Nakanishi, 1973). One of the most characteristic features of the polymerization is that the polymer obtained is three-dimensionally oriented. In order to clarify the polymerization mechanism, we have studied the crystal structures of the diolefins and their polymers and discussed the mechanism on the basis of the crystallographic results and polymerization behaviour (Nakanishi, Hasegawa & Sasada, 1977).

p-Phenylenediacrylic acid diethyl ester (*p*-PDAEt) is an interesting diolefin whose polymerization behaviour has been investigated over a wide temperature range including the crystal transition point (56°C) and the melting point (96°C) (Nakanishi, Nakanishi, Suzuki & Hasegawa, 1973). The present paper deals with the crystal structure of *p*-PDAEt below the transition point and with some structural characteristics found in the series of structure analyses of the diolefins.

Experimental

p-PDAEt was synthesized according to Suzuki, Suzuki, Nakanishi & Hasegawa (1969). Colourless plate-like crystals were grown from an ethanol solution by slow evaporation. The specimen used was a fragment of a plate 0·10 × 0·20 × 0·20 mm. The space group was determined from photographs. The precise lattice constants and intensity data were derived from measurements on a Rigaku computer-controlled four-circle diffractometer, with graphite-monochromatized Mo $K\alpha$ radiation. All reflexions within the range $2\theta < 60°$ were collected with the $2\theta–\omega$ scan mode and a scanning rate of 2° min^{-1}. Stationary background counts were accumulated for 10 s before and after each scan. Of 2136 reflexions, 1219 were greater than $3\sigma(|F_o|)$ and used for the structure determination. No correction was made for absorption. Crystallographic data of *p*-PDAEt are: $C_{16}H_{18}O_4$, $M_r = 274.3$, monoclinic, $P2_1/a$, $a = 7.399$ (2), $b = 9.894$ (4), $c = 10.167$ (4) Å, $\beta = 99.74$ (4)°, $U = 733.6$ Å^3, $Z = 2$, $D_x = 1.242$, $D_m = 1.24$ g cm^{-3}, μ(Mo $K\alpha$) = 1.04 cm^{-1}.

Structure determination and refinement

The space group and Z indicate that the molecule has a centre of symmetry. By iterative symbolic addition procedures, the signs of 253 reflexions (of 287 with $|E| \geq 1.5$) were determined in terms of one symbol. One of the corresponding E maps revealed the positions of all the non-hydrogen atoms. The parameters were refined by the block-diagonal least-squares method using $w = 0.5$ for $|F_o| \leq 1.0$, 1.0 for $|F_o| > 1.0$. Isotropic H atoms were first located geometrically and then refined. The final R value was 0.050.* Atomic scattering factors were taken from *International Tables for X-ray*

Table 1. *Fractional atomic coordinates* ($\times 10^4$ *for* C, O; $\times 10^3$ *for* H)

Estimated standard deviations are in parentheses.

	x	y	z
C(1)	9984 (3)	−1216 (2)	646 (2)
C(2)	8727 (3)	977 (2)	160 (2)
C(3)	8684 (2)	−249 (2)	817 (2)
C(4)	7328 (3)	−576 (2)	1666 (2)
C(5)	5905 (3)	156 (2)	1847 (2)
C(6)	4642 (3)	−333 (2)	2726 (2)
O(1)	3492 (2)	640 (2)	2956 (2)
O(2)	4629 (2)	−1454 (2)	3169 (2)
C(7)	2236 (3)	283 (3)	3865 (2)
C(8)	1212 (4)	1523 (3)	4077 (3)
H(C1)	997 (3)	−208 (2)	112 (2)
H(C2)	786 (3)	166 (2)	26 (2)
H(C4)	750 (3)	−144 (2)	215 (2)
H(C5)	559 (2)	101 (2)	143 (2)
H(C7)1	300 (3)	−6 (2)	474 (2)
H(C7)2	142 (3)	−51 (2)	344 (2)
H(C8)1	36 (4)	131 (3)	475 (3)
H(C8)2	67 (5)	189 (4)	319 (3)
H(C8)3	210 (4)	222 (3)	451 (3)

Crystallography (1962). Final atomic coordinates are given in Table 1.

Results and discussion

Bond lengths and angles

The molecular structure and the numbering system of *p*-PDAEt are shown in Fig. 1. The structure is compared with those of related compounds in Table 2, where abbreviations of the compounds are also given.

Although the double-bond length varies widely, the other bond lengths and angles of the four esters are nearly identical within a deviation of 3σ, except for those of the ester moiety of *p*-PDAPh.

As far as the partial structure about the single bond between benzene and the ethylenic double bond is concerned, the molecular dimensions (other than the double-bond length) of all seven compounds in Table 2 are quite similar. It is noteworthy that the bond length C(3)–C(4) and the angles C(1)–C(3)–C(2), C(2)–C(3)–C(4) and C(3)–C(4)–C(5) do not depend on the internal rotation about C(3)–C(4), which ranges from 2·2 to 17·2° (θ_1 in Fig. 2). Angular contraction of the benzene ring at the substituted atom is due to the nonbonded interaction and the conjugation effect, as discussed by Domenicano, Vaciago & Coulson (1975).

Planarity

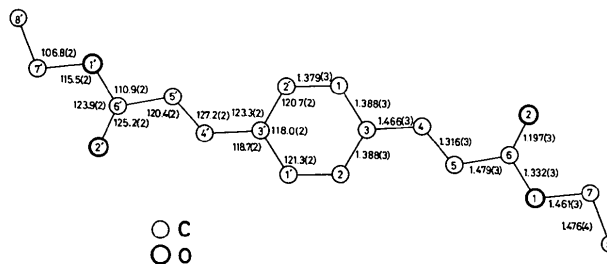The equations of the mean planes and the displacements of atoms from each plane are given in Table 3.

Fig. 1. Bond lengths (Å) and angles (°) of *p*-PDAEt. The estimated standard deviations are in parentheses.

Table 2. *Bond lengths* (Å) *and angles* (°) *of p-phenylenediacrylic acid derivatives and related compounds*

	p-PDAMe[a]	*p*-PDAEt[b]	*p*-PDAPh[c]	HNCMe[d]	DSP(α)[e]	DSP(γ)[f]	P2VB[g]
C(1)–C(3)	1·391 (4)	1·388 (3)	1·387 (9)	1·398 (3)	1·400 (3)	1·391 (8)*	1·383 (5)
C(2)–C(3)	1·385 (4)	1·388 (3)	1·399 (9)	1·386 (3)	1·391 (3)	1·397 (8)*	1·403 (5)
C(3)–C(4)	1·463 (4)	1·466 (3)	1·468 (9)	1·468 (3)	1·469 (3)	1·461 (8)*	1·459 (5)
C(4)–C(5)	1·330 (4)	1·316 (3)	1·325 (3)	1·308 (4)	1·333 (3)	1·333 (8)*	1·333 (5)
C(5)–C(6)	1·476 (4)	1·479 (3)	1·468 (9)	1·471 (3)	(1·455 (3))†	(1·460 (8))*†	(1·464 (5))†
C(6)–O(2)	1·194 (4)	1·197 (3)	1·182 (8)	1·188 (3)			
C(6)–O(1)	1·335 (4)	1·332 (3)	1·368 (8)	1·341 (3)			
O(1)–C(7)	1·443 (4)	1·461 (3)	1·412 (8)	1·442 (4)			
C(1)–C(3)–C(2)	117·9 (3)	118·0 (2)	117·4 (6)	117·6 (2)	118·4 (2)	118·2 (5)*	118·0 (3)
C(1)–C(3)–C(4)	118·8 (2)	118·7 (2)	119·7 (6)	119·6 (2)	118·7 (2)	119·0 (5)*	119·2 (3)
C(2)–C(3)–C(4)	123·3 (3)	123·3 (2)	122·9 (6)	122·8 (2)	122·9 (2)	122·7 (5)*	122·8 (3)
C(3)–C(4)–C(5)	127·2 (3)	127·2 (2)	125·9 (6)	126·4 (2)	125·9 (2)	126·8 (5)*	127·6 (4)
C(4)–C(5)–C(6)	119·3 (3)	120·4 (2)	119·6 (6)	121·6 (2)	(124·7 (2))†	(124·4 (5))*†	(124·2 (4))†
C(5)–C(6)–O(1)	110·8 (2)	110·9 (2)	108·8 (5)	111·0 (2)			
C(5)–C(6)–O(2)	126·0 (3)	125·2 (2)	127·3 (6)	126·4 (2)			
O(1)–C(6)–O(2)	123·2 (3)	123·9 (2)	123·9 (6)	122·6 (2)			
C(6)–O(1)–C(7)	115·0 (2)	115·5 (2)	117·6 (5)	116·4 (2)			

(a) *p*-Phenylenediacrylic acid dimethyl ester (Ueno, Nakanishi, Hasegawa & Sasada, 1978). (b) *p*-Phenylenediacrylic acid diethyl ester (present work). (c) *p*-Phenylenediacrylic acid diphenyl ester (Nakanishi, Ueno & Sasada, 1978). (d) Methyl 4-hydroxy-3-nitrocinnamate (Hanson, 1975). (e) 2,5-Distyrylpyrazine(α). The structural parameters of Sasada, Shimanouchi, Nakanishi & Hasegawa (1971) have been further refined on the basis of intensity data collected on a four-circle diffractometer. (f) 2,5-Distyrylpyrazine(γ) (Nakanishi, Ueno & Sasada, 1976a). (g) 1,4-Bis[β-(2-pyridyl)vinyl]benzene (Nakanishi, Ueno, Hasegawa & Sasada, 1972).

* The mean value of two equivalent structures.

† The single bond to another aromatic ring, in contrast to that to the carbonyl group in *p*-PDA esters.
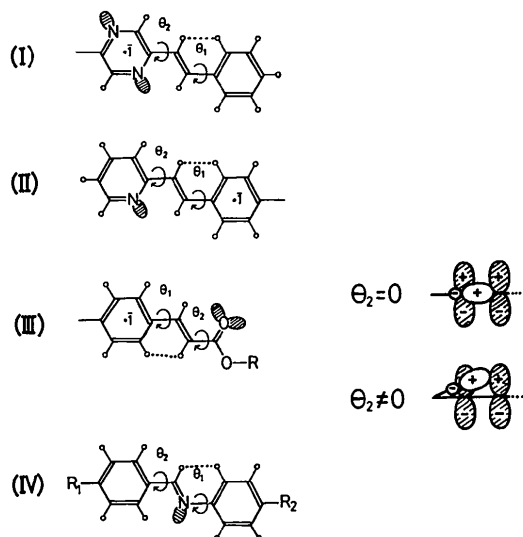
Fig. 2. Molecular structures of diolefins and benzylideneanilines, and schematic drawing of the electronic interaction between the electrons of the lone pair and the double bond, viewed along the ethylenic plane. The π-electron lobes of ethylene are hatched.

Table 3. *Deviations* (Å) *of atoms from some least-squares planes*

The equations of the planes are expressed in the form $AX + BY + CZ + D = 0$, where X, Y and Z are in Å referred to the orthogonal axes a, b and c^*.

	P1†	P2	P3	P4†	P5†
A	−0·497	−0·436	−0·522	−0·479	−0·502
B	−0·370	−0·455	−0·286	−0·337	−0·282
C	−0·785	−0·776	−0·804	−0·811	−0·818
D	3·676	3·268	3·646	3·543	3·712
C(1)	−0·002	0·143‡		−0·061	−0·129
C(2)	−0·002	−0·099‡		0·009	0·083
C(3)	0·002	0·006	−0·221‡	−0·047	−0·042
C(4)	0·025‡	−0·007	−0·213‡	−0·078	−0·070
C(5)	0·154‡	−0·004	0·000	0·051	0·122
C(6)		0·005	−0·003	0·020	0·083
O(1)		−0·225‡	0·001	−0·060	0·069
O(2)		0·202‡	0·001	0·073	0·074
C(7)			−0·064‡	−0·165‡	−0·031
C(8)			−0·171‡	−0·370‡	−0·152

† For these planes the equivalent atoms related by the centre of symmetry at (1,0,0) have also been included in the evaluation.

‡ Atoms not included in the plane calculations.

Table 4. *Internal rotation* (°) *in the conformationally flexible but conjugated molecules with lone-pair electrons*

Compound	Structural formula*		θ_2	θ_1	Reference
DSP(α)	(I)		9·0	−3·2	(a)
DSP(γ)	(I)		8·6	−13·0	(b)
			10·9	−17·2	
P2VB	(II)		11·8	1·9	(c)
p-PDAMe	(III)	(R = CH₃)	7·2	2·2	(d)
p-PDAEt	(III)	(R = C₂H₅)	10·9	6·0	(e)
p-PDAPh	(III)	(R = C₆H₅)	10·8	−15·9	(f)
Benzylideneanilines					
	(IV)	(R₁ = R₂ = H)	10·3	53·3	(g)
	(IV)	(R₁ = COOH, R₂ = H)	12·5	40·9	(g)
	(IV)	(R₁ = NO₂, R₂ = CH₃)	9·9	47·0	(g)

References: (a) The structural parameters of Sasada, Shimanouchi, Nakanishi & Hasegawa (1971) have been further refined on the basis of intensity data collected on a four-circle diffractometer. (b) Nakanishi, Ueno & Sasada (1976a). (c) Nakanishi, Ueno, Hasegawa & Sasada (1972). (d) Ueno, Nakanishi, Hasegawa & Sasada (1978). (e) Present work. (f) Nakanishi, Ueno & Sasada (1978). (g) Bürgi & Dunitz (1970).

* See Fig. 2.

The benzene ring, and the ethylene and carbonyl groups are planar. The benzene ring rotates 6·0° about C(3)—C(4) from the ethylenic plane, and the carbonyl rotates 10·9° about C(5)—C(6) in the same direction. Thus, the molecular skeleton consisting of the above three groups is nearly planar, within a deviation of 0·08 Å from the mean plane. The ethyl group rotates 5·0° about O(1)—C(7).

Characteristic conformation of diolefins

The molecular skeleton of all the diolefinic compounds analysed consists of three kinds of planar groups. Two are the benzene ring and ethylene, and the

other with lone-pair electrons is pyrazinyl for DSP, 2-pyridyl for P2VB, or carbonyl for all esters of p-phenylenediacrylic acid (p-PDA). These three groups form a conjugated system through two intervening single bonds: bond A between the benzene and ethylene moieties, and bond B between ethylene and the last planar group. Molecular structures of these diolefins are drawn schematically in Fig. 2, together with the definition of internal rotation (θ_1 and θ_2 around the single bonds A and B respectively).

There are two prominent features of the molecular conformation of these diolefins. (1) The atom with the lone-pair electrons is always situated at the same side as the ethylenic double bond with respect to bond B. It

follows that the lone-pair electrons extend parallel to the double bond. (2) The internal rotation θ_2 is almost fixed at 10·0° for all compounds, while θ_1 varies widely (Table 4).

The internal rotation θ_1 is generally explained by the nonbonded interaction between ethylenic H and the *ortho* H atom of the benzene ring (dotted line in Fig. 2), as in the case of stilbene (Robertson & Woodward, 1937; Finder, Newton & Allinger, 1974). Since there are no such interactions for θ_2, the small but definite value of θ_2 and the common orientation of the lone-pair electrons should be explained by some other factors. In the present conformation, there is an electronic interaction between lone-pair and π electrons (especially of ethylenic double bonds) (Fig. 2). This would be enough to cause resonance stabilization of the molecule. Such an electronic interaction does not exist in the planar conformation, and is much weaker in the alternative conformation where the atom with the lone-pair electrons is positioned on the opposite side around bond *B*. Such an interaction increases with increasing θ_2 (up to a certain level), whereas π conjugation through the entire molecule decreases uniformly. Thus, at θ_2 near 10° these two opposing factors are balanced in these diolefins.

Benzylideneanilines have a similar type of conjugated system, as shown in Fig. 2. Although a large internal rotation, θ_1, was interpreted as the nonbonded interaction (dotted line in Fig. 2) (Bürgi & Dunitz, 1971), a smaller θ_2 has not yet been noted. We suggest that the electronic interaction mentioned above is also present in these molecules since the values are in the same range as those in the diolefins. This is the case in some other compounds, *e.g.* azobenzene (Brown, 1966), terephthalic acid (Bailey & Brown, 1967), and even nitrobenzaldehyde (Coppens & Schmidt, 1964). The optimum angle depends on the magnitude of the two opposing factors as well as on the packing. The variation of θ_1 in the diolefins may reflect the effect of packing.
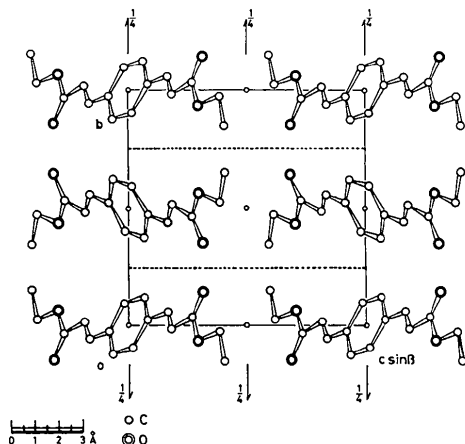
Crystal structure

The arrangements of the molecules in the *p*-PDAEt crystal viewed along the *a* and *b* axes are shown in Figs. 3 and 4 respectively. Unusually short contacts are not observed in this crystal.

The molecules are oriented in such a way that their long axes are nearly perpendicular to the *b* axis (Fig. 3), and the molecules spaced by the *a* translation are also related by a centre of symmetry, the corresponding planar parts in these molecules being parallel to each other. As the long axis of the molecule makes an angle of about 30° to the *a* axis, the molecules are piled up infinitely, displaced in the direction of the long axis by about half a molecule, to form a parallel plane-to-plane stack (Fig. 4), as is seen in Fig. 5.
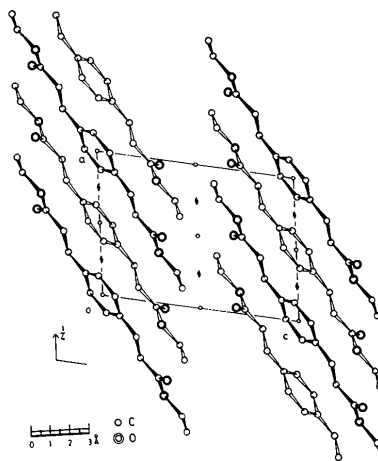
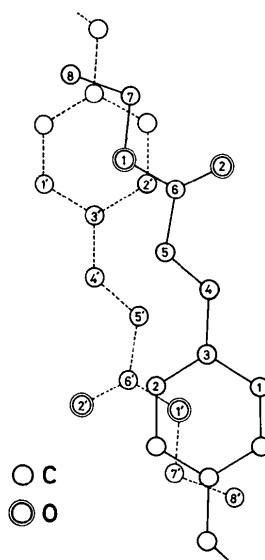Fig. 4. The crystal structure of *p*-PDAEt viewed along the *b* axis.

Fig. 3. The crystal structure of *p*-PDAEt viewed along the *a* axis.

Fig. 5. The overlapping of reacting molecules viewed along the normal of the mean plane of the molecule.

Table 5. *Intermolecular distances* (Å) *between double bonds*

$C(4^i)\cdots C(4'^{ii})$	4·549	$C(4^i)\cdots C(4''^v)$	6·026
$C(4^i)\cdots C(5'^{ii})$	3·970	$C(4^i)\cdots C(5''^v)$	6·943
$C(5^i)\cdots C(5''^{ii})$	3·780	$C(5^i)\cdots C(4''^v)$	5·820
$C(4^i)\cdots C(4'^{iii})$	7·336	$C(5^i)\cdots C(5''^v)$	6·866
$C(4^i)\cdots C(5'^{iii})$	7·588	$C(4^i)\cdots C(4^v)$	7·123
$C(5^i)\cdots C(5'^{iii})$	8·049	$C(4^i)\cdots C(5^v)$	7·188
$C(4^i)\cdots C(4'^{iv})$	8·187	$C(5^i)\cdots C(4^v)$	5·969
$C(4^i)\cdots C(5'^{iv})$	7·398	$C(5^i)\cdots C(5^v)$	5·933
$C(5^i)\cdots C(5'^{iv})$	6·775		

Symmetry code [reference molecule (i) is at the centre of symmetry (1,0,0)]

(i)		$x,$	$y,$	z	(iv)	$-1+x,$		$y,$	$1+z$
(ii)	$-1+x,$	$y,$		z	(v)	$-\frac{1}{2}+x,$	$\frac{1}{2}-y,$		z
(iii)		$x,$	$y,$	$1+z$					

Ethylenic double bonds of two adjacent molecules in the stack, which are antiparallel to each other, approach at a distance of 3·970 Å. This intermolecular distance between double bonds is the shortest. The next shortest contacts, greater than 5 Å, are found between molecules which are related by the *a* glide and are not parallel to each other (Table 5). Therefore, it is most probable that the double bonds in the stack react to form a cyclobutane ring upon photoirradiation, resulting in a linear polymer elongated along the *a* axis. This has been confirmed by an X-ray crystallographic study of the partially polymerized crystal (Nakanishi, Hasegawa & Sasada, 1977).

The shortest distance (3·970 Å) in the present crystal is slightly longer than those in other photopolymerizable crystals [*e.g.* 3·939 for DSP(a), 3·910 for P2VB, 3·937 for *p*-PDAMe, 3·928 for *p*-PDAPh, and 3·931 Å for *p*-phenylenedi(α-cyanoacrylic acid) di-*n*-propyl ester (*p*-CPAnPr) (Nakanishi, Ueno & Sasada, 1976*b*)]. However, it is impossible to find any correlation between photoreactivity and simple geometrical parameters such as the above-mentioned distance and the relative orientation of the double bonds.

Characteristic packing of the diolefins

As an extension of solid-state photodimerization many compounds with two or more cinnamic acid moieties were synthesized in order to examine whether they are photopolymerizable. Only *p*-PDA derivatives give crystalline polymers; dicinnamates and dicinnamides containing alkylene units between two cinnamic moieties, and *m*-phenylenediacrylic acid derivatives produce amorphous oligomers (Hasegawa *et al.*, 1973; Miura, Kitami & Nagakubo, 1968; Holm & Zienty, 1972). From the view of crystal design and/or crystal engineering (Schmidt, 1971), it is of great interest to examine why the rigid rod-like molecules such as *p*-PDA derivatives only favour this type of polymerization (Nakanishi, Hasegawa & Sasada, 1972).

In order to investigate the contacts between the reacting molecules in Fig. 5 a molecule is projected on the mean plane of the adjacent molecule in the same stack. The ester O atom with lone-pair electrons approaches the electron-deficient benzene ring. Intermolecular contacts of this type are common to three *p*-PDA esters, although the close contact between the carbonyl group and the benzene ring has been found in the α-cyano derivative (*p*-CPAnPr). In a wider field this is also the case for DSP(α) and P2VB where two unlike aromatic rings approach each other. No such contacts have been found in the photostable modification of DSP(*y*).

Since all the photopolymerizable diolefins are nearly planar and have two functional groups with their dipoles in opposite directions, they can form a stable plane-to-plane stack only by being displaced by about half a molecule along the molecular long axis, the centre of gravity of the molecules being separated by about 7 Å. This results in packing quite favourable for polymerization. Therefore, the intermolecular contacts between electron-rich and electron-deficient moieties are a predominant motif for the formation of photopolymerizable crystals of this kind. The same type of intermolecular contact also appears in the photodimerizable crystal of cinnamic acid (α) (Schmidt, 1964).

Thus, the conditions for obtaining photopolymerizable crystals are that the rigid rod-like molecule should be nearly planar and the two functional groups have mutually opposite dipole directions, although they need not necessarily be equal (Addadi, Cohen & Lahav, 1975). Such a hypothesis has recently been exemplified by the four-centre-type photopolymerization of *p*-phenylenedibutadienoic acid derivatives which give rise to some novel rod-like polymers with a pendant olefin every 7·5 Å. A report of this will be published elsewhere.

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The Crystal Structure of the Molecular Complex between Triphenylmethyl Dimer and Ethyl Acetate

BY J. ALLEMAND AND R. GERDIL*

Département de Chimie Organique et Laboratoire de Cristallographie aux Rayons-X, Université de Genève, 30 quai Ernest Ansermet, 1211 Genève, Switzerland

Triphenylmethyl radicals produced in ethyl acetate give rise to a crystalline 1:1 solvate. $[C_{38}H_{30}.C_4H_8O_2]$ is triclinic ($P\bar{1}$) with $a = 13.690$ (9), $b = 12.198$ (9), $c = 10.776$ (7) Å; $\alpha = 81.96$ (8), $\beta = 79.06$ (8), $\gamma = 70.15$ (8)°; $Z = 2$. Diffracted intensities were measured on an automated four-circle diffractometer. The structure was solved in a stepwise manner by direct methods and refined to a final R of 0.058. H atoms were located from a difference synthesis and their positions refined. The dimer is 1-diphenylmethylene-4-triphenyl-methyl-2,5-cyclohexadiene resulting from the unsymmetrical coupling of the central C of one radical with the *para* C atom of one phenyl nucleus of another radical. The newly formed bond has a length of 1.589 Å. The packing of the irregular-shaped dimer molecules entails the presence of cavities large enough to accommodate guest molecules. The solvent molecules are not single-positioned in the cavities, but rather assume two definite orientations statistically distributed in a 1:1 ratio. This type of disorder is best accounted for by an ethyl acetate model having the ethyl group twisted out of the plane of the CH_3CO_2· fragment.

Introduction

At the beginning of the century the discovery of triphenylmethyl by Gomberg (1900) demonstrated the existence of stable free radicals in solution and was the start of numerous subsequent studies, which are still being carried out, on the lability of the single C—C bond in highly substituted ethanes. The triphenyl-methyl radicals exist in equilibrium with the molecular

compound according to 2Ph₃C· ⇌ dimer (TPMD). Soon after Gomberg's discovery Jacobson (1905) rightly suggested that the dimer was not hexaphenyl-ethane but had a methylenecyclohexadiene structure resulting from the unsymmetrical coupling of the central atom of one radical with the *para* C atom of one phenyl nucleus of another radical. This view was, however, rejected by later investigators and the hexa-phenylethane structure was considered valid for over 60 years (review: McBride, 1974) till Lankamp, Nauta & McLean (1968), as well as Staab, Brettschneider &

* Author to whom correspondence should be addressed.