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

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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-triphenylmethyl-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 triphenylmethyl radicals exist in equilibrium with the molecular

compound according to 2Ph$_3$C· ⇌ dimer (TPMD). Soon after Gomberg's discovery Jacobson (1905) rightly suggested that the dimer was not hexaphenylethane 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 hexaphenylethane structure was considered valid for over 60 years (review: McBride, 1974) till Lankamp, Nauta & McLean (1968), as well as Staab, Brettschneider &

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Brunner (1970), were able to confirm that the dimer was actually 1-diphenylmethylene-4-triphenylmethyl-2,5-cyclohexadiene.

Following the experimental setting described by Staab *et al.* (1970) we have carried out ^{1}H NMR measurements on the dimer prepared from triphenylchloromethane in acetone, benzene and carbon tetrachloride and obtained spectra consistent with the assumed structure. By evaporation of the solutions powdery residues were left, which upon dissolving again displayed the same ^{1}H NMR spectrum as the original solution. By this route, however, we were unable to grow any sizeable crystal of the pure dimer amenable to X-ray analysis. Therefore, we turned to the description reported by Gomberg (1901) of so-called 'compounds' generated by the interaction of triphenylmethyl with oxygen-containing solvents such as ethers or esters. In these cases it seemed most likely to us that the author had been confronted with dimer–solvent molecular complexes. Following Gomberg's procedure large crystals can indeed be grown and isolated from the reaction mixtures under adequate experimental conditions. The crystals are diamagnetic and generate a paramagnetic solution when dissolved in the appropriate solvent.

Experimental and structure determination

To a solution of triphenylchloromethane in dry ethyl acetate zinc turnings were added and the mixture was allowed to stand for several days under an atmosphere of dry nitrogen. Plate-shaped, yellowish prisms slowly grew at the metal–solution interface and on the walls of the reaction vessel (Schlenk tube). During the removal of the crystals from the reaction mixture care must be taken to avoid any contact with air or moisture. The crystal density was measured by flotation in a mixture of methylene chloride and ethyl acetate. ^{1}H NMR spectra were recorded at 34 °C with a Varian XL-100 spectrometer using tetramethylsilane as internal standard in $CDCl_3$: the aliphatic proton and olefinic protons form an $|AA'BB'C|$ system ($^3J_{AB} = 10$ Hz) with signals at [δ p.p.m.] 6·40 (A,2H), 6·09 (B,2H) and 5·18 (C,1H). The magnetic properties of a sample of crystals were tested and good evidence of their diamagnetism was obtained. Dissolving the sample in ethyl acetate produced a paramagnetic solution whose ESR spectrum was measured with a JEML ME-1X recording spectrometer (10 kH, field modulation) and found to be identical with that of triphenylmethyl (Schreiner, Berndt & Baer, 1973).

The crystal selected for X-ray analysis was cut to 0·36 × 0·33 × 0·21 mm and sealed in a Lindemann capillary containing a cellulose fibre impregnated with ethyl acetate. Lattice parameters and diffracted intensities were measured at room temperature on an automated four-circle Philips PW1100 diffractometer with graphite-monochromated Mo $K\bar{\alpha}$ radiation using the ω-scan technique at 2·4° min^{-1} in ω (scan width 1°).

Crystal data

$[C_{38}H_{30}.C_4H_8O_2]$ (crystals decompose between 80–90 °C). Triclinic; space group $P\bar{1}$, $a = 13·690$ (9), $b = 12·198$ (9), $c = 10·776$ (7) Å, $\alpha = 81·96$ (8), $\beta = 79·06$ (8), $\gamma = 70·15$ (8)°; $Z = 2$; $D_m = 1·157$, $D_x = 1·160$ g cm^{-3}; $\mu = 0·772$ cm^{-1}; $F(000) = 612$.

Of the 5253 reflections measured in the range $3° < \theta < 25°$, 4976 were independent. A monitor reflection measured at constant intervals showed no signs of crystal degradation. After the usual corrections and averaging, the reflections were considered observed at the $4\sigma(F)$ level and merged into a set of 2937 structure amplitudes which were used in the structure analysis. No absorption correction was applied. The structure was solved by direct methods using the XRAY system (1976) series of programs. 6113 relationships were derived for 526 reflections with $|E| > 1·6$. The initial E map revealed only a small recognizable molecular fragment which was further extended in a stepwise manner by successive E syntheses till the whole molecular frame became apparent. At this stage ($R = 0·33$) the location of the solvent was found from a difference synthesis. Positional and anisotropic thermal parameters were refined by least-squares analysis. The function minimized was $\sum w\Delta F^2$ where $w = 1$ for $F_o \leq 32$ and $w = (32/F_o)^2$ for $F_o > 32$. When the R value was reduced to 0·10 a difference electron-density distribution revealed all the H atoms of the dimer and average positions for some of those of the ethyl acetate.
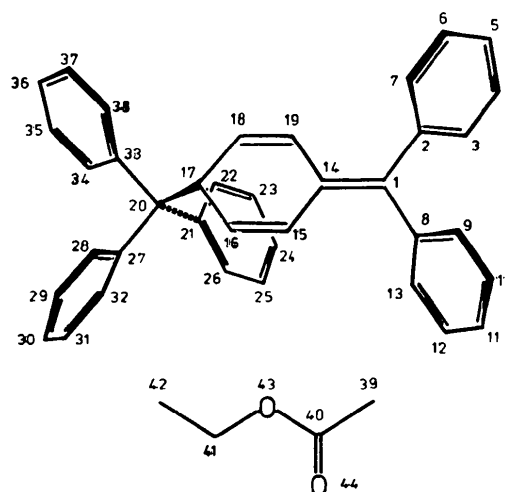

Fig. 1. The atom-numbering system.

Table 1. *Final positional parameters* (×10⁴) *of the dimer, with standard deviations in parentheses*

	x	y	z		x	y	z
C(1)	8434 (3)	7748 (3)	1037 (3)	C(20)	4238 (3)	7989 (3)	1907 (3)
C(2)	9151 (3)	7468 (3)	−186 (3)	C(21)	4928 (3)	6709 (3)	2172 (3)
C(3)	9997 (3)	6435 (4)	−229 (4)	C(22)	5228 (3)	5939 (4)	1238 (4)
C(4)	10678 (3)	6134 (4)	−1345 (4)	C(23)	5939 (4)	4821 (4)	1415 (5)
C(5)	10540 (3)	6874 (5)	−2427 (4)	C(24)	6362 (4)	4466 (4)	2517 (6)
C(6)	9716 (4)	7919 (5)	−2389 (4)	C(25)	6082 (4)	5215 (4)	3454 (5)
C(7)	9023 (3)	8221 (4)	−1281 (4)	C(26)	5374 (3)	6331 (3)	3273 (4)
C(8)	8986 (3)	7680 (4)	2122 (4)	C(27)	3499 (3)	8521 (3)	3093 (3)
C(9)	9676 (3)	8321 (5)	2027 (4)	C(28)	3127 (3)	9724 (4)	3180 (4)
C(10)	10241 (4)	8240 (7)	3003 (7)	C(29)	2432 (3)	10221 (4)	4226 (4)
C(11)	10113 (5)	7499 (9)	4037 (7)	C(30)	2076 (3)	9530 (5)	5185 (4)
C(12)	9443 (5)	6882 (7)	4211 (5)	C(31)	2402 (4)	8346 (5)	5107 (4)
C(13)	8856 (3)	6955 (5)	3213 (4)	C(32)	3104 (3)	7840 (4)	4066 (4)
C(14)	7373 (3)	8031 (3)	1148 (3)	C(33)	3501 (2)	8097 (3)	943 (3)
C(15)	6669 (3)	8458 (3)	2306 (3)	C(34)	2869 (3)	7385 (3)	1168 (3)
C(16)	5624 (3)	8771 (3)	2415 (3)	C(35)	2152 (3)	7483 (4)	367 (4)
C(17)	5041 (3)	8692 (3)	1399 (3)	C(36)	2048 (3)	8289 (4)	−668 (4)
C(18)	5797 (3)	8207 (4)	253 (3)	C(37)	2656 (3)	9005 (4)	−899 (4)
C(19)	6832 (3)	7940 (4)	134 (3)	C(38)	3370 (3)	8916 (3)	−89 (4)

Table 2. *Final positional and isotropic thermal parameters* (×10³) *of the hydrogen atoms*

The atoms are labelled according to the C to which they are bonded.

	x	y	z	U (Å²)		x	y	z	U (Å²)
H(3)	1011 (3)	592 (3)	59 (3)	86 (13)	H(22)	497 (3)	620 (3)	39 (3)	85 (14)
H(4)	1131 (3)	534 (3)	−136 (4)	109 (14)	H(23)	615 (3)	438 (3)	71 (4)	113 (14)
H(5)	1101 (3)	665 (3)	−326 (3)	88 (13)	H(24)	690 (3)	366 (3)	258 (3)	102 (14)
H(6)	961 (3)	847 (3)	−314 (3)	93 (13)	H(25)	636 (3)	505 (3)	425 (3)	81 (13)
H(7)	845 (3)	904 (3)	−119 (3)	90 (13)	H(26)	515 (2)	684 (2)	394 (3)	51 (11)
H(9)	971 (4)	890 (4)	111 (4)	121 (15)	H(28)	336 (3)	1025 (3)	237 (3)	96 (14)
H(10)	1078 (4)	874 (5)	282 (5)	147 (17)	H(29)	218 (3)	1112 (4)	418 (4)	116 (15)
H(11)	1052 (4)	751 (5)	470 (5)	167 (18)	H(30)	160 (3)	983 (4)	599 (4)	122 (15)
H(12)	933 (4)	638 (5)	494 (5)	149 (15)	H(31)	216 (3)	789 (3)	579 (4)	102 (14)
H(13)	836 (3)	644 (3)	320 (4)	92 (14)	H(32)	331 (2)	697 (3)	400 (3)	65 (12)
H(15)	698 (2)	857 (2)	302 (3)	55 (11)	H(34)	297 (3)	676 (3)	188 (3)	78 (14)
H(16)	521 (2)	905 (2)	326 (3)	55 (11)	H(35)	168 (3)	698 (3)	64 (3)	98 (15)
H(17)	458 (2)	955 (3)	115 (3)	60 (12)	H(36)	153 (3)	833 (3)	−124 (3)	95 (14)
H(18)	550 (2)	810 (2)	−46 (3)	54 (11)	H(37)	257 (3)	967 (3)	−165 (3)	87 (13)
H(19)	726 (2)	767 (2)	−65 (3)	54 (11)	H(38)	380 (2)	944 (3)	−27 (3)	58 (12)

Their coordinates were included in the structure model and isotropically refined. The final R value based on 2851 reflections was 0·058. The numbering system is given in Fig. 1. The final positional parameters are listed in Tables 1 and 2.*

Discussion of the results

The bond lengths and angles are given in Table 3. With regard to its special situation as a guest molecule ethyl acetate will be discussed separately further below.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33433 (36 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The C—H lengths measured on the dimer range from 0·94 to 1·07 Å, mean value 1·01 (5) Å; a stereoscopic view of the molecule is shown in Fig. 2. The cyclohexadiene ring (atoms 14, 15, 16, 17, 18, 19) is planar with an e.s.d. of 0·014 Å of the atoms from the plane. The exocyclic methylene C is shifted by 0·025 Å from this plane, away from the triphenylmethyl group, with a concomitant torsion of about 9° of the double bond, as defined by the orientation of the bonds to the two adjacent phenyl rings. This torsion is caused mainly by repulsion between C(7)···H(19) and C(13)···H(15) separated by 2·66 and 2·67 Å respectively. Correspondingly, C(1)—C(14) appears a little longer than the other two olefinic bonds. The twist angles of the phenyl rings about C(1)—C(2) and C(1)—C(8) are 53·1 and 55·3° respectively. They are best defined by the

Table 3. *Molecular parameters of the dimer*

Bond distances are in Å, angles in degrees.

|			
C(1) C(2) 1·491 (5)	C(21) C(26) 1·387 (6)	C(4) C(5) C(6) 119·4 (4)	C(27) C(20) C(33) 104·7 (3)
C(1) C(8) 1·486 (6)	C(22) C(23) 1·392 (6)	C(5) C(6) C(7) 121·0 (4)	C(20) C(21) C(22) 120·1 (3)
C(1) C(14) 1·360 (5)	C(23) C(24) 1·371 (8)	C(2) C(7) C(6) 119·8 (4)	C(20) C(21) C(26) 121·9 (4)
C(2) C(3) 1·392 (5)	C(24) C(25) 1·369 (8)	C(1) C(8) C(9) 119·6 (4)	C(22) C(21) C(26) 117·5 (3)
C(2) C(7) 1·391 (6)	C(25) C(26) 1·391 (6)	C(1) C(8) C(13) 121·0 (5)	C(21) C(22) C(23) 120·7 (4)
C(3) C(4) 1·384 (6)	C(27) C(32) 1·389 (6)	C(9) C(8) C(13) 119·4 (4)	C(22) C(23) C(24) 120·6 (5)
C(4) C(5) 1·373 (7)	C(27) C(28) 1·390 (6)	C(8) C(9) C(10) 121·2 (5)	C(23) C(24) C(25) 119·8 (4)
C(5) C(6) 1·385 (7)	C(28) C(29) 1·391 (6)	C(9) C(10) C(11) 117·5 (7)	C(24) C(25) C(26) 119·4 (5)
C(6) C(7) 1·384 (6)	C(29) C(30) 1·364 (7)	C(10) C(11) C(12) 124·7 (7)	C(21) C(26) C(25) 121·9 (4)
C(8) C(9) 1·400 (8)	C(30) C(31) 1·369 (8)	C(11) C(12) C(13) 118·5 (6)	C(20) C(27) C(32) 121·8 (4)
C(8) C(13) 1·390 (6)	C(31) C(32) 1·394 (6)	C(8) C(13) C(12) 118·7 (6)	C(20) C(27) C(28) 120·9 (3)
C(9) C(10) 1·395 (9)	C(33) C(34) 1·390 (6)	C(1) C(14) C(15) 122·3 (4)	C(28) C(27) C(32) 117·0 (3)
C(10) C(11) 1·357 (11)	C(33) C(38) 1·382 (5)	C(1) C(14) C(19) 123·6 (3)	C(27) C(28) C(29) 121·7 (4)
C(11) C(12) 1·343 (14)	C(34) C(35) 1·391 (6)	C(15) C(14) C(19) 114·2 (3)	C(30) C(29) C(28) 120·1 (4)
C(12) C(13) 1·437 (9)	C(35) C(36) 1·374 (6)	C(14) C(15) C(16) 122·9 (4)	C(29) C(30) C(31) 119·6 (4)
C(14) C(15) 1·463 (5)	C(36) C(37) 1·369 (8)	C(15) C(16) C(17) 124·6 (3)	C(32) C(31) C(30) 120·7 (5)
C(14) C(19) 1·467 (6)	C(37) C(38) 1·399 (7)	C(16) C(17) C(18) 110·5 (3)	C(27) C(32) C(31) 120·9 (4)
C(15) C(16) 1·335 (5)		C(16) C(17) C(20) 112·1 (3)	C(20) C(33) C(34) 118·4 (3)
C(16) C(17) 1·503 (6)	C(2) C(1) C(8) 113·9 (3)	C(18) C(17) C(20) 112·6 (3)	C(20) C(33) C(38) 124·2 (4)
C(17) C(18) 1·500 (5)	C(2) C(1) C(14) 122·9 (4)	C(17) C(18) C(19) 124·5 (4)	C(34) C(33) C(38) 117·2 (4)
C(17) C(20) 1·589 (6)	C(8) C(1) C(14) 123·2 (3)	C(14) C(19) C(18) 123·3 (3)	C(33) C(34) C(35) 121·0 (3)
C(18) C(19) 1·327 (5)	C(1) C(2) C(3) 119·2 (3)	C(17) C(20) C(21) 105·3 (3)	C(34) C(35) C(36) 120·9 (4)
C(20) C(21) 1·545 (5)	C(1) C(2) C(7) 122·3 (3)	C(17) C(20) C(27) 109·9 (3)	C(35) C(36) C(37) 119·0 (5)
C(20) C(27) 1·542 (5)	C(3) C(2) C(7) 118·6 (3)	C(17) C(20) C(33) 112·0 (3)	C(36) C(37) C(38) 120·2 (4)
C(20) C(33) 1·543 (5)	C(2) C(3) C(4) 121·2 (3)	C(21) C(20) C(27) 113·2 (3)	C(33) C(38) C(37) 121·6 (4)
C(21) C(22) 1·382 (6)	C(3) C(4) C(5) 120·0 (4)	C(21) C(20) C(33) 111·8 (3)	
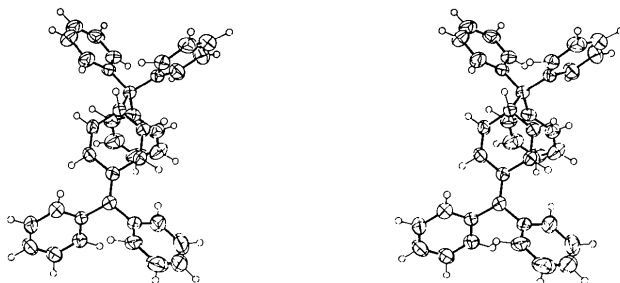
Fig. 2. Stereoscopic view of the molecular conformation.

dihedral angles between the plane through 1—2—8—14 (e.s.d. 0·002 Å) and the mean plane through Ph(2) and Ph(8) [for convenience the phenyl rings are denoted, in the following, by Ph(*i*) where *i* is the label of the *ipso* C atom]. Furthermore, the dihedral angle between Ph(2) and Ph(8) is 83·5° as compared with 56° in benzophenone (Fleischer, Sung & Hawkinson, 1968).

The activation energy of the C(17)—C(20) bond homolysis amounts to about 19 kcal mol⁻¹ with a dissociation energy of 12 kcal mol⁻¹ (Ingold, 1973). In view of these low values a bond length of 1·589 Å does not appear exceedingly long. It lies close to the value, 1·582 Å, found for hexamethylethane (Bartell & Boates, 1976) whose thermolysis involves an activation energy of 68·5 kcal mol⁻¹ (Tsang, 1966). Pentaphenylethane (PPE), which can be regarded as a true ethane at room temperature, only splits into radicals

above 105 °C (Bachmann & Wiselogle, 1936) with an activation energy of 27·6 kcal mol⁻¹. Empirical forcefield calculations (EFF) have recently been performed to determine strain energies and geometries of hexaphenylethane (HPE) and similar strained hydrocarbons (Hounshell, Dougherty, Hummel & Mislow, 1977). The calculated central bond length of PPE is 1·595 Å, probably an underestimated value owing to the approach used in the EFF parametrization. Comparison with C(17)—C(20) in TPMD suggests that the spontaneous dissociation of the latter at room temperature does not reflect essentially the internal molecular strain in the ground state, but rather a favourable electron redistribution in the transition state (low activation energy). Therefore, bond lengths calculated by EFF methods are not necessarily representative of the tendency to homolysis.

The triphenylmethyl group is characterized by very different twist angles of the phenyl rings about the bonds joining C(20) to C(21), C(27) and C(33); the angles are 84·7, 35·2 and 12·2° respectively. The cyclohexadiene ring and Ph(21) almost have a common bisector plane passing through atoms 14—17—20—21. This reciprocal orientation minimizes the front strain as evidenced by the distances C(18)···C(22) = 3·117 and C(16)···C(26) = 3·103 Å, and by the small C(17)—C(20)—C(21) angle of 105·3°. The front strain of Ph(27) and Ph(33) with the cyclohexadienyl moiety is more important leading to larger values for the angles C(21)—C(20)—C(27) (113·2°) and C(21)—C(20)—C(33) (111·8°), and subsequent decrease of C(27)—
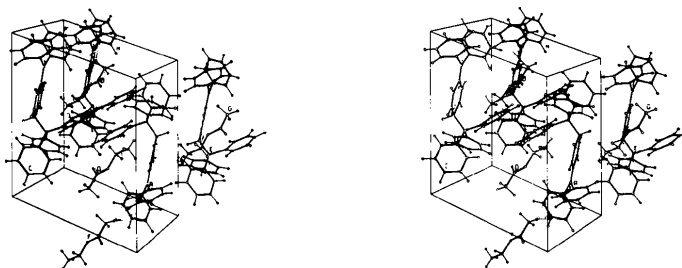
Fig. 3. Stereoscopic view of some aspects of the molecular packing. The origin is in the upper rear corner. The a, b and c axes respectively point downward, to the right and to the left. The basic molecules with positions x,y,z are denoted by A and B. The dotted lines stress the closest intermolecular approaches. The following distances, between one H and one unsaturated ring, are averaged over the six depicted H$\cdots$C contacts: H(E)$\cdots A$ = 3·11 (5); H(F)$\cdots A$ = 3·32 (18); H(B)$\cdots$H = 3·30 (11) Å. Relevant diatomic contacts are: H(A)$\cdots$O(D) = 2·70; H(A)$\cdots$H(H) = 2·43 Å.

C(20)–C(33) to 104·7°. A strong repulsion prevails between H(17) and the proximal atoms H(28) and H(38) at 1·94 and 2·07 Å, respectively, as well as between C(27)$\cdots$H(16) and C(26)$\cdots$H(32) separated by 2·68 and 2·66 Å, respectively. The phenyl rings Ph(27) and Ph(33) are further locked in their present orientation by van der Waals contacts between the distal H(32) and H(34).

Molecular packing and disordered guest molecule

Some aspects of the molecular packing are shown in Fig. 3. There are no contacts shorter than the sum of the van der Waals radii. The shortest intermolecular distances are H(5)$\cdots$H'(11) = 2·41 and C(35)$\cdots$C'(9) = 3·404 Å between molecules related by a translation unit along c and a respectively.

The antagonistic internal non-bonded interactions confer a definite rigidity on the host molecule. The packing of such irregular shaped units entails the presence of cavities large enough to accommodate molecules of ethyl acetate. The refined positional parameters of the latter (Table 4) lead to a planar molecule (e.s.d. 0·015 Å) with anomalous bond distances which are too short [e.g. C(41)–C(42) = 1·290; C(40)–C(43) = 1·296 Å; etc.] whereas the bond angles fall in the expected ranges [e.g. C(42)–C(41)–O(43) = 108·2; C(39)–C(40)–O(44) = 125·6°; etc.]. The observed atoms display highly anisotropic thermal motion with conspicuously high amplitudes perpendicular to the molecular plane (Fig. 4). These correspond to r.m.s. values ranging from 0·41 Å for C(40) to 0·69 Å for C(42), which are obviously prohibitive values likely to be related to some localized disorder in the atomic locations. In an attempt to obtain more information about this disorder a ΔF synthesis was calculated with F_c values from which the contribution of the ethyl acetate molecule had been omitted. Sections passing

Table 4. Average positional parameters ($\times 10^3$) of ethyl acetate, located from a difference synthesis

	x	y	z
C(39)	185	456	221
C(40)	261	429	309
C(41)	404	298	385
C(42)	484	183	362
O(43)	335	329	294
O(44)	265	490	382
H1(39)	134	540	241
H2(39)	152	386	229
H3(39)	227	447	118
H1(41)*	443	364	378
H2(41)*	359	294	480
H1(42)	540	170	403
H2(42)	454	101	352
H3(42)	521	173	273

* Calculated coordinates.

through the various atoms are shown in Fig. 4. With the exception of C(40) the electron density of all the atoms is considerably elongated in a direction perpendicular to the 'observed' molecular plane. The electron density along the different axes is approximately Gaussian and accordingly could be fitted by a sum of a number of smaller peaks. The simplest hypothesis, somewhat implied by the constraint of having longer bonds, was to assume the presence of two conformational models distributed statistically in the ratio 1 : 1 over the available sites. For the purpose of semi-quantitative discussion the electron density along the radius of spherical C and O atoms was calculated for an average temperature factor of 5 Å^2 (initial Wilson plot) over 1500 terms of the Mo sphere of reflection. The peaks resulting from the sum of two transform profiles placed at various distances $\pm|\delta|$ from the average position of each atom were drawn and the δ value corresponding to the best fit with the experimental profile was retained (Fig. 5). The set of empirical δ_i values can be used to assign two new alternative pos-
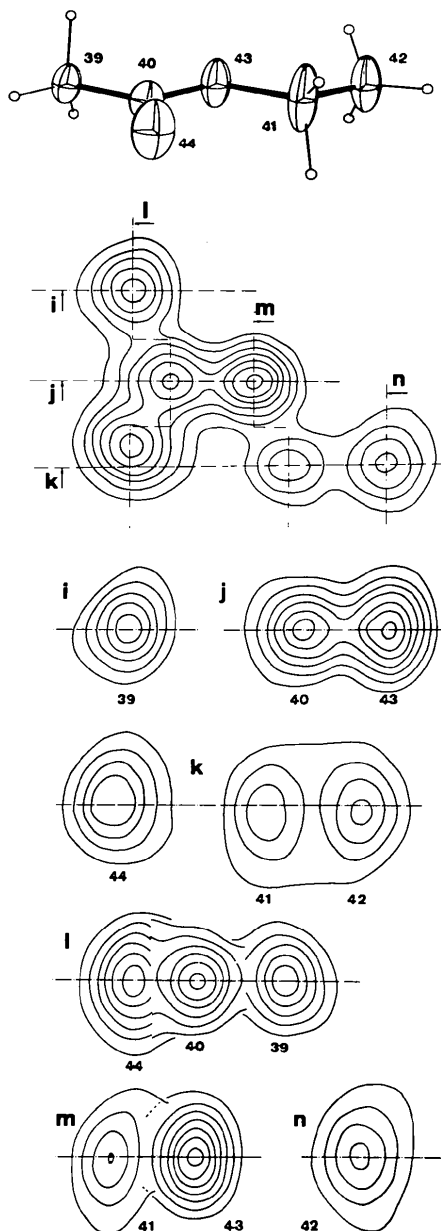
Fig. 4. Ethyl acetate. Molecular frame and thermal ellipsoids after refinement of the coordinates resulting from a ΔF synthesis in which the contribution of the molecule had been omitted. Various sections through the difference map are shown below. The main section is coincident with the molecular plane; the other sections are perpendicular to this plane. The contours are at intervals of 0·4 e Å^{-3}, starting at 0·4 e Å^{-3}.
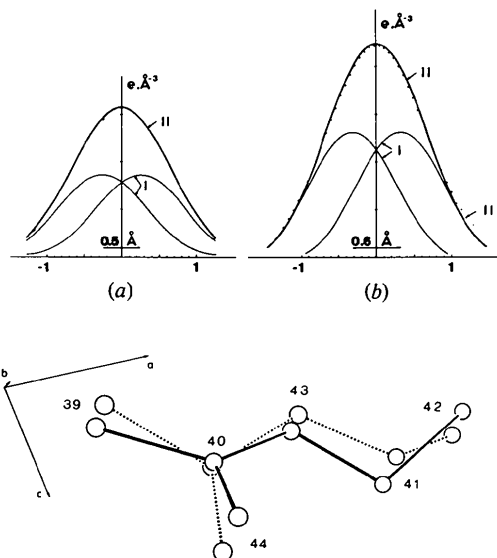

Fig. 5. Electron density profiles (II) along lines perpendicular to the molecular plane and passing through the centre of (a) C(42) and (b) O(44). The compound peak (III) obtained by the summation of two corresponding transform profiles is shown when not coincident with (II). The separation of the transform profiles (δ value) is indicated near the origin of the coordinate axes. The two alternative orientations for the ethyl acetate model are illustrated below with respect to the crystallographic axes.

itions $\mathbf{r}'_i = \mathbf{r}_i + \boldsymbol{\delta}'_i$ or $\mathbf{r}''_i = \mathbf{r}_i + \boldsymbol{\delta}''_i$ to each atom, where the vectors $\boldsymbol{\delta}'_i$ ($\Delta x, \Delta y, \Delta z$) and $\boldsymbol{\delta}''_i$ ($-\Delta x, -\Delta y, -\Delta z$) are parallel to the normal to the observed molecular plane. The endpoints of the positional vectors $\mathbf{r}_i$ can be chosen either at the peaks resulting from the ΔF synthesis or at their projections on the mean molecular plane. Owing to the approximations involved in our approach we adopted

the latter alternative giving rise to a single average geometry substantiated by two enantiomeric models (Fig. 5). This in no way precludes the actual occurrence of two 'distinct' conformers in agreement with the asymmetry of the cavity.

Among the numerous ways of linking pairs of atoms in the new set of atomic positions, only one arrangement of bonds gives rise to a structurally satisfactory model. Let us denote by the same subscript (1 or 2) all the available atomic positions on the same side of the plane, then one sequence of adequate locations is $\{39_1, 40_2, 41_1, 42_2, 43_1, 44_2\}$ leading to the following bond distances and angles: C(39)—C(40) = 1·48, C(40)—O(43) = 1·32, C(40)—O(44) = 1·20, O(43)—C(41) = 1·42, C(41)—C(42) = 1·56 Å; C(39)—C(40)—C(43) = 111, C(39)—C(40)—C(44) = 128, O(43)—C(40)—O(44) = 121, C(42)—C(41)—O(43) = 107, C(40)—O(43)—C(41) = 114°. The atoms 39—40—43—44 are reasonably coplanar (e.s.d. 0·018 Å). Their mean plane subtends an angle of 10° with the plane defined by the atoms 42—41—43, thus affording an average value for the torsion angle about C(40)—O(43) in agreement with the mean value 25° observed for methyl acetate in the gas phase (O'Gorman, Shand & Schomaker, 1950). The ethyl group is further twisted around O(43)—C(41) by an angle of 151°.

As depicted in Fig. 4, it was possible, in spite of the disorder, to determine from the ΔF synthesis the

orientation and an approximate geometry for both CH_3 groups of ethyl acetate. The H peaks are diffuse but their analytical centre bears some significance, leading to the following average geometry taken over the two groups: C–H $= 1.07$ (11) Å; C–C–H $= 112$ (5), H–C–H $= 106$ (13)°.

A test of the above disordered model ($B = 5$ Å^2 for all the atoms), based on structure factor calculations showed an increase in the value of $[\sum w\Delta^2/(m-n)]^{1/2}$ of about 20% and yielded an R factor of 0·078. As we have pointed out, the refined planar model (Fig. 4) does not represent a single molecule and must be rejected as such. On the other hand, the model arrived at empirically by considering the aspherical electron distribution at the atomic sites of the solvent is a constrained limiting case implying a minimum number of parameters. It is clear that the introduction of additional parameters (e.g. a weighted population of conformers) could reduce $\sum w\Delta^2$ to any desired value without necessarily increasing the physical significance of the results. This was demonstrated in refining aniso-tropically the disordered model in Fig. 5, considering two independent molecules with a constant weight of $\frac{1}{2}$. Introduction of a damping factor decreased R to 0·055 after only two cycles of refinement (planar model $R = 0·058$). The initial model did not collapse into a single 'average' molecule but afforded two new different conformers slightly displaced from the initial ones. No undue values of the thermal parameters were to be noted. The geometries, though physically inconsistent, show some improvement over that of the planar model. This test might add further support to the type of disorder suggested above in an oversimplified manner. The number of parameters to be handled and the inaccuracy of the data make the least-squares method

unrealistic in the present case and we think that results obtained from a simple interpretation of the difference synthesis are more trustworthy.

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The Conformation of Heterocyclic Spiro Compounds.
III. The Crystal and Molecular Structure of N-(β-Hydroxyethyl)granatanine-3-spiro-5'-hydantoin

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N-(β-Hydroxyethyl)granatanine-3-spiro-5'-hydantoin, $C_{13}H_{19}N_3O_3$, is monoclinic, $a = 9·326$ (1), $b = 11·720$ (1), $c = 12·166$ (1) Å, $\beta = 109·23$ (1)°, $Z = 4$, space group $P2_1/c$. The atomic positions were determined by direct methods and refined by full-matrix least squares to an R of 0·044 for 1955 reflections. The bicyclo[3.3.1]nonane system adopts a boat–chair conformation. The structure is held together by a system of hydrogen bonds.