124. The Crystal Structure of the Pentaphenylethane/Acetone Solvate by X-Ray Analysis

by **Gerald Bernardinelli** and **Raymond Gerdil**[1])

Département de Chimie Organique et Laboratoire de Radiocristallographie, Université de Genève, 30, quai Ernest-Ansermet, CH-1211 Genève 4

(30.III.81)

Summary

The crystal structure of the acetone solvate of pentaphenylethane ($C_{32}H_{26} \cdot \frac{1}{2} C_3H_6O$; monoclinic, $a = 8.625$, $b = 16.587$, $c = 16.961$ Å, $\beta = 95.75°$, space group $P2_1/c$, $Z = 4$) has been determined by X-ray analysis. The structure was solved by direct methods and refined to a final R of 0.056. The central ethane bond has a length of 1.612(3) Å. The cavity enclosing the solvent retains the inversion centre in the crystal: as a consequence, a two-fold disordered orientation was observed for the acetone molecule. The rotational orientation of the methyl groups was found to be staggered with respect to the C, O-bond.

Introduction. - As part of our interest in the stereochemistry of polyarylmethanes and polyarylethanes [1] we have turned our attention to the X-ray structure of pentaphenylethane (PPE) in order to compare the solid state geometry of this highly strained molecule with the ground-state conformation calculated by *Mislow et al.* [2]. At the time the present work was being completed the X-ray structure of the PPE/tetrahydrofuran solvate was independently published by *Simonetta et al.* [3]. The present account stresses some basic features of the PPE/acetone solvate with

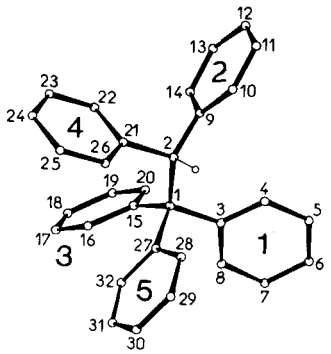

Fig. 1. *The atom- and phenyl-numbering systems.* The H-atoms are numbered according to the convention C(i)–H(i).

[1]) To whom correspondence should be addressed.

0018-019X/81/5/1365-07$01.00/0 © 1981 Schweizerische Chemische Gesellschaft

special emphasis on the molecular packing of the host PPE with the enclosed solvent. In a following paper [4] some dynamic aspects of the stereoisomerization of PPE will be studied by empirical force field methods.

Experimental Part. - Colorless crystals of the acetone solvate [$C_{32}H_{26} \cdot \frac{1}{2}\ C_3H_6O$] were grown from an acetone solution by slow evaporation. The crystallographic data are: $a = 8.625(2)$, $b = 16.587(6)$, $c = 16.961(4)$ Å, $\beta = 95.75(2)°$, space group $P2_1/c$; $Z = 4$; $d_{obs} = 1.207$, $d_{calc} = 1.209$ g cm^{-3}. Lattice parameters and diffracted intensities were measured at RT. on an automated four-circle PW1100 diffractometer with graphite monochromated Mo$K\alpha$-radiation ($\omega - 2\theta$ scan). A data set of 2612 independent structure amplitudes, with $|F_o| > 3\sigma(F_o)$, was used in the structure analysis.

The structure was solved by direct methods using the SINGEN and TANGEN programs of the XRAY system [5]. The first E synthesis revealed the whole molecular frame, except for C(5), the position of which was calculated together with those of the H-atoms of the phenyl rings. After a few cycles of anisotropic block-diagonal refinement (isotropic for the H-atoms) a difference synthesis revealed a planar distribution[2]) of smeared out atomic peaks (non-H-atoms) for the disordered acetone molecule, in accordance with its special position on a centre of symmetry. The H(2)-atom was located

Table 1. *Final positional and isotropic thermal parameters* ($\times 10^4$ for non-hydrogen atoms and $\times 10^3$ for hydrogen atoms)

Atom	x	y	z	U(Å^2)	Atom	x	y	z	U(Å^2)
C(1)	4839(3)	2770(1)	3204(1)	394	H(2)	620(3)	337(2)	411(1)	57
C(2)	5439(3)	2868(1)	4130(1)	404	H(4)	405(3)	430(1)	374(1)	48
C(3)	3936(3)	3513(1)	2841(1)	396	H(5)	283(3)	540(2)	312(2)	85
C(4)	3703(3)	4226(1)	3232(1)	521	H(6)	186(3)	524(2)	175(2)	83
C(5)	2942(3)	4873(2)	2847(2)	620	H(7)	226(4)	406(2)	104(2)	88
C(6)	2396(3)	4821(2)	2062(2)	626	H(8)	358(3)	297(1)	175(2)	61
C(7)	2631(3)	4119(2)	1658(2)	602	H(10)	566(3)	402(1)	515(1)	53
C(8)	3393(3)	3477(1)	2043(1)	505	H(11)	418(3)	444(2)	619(2)	72
C(9)	4266(3)	3120(1)	4696(1)	436	H(12)	163(4)	376(2)	631(2)	100
C(10)	4693(3)	3741(2)	5233(1)	532	H(13)	93(4)	261(2)	539(2)	95
C(11)	3761(4)	3971(2)	5812(2)	642	H(14)	252(3)	226(1)	441(1)	61
C(12)	2376(4)	3581(2)	5881(2)	683	H(16)	564(3)	119(1)	320(1)	52
C(13)	1914(3)	2972(2)	5360(2)	674	H(17)	403(3)	2(2)	308(2)	72
C(14)	2845(3)	2740(2)	4776(1)	558	H(18)	119(4)	14(2)	292(2)	88
C(15)	3802(3)	2007(1)	3092(1)	377	H(19)	0(3)	145(2)	284(2)	70
C(16)	4447(3)	1237(1)	3136(1)	440	H(20)	170(3)	263(1)	296(1)	52
C(17)	3508(3)	555(1)	3069(1)	529	H(22)	469(3)	156(2)	499(2)	66
C(18)	1915(3)	628(2)	2979(2)	564	H(23)	597(4)	47(2)	546(2)	116
C(19)	1249(3)	1383(2)	2934(1)	525	H(24)	870(4)	31(2)	525(2)	96
C(20)	2193(3)	2065(1)	2981(1)	436	H(25)	995(4)	138(2)	456(2)	104
C(21)	6383(3)	2136(1)	4464(1)	444	H(26)	847(3)	246(2)	411(1)	56
C(22)	5729(3)	1525(2)	4880(2)	595	H(28)	725(3)	381(2)	321(2)	69
C(23)	6610(4)	873(2)	5181(2)	706	H(29)	955(3)	382(2)	252(2)	60
C(24)	8160(4)	815(2)	5074(2)	677	H(30)	980(3)	287(2)	148(2)	62
C(25)	8839(3)	1415(2)	4669(2)	656	H(31)	778(3)	189(1)	125(1)	49
C(26)	7965(3)	2069(2)	4375(1)	539	H(32)	563(3)	181(1)	198(1)	50
C(27)	6298(3)	2748(1)	2728(1)	377					
C(28)	7414(3)	3350(1)	2841(1)	471					
C(29)	8676(3)	3385(2)	2395(2)	524					
C(30)	8816(3)	2835(2)	1800(2)	553					
C(31)	7677(3)	2257(2)	1654(1)	567					
C(32)	6443(3)	2212(1)	2113(1)	454					

[2]) Equation of the mean plane: $0.6026\,x + 0.6844\,y + 0.4106\,z = 0$.

Table 2. *Final positional and thermal parameters* ($\times 10^4$) *for the acetone molecule*

The average thermal parameters U for hydrogen atoms is 0.175 (Å^2)

Atom	x	y	z	U(Å^2)
O(1)	1530	−652	−97	1390
C(33)	447	−190	−31	797
C(34)	−94	395	−680	1037
C(35)	−404	−183	703	952
H(34A)	−1066	745	−497	
H(34B)	−470	65	−1221	
H(34C)	859	799	−788	
H(35A)	−1320	272	634	
H(35B)	409	−38	1217	
H(35C)	−919	−773	785	

from a difference synthesis at a further stage of the refinement and included in the model. Subsequently, the structure was refined by full-matrix least-squares assuming a rigid model with a weight of ½ for the acetone molecule [6]. Convergence was obtained at $R = 0.056$ and $R_w = 0.074$. The use of two identical rigid acetone molecules, the positions of which were independently refined with a weight of ¼, reduced the R and R_w factors to 0.051 and 0.068, respectively. The positional parameters reported in *Tables 1* and *2* were obtained from the structure model considering only one rigid body for the acetone molecule.

Discussion of the crystal structure of PPE. - The acetone and tetrahydrofuran (THF) solvates crystallize in isomorphous systems. The unit cell volume of the THF solvate is about 1.3% larger than that of the acetone solvate, in accordance with the larger space filling contribution of THF. The molecular packings are very similar thus implying a close conformational resemblance between the host molecules of both solvates. Most of the differences between the bond lengths and angles of the two models lie within two to three times the *esd*'s. Larger discrepancies are found between the torsional angle values of those phenyl rings which are in contact with the enclosed solvent molecule. Several relevant structural features of PPE have already been reported [3] and will not be discussed again here. We shall be content with a few remarks which are pertinent to the dynamic approach to the stereoisomerization of PPE [4]. A view of the molecule with the numbering system is given in *Figure 1*.

The steric repulsion between the trityl and diphenylmethyl moieties is evidenced by the major stretching of the ethane bond to a value of 1.612(3) Å, whereas the C_{ethane}-C_{ethane}-C_{phenyl} angles suffer moderate to high degrees of deformation when compared with the 'reference' value 106° observed in the unstrained trigonal triphenylmethane, chloro- and bromotriphenylmethane [7]. The opening of the C(2)–C(1)–C(3) and C(1)–C(2)–C(9) angles up to values of 114° and 118°, respectively, is consequent upon the front strain of Ph(1)[3]) and Ph(3) with Ph(2) as evidenced by the short contacts C(20)...H(14) (2.44), C(9)...H(4) (2.53) and C(4)...C(9) (3.087 Å). These contacts are also of prime importance in locking Ph(1) in an eclipsed position ($R_1 = 2°$)[4]) with respect to the central ethane bond. The

[3]) For convenience the phenyl rings are denoted, in the following, by Ph(i) where i is the ring label shown in *Figure 1*.

[4]) The rotational orientation of a phenyl ring is defined by the dihedral angle R_i (C_{ethane}-C_{ethane}-C_{ipso}-C_{ortho}), where i refers to the ring label.

expansion of the C_{ethane}-C_{ethane}-C_{phenyl} angles brings about a concomitant closing of the C_{phenyl}-C_{ethane}-C_{phenyl} angles. The resulting angular strain is particularly severe for C(3)–C(1)–C(27) = 102° in the trityl group (the equivalent bond angle at the apical C-atom of trigonal triphenylmethane is 112°). The rotational orientation of Ph(2) and Ph(5), with $R_2 = 51°$ and $R_5 = -47°$, is severely controlled by the repulsive interactions between the apical H(2)-atom and the proximal H(10)- and H(28)-atoms at 2.16(4) and 1.99(4) Å, respectively. A concomitant distorsion of Ph(5) from planarity ensues, resulting in opposite out-of-plane displacements of about 0.02 Å for C(27) and C(28). There are no significant short *van der Waals* contacts between the PPE molecules.

Visualization of the cage and of the enclosed acetone molecule. - Let us consider an acetone molecule lying on an inversion centre at (0,0,0), in the middle of a

Table 3. *Molecular parameters of PPE.* For atom-numbering system, see *Figure 1*

Bond distances (Å). Standard deviations (× 10^3) are in parentheses. The average C_{Ar}-H distance is 1.00(4) Å.

C(1)–C(2)	1.612(3)	C(9)–C(10)	1.400(3)	C(21)–C(22)	1.386(4)
C(1)–C(3)	1.553(3)	C(9)–C(14)	1.396(4)	C(21)–C(26)	1.393(4)
C(1)–C(15)	1.549(3)	C(10)–C(11)	1.384(4)	C(22)–C(23)	1.390(4)
C(1)–C(27)	1.563(3)	C(11)–C(12)	1.374(5)	C(23)–C(24)	1.370(5)
C(2)–H(2)	1.060(30)	C(12)–C(13)	1.375(4)	C(24)–C(25)	1.374(5)
C(2)–C(9)	1.521(3)	C(13)–C(14)	1.391(4)	C(25)–C(26)	1.386(4)
C(2)–C(21)	1.538(3)	C(15)–C(16)	1.392(3)	C(27)–C(28)	1.387(3)
C(3)–C(4)	1.380(3)	C(15)–C(20)	1.386(3)	C(27)–C(32)	1.385(3)
C(3)–C(8)	1.388(3)	C(16)–C(17)	1.389(4)	C(28)–C(29)	1.388(4)
C(4)–C(5)	1.386(4)	C(17)–C(18)	1.373(4)	C(29)–C(30)	1.375(4)
C(5)–C(6)	1.371(4)	C(18)–C(19)	1.376(4)	C(30)–C(31)	1.377(4)
C(6)–C(7)	1.377(4)	C(19)–C(20)	1.392(4)	C(31)–C(32)	1.382(4)
C(7)–C(8)	1.380(4)				

Bond angles (°). The average standard deviations for the C–C–C and C–C–H angles are 0.3° and 1.3°, respectively.

C(2)–C(1)–C(3)	113.9	C(6)–C(7)–C(8)	120.2	C(15)–C(20)–C(19)	121.6
C(2)–C(1)–C(15)	109.1	C(3)–C(8)–C(7)	121.8	C(2)–C(21)–C(22)	122.5
C(2)–C(1)–C(27)	108.0	C(2)–C(9)–C(10)	117.7	C(2)–C(21)–C(26)	120.7
C(3)–C(1)–C(15)	109.8	C(2)–C(9)–C(14)	127.7	C(22)–C(21)–C(26)	116.8
C(3)–C(1)–C(27)	102.2	C(10)–C(9)–C(14)	116.4	C(21)–C(22)–C(23)	121.4
C(15)–C(1)–C(27)	113.8	C(9)–C(10)–C(11)	122.0	C(22)–C(23)–C(24)	120.7
C(1)–C(2)–H(2)	101.2	C(10)–C(11)–C(12)	120.2	C(23)–C(24)–C(25)	119.1
C(1)–C(2)–C(9)	118.3	C(11)–C(12)–C(13)	119.3	C(24)–C(25)–C(26)	120.2
C(1)–C(2)–C(21)	112.7	C(12)–C(13)–C(14)	120.7	C(21)–C(26)–C(25)	121.8
C(9)–C(2)–H(2)	104.7	C(9)–C(14)–C(13)	121.3	C(1)–C(27)–C(28)	119.7
C(21)–C(2)–H(2)	108.8	C(1)–C(15)–C(16)	121.3	C(1)–C(27)–C(32)	122.8
C(9)–C(2)–C(21)	110.2	C(1)–C(15)–C(20)	121.2	C(28)–C(27)–C(32)	116.9
C(1)–C(3)–C(4)	125.6	C(16)–C(15)–C(20)	117.4	C(27)–C(28)–C(29)	121.7
C(1)–C(3)–C(8)	117.4	C(15)–C(16)–C(17)	121.1	C(28)–C(29)–C(30)	120.3
C(4)–C(3)–C(8)	117.0	C(16)–C(17)–C(18)	120.4	C(29)–C(30)–C(31)	118.7
C(3)–C(4)–C(5)	121.5	C(17)–C(18)–C(19)	119.6	C(30)–C(31)–C(32)	120.8
C(4)–C(5)–C(6)	120.6	C(18)–C(19)–C(20)	119.8	C(27)–C(32)–C(31)	121.5
C(5)–C(6)–C(7)	118.9				

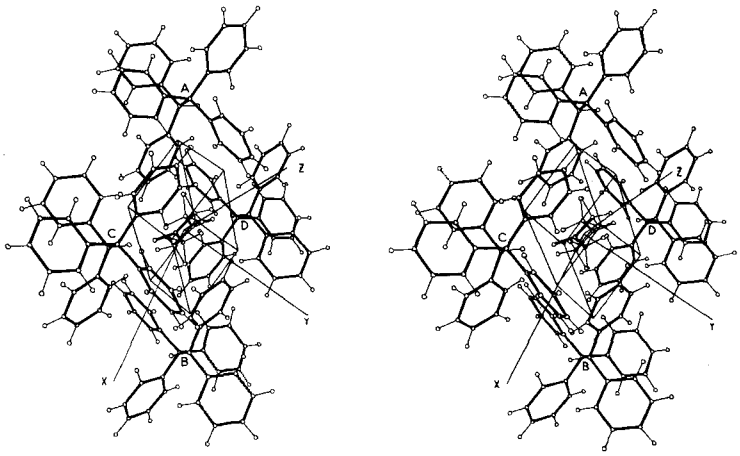

Fig. 2. *Stereoscopic view of a simplified prismatic representation of the cage centered on the inversion centre at (0,0,0).* The two-fold positional disorder of the acetone molecule, constrained to lay on the inversion centre, is depicted in the centre of the prism.

centrosymmetric cage formed by two pairs of enantiomeric PPE molecules (A, B and C, D in *Fig. 2*). Space group considerations and the PPE/acetone molecular ratio of 2:1 require a two-fold disorder for the solvent molecule as depicted in *Figure 2.*

A simple way to visualize the cavity and its orientation with respect to the crystallographic axis is to consider an oblique prism whose faces are either parallel or perpendicular to those phenyl groups in close contact with the guest molecule. The prism is expanded so that its faces are at *van der Waals* distances from the bordering atomic clusters of the host molecules. In this way the prism size ($3.36 \times 4.06 \times 6.61$ Å; 81 Å^3) gives a somewhat underestimated value for the volume accessible to the acetone molecule (molecular volume 66 Å^3), in accordance with the fairly high *Kitaigorodsky*-packing coefficient [8] of 0.81 associated with the insertion of an acetone molecule in a void space having the prism volume (the packing coefficient of the solvate is 0.757). A more realistic visualization of the cavity shape is obtained by drawing contours in sections through the *van der Waals* envelope of those PPE atoms nearest to the enclosed molecule. A stereoscopic view of the contours is shown in *Figure 3,* where it can be noticed that the prism size, as defined above, actually underestimates the volume accessible to the guest molecule.

A difference synthesis calculated within the cavity revealed a planar distribution of elongated peaks consistent with the superimposition of two acetone molecules related by an inversion centre *(Fig. 4a).* In the subsequent refinements one acetone molecule was attributed a weight of ½ and considered as a rigid body whose geometry was that derived by *Nelson & Pierce* [6]. Tetrahedral angular symmetry was assumed for the methyl groups (C–H = 1.09 Å). Evidence for a motional disorder restricted to an in-plane rocking of acetone is reflected in the elongated electron distribution of the O-atom in a direction perpendicular to the

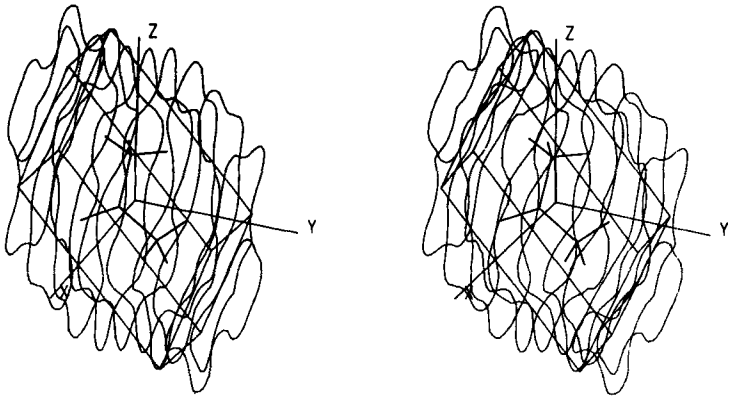

Fig. 3. *Stereoscopic view of the shape of the cavity enclosing the acetone molecule.* The contours are drawn in sections parallel to the (0 1 0) plane and are at intervals of 0.66 Å. The sections are representative of the bordering *van der Waals* envelopes of the stacked PPE molecules.

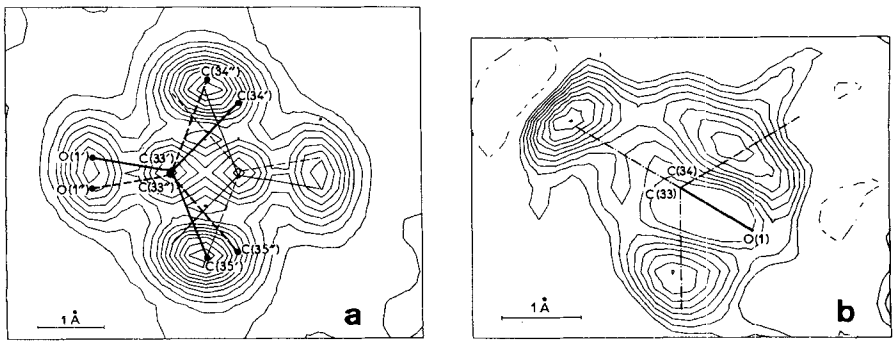

Fig. 4. *Sections through difference maps.* (a) The section is coincident with the mean plane of the acetone molecule, whose contribution has been omitted in the ΔF synthesis. The two alternative positions accounting for the reorientation mode of the guest molecule are respectively represented by solid and dashed lines. (b) The section is coincident with the plane containing the H-atoms of a methyl group. The dashed lines represent the C,H-bonds directions of a trigonal group staggering the C(33)–O(1) bond, whose projection is shown on the section plane (solid line).

mean C,O-bond direction. This disorder was accounted for by a simple model consisting of two identical rigid acetone molecules tilted to each other and refined independently with a weight of $\frac{1}{4}$. It is noteworthy that both models remained coplanar during the refinement. Following this procedure the R and R_w factors decreased slightly to final values of 0.051 and 0.068, respectively. The two 'independent' acetone skeletons converged on final positions tilted to each other by an angle of 24° (see *Fig. 4a*).

A difference map coincident with the plane passing through the three H-atoms of each methyl group provided, in each case, a trigonal pattern of peaks consistent with the methyl groups staggering the C,O-bond (see *Fig. 4b*). This contrasts with the eclipsed arrangement reported for the gas phase [6]. Quantum mechanical

calculations have also shown that the structure benefits from favorable stabilizing interactions when one C,H-bond eclipses the C,O-bond [9], with a barrier to rotation of about 1 to 1.5 kcal/mol. The small destabilizing influence in the staggered rotamer is apparently compensated by a more favorable packing within the cage. This can be roughly checked as follows: the number of close contacts ($H \ldots H \leqq 2.6$; $C_{ar} \ldots H \leqq 3.2$; $O \ldots H \leqq 2.8$ Å) arising from the insertion of one rotamer in the cavity is 19 for the eclipsed conformation (with a short $H \ldots H = 2.2$ Å) as against 15 for the staggered conformation (no short $H \ldots H$ contacts).

Copies of the lists of structure factors and anisotropic thermal parameters may be obtained from the authors.

REFERENCES

[1] *J. Allemand & R. Gerdil,* Acta Cristallogr. B*34,* 2214 (1978).
[2] *W. D. Hounshell, D. A. Dougherty, J. P. Hummel & K. Mislow,* J. Am. Chem. Soc. *99,* 1916 (1977).
[3] *R. Destro, T. Pilati & M. Simonetta,* J. Am. Chem. Soc. *110,* 6507 (1978).
[4] *G. Bernardinelli & R. Gerdil,* Helv. Chim. Acta. *64,* 1372 (1981).
[5] XRAY system. Version of March 1976. Tech. Rep. TR-446. Univ. of Maryland, College Park, Maryland.
[6] *R. Nelson & L. Pierce,* J. Mol. Spectrosc. *18,* 344 (1965).
[7] *A. Dunand,* Thèse de Doctorat No 1778, Univ. de Genève, 1977.
[8] *A. I. Kitaigorodsky,* 'Molecular Crystals and Molecules', Academic Press, London 1973.
[9] *A. Veillard,* in 'Quantum Mechanics of Molecular Conformations', ed. B. Pullman, J. Wiley & Sons, London 1976, ch. 1.