A Refinement of the Crystal Structure of Tetraphenylmethane: Three Independent Redeterminations

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Tetraphenylmethane, $C_{25}H_{20}$, tetragonal, $P\bar{4}2_1c$ (D_{2d}^4), $a = 10\cdot896$ (2), $c = 7\cdot280$ (1) Å at 20°C; $Z = 2$, molecular symmetry $\bar{4}$, $D_m = 1\cdot217$, $D_x = 1\cdot226$ g cm^{-3}. Three independent three-dimensional refinements of an earlier two-dimensional analysis. The structural parameters are $\psi = 7\cdot5$, $\theta = 49\cdot2°$. The central C–C bonds are $1\cdot553$ (3) Å (corrected) and the central valence angles are unequal; $106\cdot7$ (2) and $110\cdot9$ (2)°. The diameters of the phenyl rings are $5\cdot0°$ from collinearity with the central C–C bonds. The phenyl C–C distances are within $\pm0\cdot012$ ($2\cdot4\sigma$) of the mean of $1\cdot393$ Å (corrected). There is a closure of the phenyl ring angle of $3\cdot0°$ (10σ) at C(1) compared with the others which average $120\cdot5°$. The small departures from planarity of the benzene ring are no greater than $0\cdot010$ Å.

Introduction

Tetraphenylmethane is a member of an isostructural series which includes the compounds with Si, Ge, Sn and Pb as the central atom (Ismailzade & Ždanov, 1952; Busetti, Mammi, Signor & Del Pra, 1967; Chieh & Trotter, 1970; Glidewell & Sheldrick, 1971; Chieh, 1971, 1972; Karipides & Haller, 1972). Because of their relative simplicity, these structures have been the object of a theoretical calculation aimed at predicting both the intramolecular geometry and the intermolecular packing (Ahmed, Kitaigorodsky & Mirskaya, 1971). The obvious deficiencies of an early two-dimensional crystal-structure analysis by Sumsion & McLachlan (1950) led three groups to decide simultaneously to refine the structure of $C(C_6H_5)_4$ using modern techniques of X-ray single-crystal diffractometry and computing. The results from one group were briefly reported (Robbins & Jeffrey, 1974).

Results

The three sets of crystal data and details of the structure refinement methods are given in Table 1. The atomic parameters are given in Table 2. The molecular dimensions and a stereo view are given in Table 3 and Fig. 1. The lattice constants at 20 and 26° correspond to α's of the order of 10^{-4} deg^{-1}, which is reasonable.

However, no corresponding systematic differences were observable in the comparison of the atomic positional or thermal parameters. The small differences in bond lengths in Table 3, suggest that the difference in cell dimensions is due, in part, to a systematic discrepancy of about 0·1%.

A rigid-body analysis based on the central carbon and one ring gave a better fit than that based on the whole molecule. The center of libration is 0·9 Å from C(0) and about midway between C(1) and C(1″) (Robbins, 1975). The r.m.s. value of U_{ij} exp$(-U_{ij}$RBM) was 0·0029 Å^2 and $\sigma(U_{ij}$RBM) = 0·0040 Å. This table of parameters is available.* A riding-motion correction increased the C–C distances by 0·002–0·004 Å. This correction is not included in the data in Fig. 1 and Table 3. The half-normal probability plots between the three sets of data are available.* There was one outlier common to two plots, C(3)β_{12} for EP. These plots have slopes ranging from 1·3 (thermal parameters WP *versus* T) to 1·8 (positional parameters EP *versus* T). When the σ's of each set were rescaled to give slopes of unity, the new σ's were 0·003 Å for C(0)–C(1) and 0·005 Å for other C–C bonds. With these values, the

mean difference in the bond lengths from the data at 20 and 26° shown in Table 3 was 0.5σ and the greatest difference was 1.5σ. The C–H bond lengths which ranged from 0.98 to 1.04 Å had $\sigma = 0.03$ Å. The bond angles had σ's of 0.2° for those about C(0) and 0.3° elsewhere, except for those involving hydrogens where $\sigma = 2°$. The three tables of observed and calculated structure factors are available.*

Discussion

The coordinates given in Table 2 correspond to large changes from the original values of Sumsion & McLachlan; they differ on average by 0.17 Å, the largest being 0.56 Å. In the new determinations, no individual parameter value differs by more than 3σ (uncorrected from least-squares refinement) from the mean.

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* See previous footnote.

Apart from the distortions from ideal tetrahedral and trigonal bond angles, discussed below, the crystal structure of $C(C_6H_5)_4$ is defined by two parameters: the angle $\psi = 7.5$ (2)° [shown in Fig. 1(a)] between C(0)–C(1) and **b**, projected down **c**; the angle $\theta = 49.2$ (2)° between the best least-squares plane of a phenyl ring viewed down its C(0)–C(1') bond and C(0)–C(1). Alternative, and more direct, parameters are the torsion angles C(1)–C(0)–C(1')–C(2') = 48.4 (2), C(1)–C(0)–C(1')–C(6') = −130.4 (2)° [shown in Fig. 1(b)].

These parameters, ψ and θ, were calculated by Ahmed, Kitaigorodsky & Mirskaya (1971) using a minimum potential method. They used Sumsion & McLachlan's cell dimensions and assumed a $\bar{4}$ molecule with C(0)–C(1) = 1.50, C–C(phenyl) = 1.39, C–H = 1.08 Å and tetrahedral and trigonal angles to obtain values of $\psi = 7.5$, $\theta = 44°$. The exact agreement in ψ reflects the effectiveness of the minimum potential method in predicting intermolecular packing.

Table 1. *Crystal and structure analysis data for tetraphenylmethane*

Tetragonal; space group $P\bar{4}2_1c$; $Z = 2$; $C_{25}H_{20}$; m.p. 280°C; molecular symmetry $\bar{4}$; molecular weight 320.44; D_m 1.217 g cm^{-3}; μ(Cu $K\alpha$) = 0.857 cm^{-1}.

	Texas	East Pa.	West Pa.
Cell parameters			
Temperature	20°C	20°C	26°C
a (Å)	10.894 (2)	10.899 (2)	10.916 (3)
c (Å)	7.280 (1)	7.279 (1)	7.287 (2)
V (Å^3)	864.1 (4)	864.7 (4)	868.3 (5)
λ(Cu $K\alpha$) = 1.5418 Å			
D_x (g cm^{-3})	1.230	1.231	1.231
Intensity data			
Crystal source	Aldrich Chem. Co.	Prof. Kurt Mislow	Aldrich Chem. Co.
Solvent for recrystallization	Benzene–toluene		Benzene
Crystal size (mm)	0.16 × 0.14 × 0.44	0.1 × 0.2 × 0.4	0.11 × 0.09 × 0.5
Diffractometer, $\theta/2\theta$ scan with graphite-monochromatized Cu $K\alpha$	Syntex $P\bar{1}$	Picker FACS 1	Nonius CAD-4
Total independent data observed	549 (140 collected in parallel mode) 439 [$I > 3\sigma(I)$]	420 (averaged from hk, kh pairs) 405 [$I > 2\sigma(I)$]	533 (averaged from hk, kh pairs) 444 [$I > 2\sigma(I)$]
2θ limit (°)	158	125	150
No absorption corrections applied			
Structure solution	Redetermination from 3D Patterson and difference syntheses	Redetermination using trial orientation in a general constraint refinement program (Chesick & Davidon, 1975)	Refinement from Sumsion & McLachlan (1950) parameters
Parameter refinement	Full-matrix least-squares refinement on $\sum w(|F_o| - |F_c|)^2$ with anisotropic carbons and isotropic hydrogens		
R_1	0.040	0.036	0.035
R_2	0.052		0.040
Goodness of fit	1.38		1.08
Weighting scheme	$\omega = 1/\sigma^2$ where $\sigma = \sum A_n T_n(|F_o|')$; A_n being coefficients from least-squares fitting of curve $||F_o| - |F_c|| = \sum A_n T_n(|F_o|')$ where T_n are the Chebyshev polynomials and a linear transformation of $|F_o|$ gives $| \leq |F_o|' \leq |$	$\omega = (0.1 + 0.000005|F_o|^3)^{-1}$	$\omega = 1/(\sigma')^2$ where $\sigma' = 1.08$ ($\sigma_{\text{counting stat.}}$)

Table 2. *Atomic coordinates and thermal parameters*

Values of C atoms are $\times 10^4$; for hydrogens $\times 10^3$; β values are $\times 10^3$; standard deviations are in parentheses; parameters are given in the order Texas, East Pa., West Pa. The temperature-factor expression used was $\exp[-10^{-4}(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B (Å²)
C(0)	(0	0	0)	61 (2)	61 (2)	126 (10)				
	(0	0	0)							2·52 (7)
	(0	0	0)							2·45 (5)
C(1)	150 (2)	1135 (2)	1270 (4)	62 (2)	64 (2)	124 (4)	−3 (1)	7 (3)	0 (3)	
	146 (2)	1129 (2)	1271 (3)	60 (4)	61 (0)	123 (8)	−7 (3)	17 (5)	−5 (5)	
	146 (2)	1131 (2)	1270 (2)	56 (1)	60 (1)	111 (3)	−5 (1)	10 (2)	0 (2)	
C(2)	987 (3)	1073 (3)	2724 (4)	79 (2)	88 (2)	148 (6)	−5 (2)	−2 (3)	−2 (3)	
	991 (2)	1071 (2)	2720 (3)	72 (0)	86 (3)	140 (9)	−16 (3)	−5 (5)	−1 (6)	
	988 (2)	1071 (3)	2722 (3)	71 (1)	83 (2)	129 (4)	−5 (1)	−4 (2)	−6 (2)	
C(3)	1159 (3)	2055 (3)	3892 (5)	87 (2)	114 (3)	151 (6)	−24 (2)	1 (3)	−23 (4)	
	1166 (2)	2055 (2)	3894 (4)	82 (1)	116 (5)	153 (13)	−55 (4)	10 (6)	−39 (7)	
	1162 (2)	2054 (2)	3895 (3)	83 (2)	111 (4)	134 (4)	−25 (2)	1 (2)	−20 (2)	
C(4)	498 (3)	3119 (3)	3665 (5)	117 (3)	91 (2)	186 (6)	−25 (2)	21 (4)	−43 (4)	
	499 (2)	3120 (2)	3655 (4)	115 (4)	89 (2)	186 (16)	−51 (4)	50 (7)	−71 (7)	
	499 (3)	3120 (2)	3662 (3)	111 (2)	86 (2)	175 (4)	−26 (2)	23 (1)	−42 (3)	
C(5)	−350 (3)	3185 (3)	2267 (5)	114 (3)	67 (2)	214 (7)	2 (2)	21 (4)	−16 (4)	
	−353 (2)	3195 (2)	2265 (4)	110 (3)	71 (3)	210 (9)	0 (4)	47 (7)	−51 (6)	
	−356 (2)	3189 (2)	2263 (3)	107 (2)	67 (2)	195 (4)	3 (2)	23 (3)	−21 (2)	
C(6)	−530 (3)	2206 (3)	1081 (5)	82 (2)	65 (2)	170 (6)	6 (2)	−2 (4)	−12 (3)	
	−525 (2)	2206 (2)	1074 (4)	81 (3)	69 (5)	162 (18)	8 (3)	4 (6)	−19 (5)	
	−526 (2)	2204 (2)	1076 (3)	76 (2)	65 (1)	144 (4)	3 (1)	4 (2)	−11 (2)	

Table 2 (*cont.*)

	x	y	z	B (Å²)
H(2)	145 (3)	32 (3)	291 (4)	3·9 (6)
	148 (2)	27 (2)	289 (3)	4·7 (4)
	145 (2)	31 (2)	292 (3)	3·4 (4)
H(3)	175 (3)	196 (3)	497 (6)	5·1 (7)
	178 (2)	196 (2)	484 (4)	4·6 (4)
	175 (2)	195 (2)	490 (4)	4·7 (4)
H(4)	62 (3)	380 (3)	448 (5)	4·9 (7)
	63 (2)	385 (2)	448 (3)	5·7 (5)
	64 (2)	384 (2)	441 (3)	5·0 (5)
H(5)	−81 (3)	389 (3)	209 (4)	4·4 (6)
	−86 (2)	396 (2)	208 (3)	4·8 (4)
	−83 (2)	393 (2)	213 (3)	4·6 (5)
H(6)	−117 (3)	230 (3)	10 (5)	4·7 (7)
	−118 (2)	227 (2)	10 (3)	4·4 (4)
	−116 (2)	228 (2)	8 (4)	4·3 (5)

Table 3. *Bond lengths* (Å) *and valence angles* (°) *in tetraphenylmethane*

(a) Mean of 20 °C data; (b) 26 °C data.

	(a)	(b)
C(0)–C(1)	1·550	1·551
C(1)–C(2)	1·401	1·403
C(2)–C(3)	1·382	1·385
C(3)–C(4)	1·378	1·381
C(4)–C(5)	1·377	1·384
C(5)–C(6)	1·391	1·392
C(6)–C(1)	1·389	1·389
C(1)–C(0)–C(1')	106·7	106·8
C(1)–C(0)–C(1'')	110·9	110·8
C(0)–C(1)–C(2)	118·8	118·7
C(0)–C(1)–C(6)	123·7	123·8
C(1)–C(2)–C(3)	121·2	121·3
C(2)–C(3)–C(4)	120·4	120·3
C(3)–C(4)–C(5)	119·4	119·3
C(4)–C(5)–C(6)	120·5	120·4
C(5)–C(6)–C(1)	120·9	121·2
C(6)–C(1)–C(2)	117·5	117·5

The deformations from ideal tetrahedral and trigonal geometry observed in the crystal structure are described below.

(i) The C(0)–C(1) bonds are 1·553 (3) Å, when the +0·003 Å riding correction is included. This is longer than usual, *e.g.* 1·525 Å. In triphenylmethane, the corresponding distances range from 1·508 to 1·556 (7) with a mean of 1·524 Å (Riche & Pascard-Billy, 1974).

(ii) The central carbon valence angles are 106·7 (2)° for the two bisected by the $\bar{4}$ axis, as shown in Fig. 1(c), and 110·9 (2)° for the other four [Fig. 1(d)]. The corresponding angles in the crystal structure of triphenylmethane are 118·8, 112·8 and 114·5°. In tetraphenyl silicon (Chieh, 1971; Glidewell & Sheldrick, 1971), germanium (Chieh, 1971; Karipides & Haller, 1972) and tin (Chieh & Trotter, 1970) these angles are 107·5 (4) and 110·4 (4), 108·8 (2) and 109·8 (2), 110·8 (9) and 108·8 (4)° respectively. It appears that as the central atom gets larger this distortion from ideal tetrahedral gets smaller and may actually reverse. The corresponding θ values are 53·1, 54·3 and 58·7°, respectively.

(iii) In addition, the diameters of the phenyl rings [*e.g.* C(1)···C(4)] are not collinear with the bonds [*e.g.* C(0)–C(1)] owing to a difference of 5·0° (17σ) between the angles C(0)–C(1)–C(2) and C(0)–C(1)–C(6) as shown in Fig. 1(a).

(iv) There is also a small closure of the phenyl ring at C(1) of 3·0° (10σ) relative to the mean of 120·5° for the other five angles (119·7 to 121·4°). A similar small closure at C(1) is observed in the tetraphenylborate ion where the angle is considerably more closed to about 114° (Cotton & Murillo, 1975). The phenyl C–C distances range from +0·013 to −0·012 Å from a mean of 1·393 Å (corrected). The bonds about

C(1) are 0·015 Å (3σ) longer than those about C(4); this is a marginal observation which occurs from all three sets of data and may be significant.

(v) The phenyl rings have a barely significant boat-twist deformation with deviations from the best least-squares plane of C(1) −0·010, C(4) −0·010, C(2)
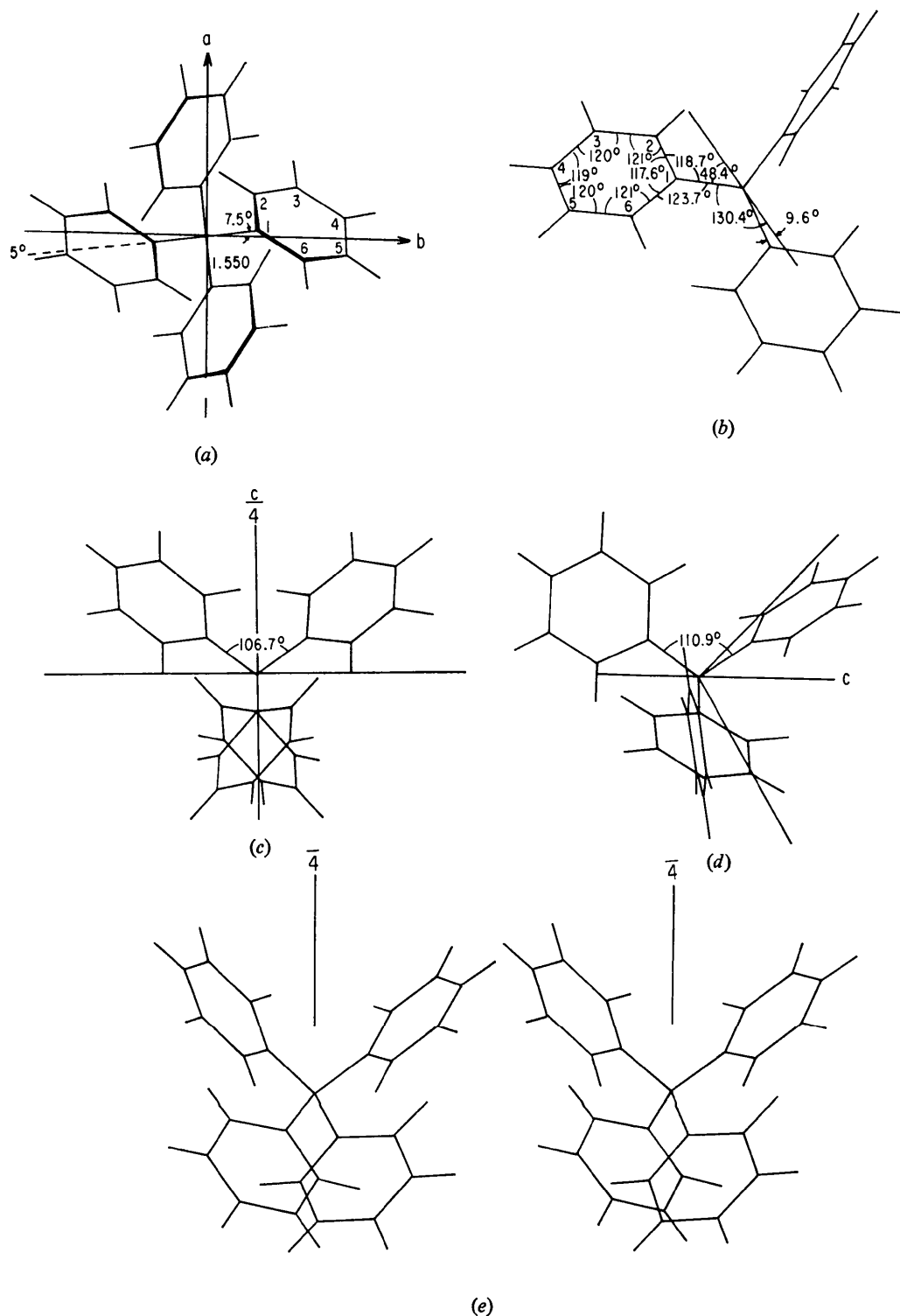

(a)

(b)

(c)

(d)

(e)

Fig. 1. Molecular geometry of tetraphenylmethane. (a) View down 4̄ axis. (b) View down C(1)–C(0). (c) View showing C(1)–C(0)–C(1′) angle bisected by 4̄ axis. (d) View showing C(1)–C(0)–C(1″) angle generated by 4̄ axis. (e) Stereo view of molecule. Diagrams produced from atomic coordinates by means of the CRYSNET PROJECT computer graphics (Bernstein et al., 1974).
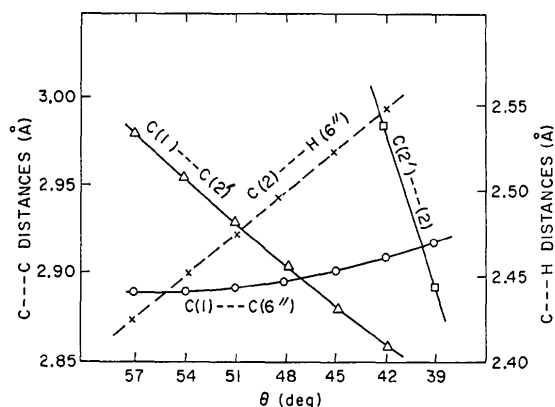
Fig. 2. Variation of the closest intramolecular distances with the torsion angle C(1)–C(0)–C(1′)–C(2′). (′) $x\bar{y}z$; (″) $\bar{y}x\bar{z}$; (‴) $y\bar{x}\bar{z}$.

+0·006, C(5) +0·006, C(3) +0·003, C(6) +0·003. The data for this plane are available.*

Tetraphenylmethane is an overcrowded molecule in a loosely packed crystal environment. Fig. 2 shows the dependence of the shortest intramolecular separations on the angle of twist of the phenyl rings. The slopes of C(1)···C(6″) and C(1)···C(2′) intersect close to the observed value of 48°, where the separations are 2·90 Å. The steeper dependency of C(1)···C(2′) is opposed by that of C(2)···H(6″), which has a value of 2·50 Å. In contrast, the shortest intermolecular distances are H···H 2·50, C···H 2·87, C···C 3·65 Å. This suggests that the conformation of the molecules in the crystal is determined mainly by the intramolecular forces.

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* See footnote on p. 2395.

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