The Structures of Bis(triphenylmethyl) Sulfide and Bis(triphenylmethyl) Ether

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Abstract

The crystal structure of bis(triphenylmethyl) sulfide, $[(C_6H_5)_3C]_2S$, $C_{38}H_{30}S$, (I), is triclinic, $P\bar{1}$, $Z = 2$, with $a = 8 \cdot 831$ (1), $b = 9 \cdot 474$ (1), $c = 17 \cdot 590$ (2) Å, $\alpha = 90 \cdot 146$ (5), $\beta = 92 \cdot 584$ (4), $\gamma = 106 \cdot 580$ (4)°. The final $R(F)$ is $0 \cdot 035$ for all observed reflections. The molecular conformation of (I) is different from that of bis(triphenylmethyl) ether, $[(C_6H_5)_3C]_2O$, $C_{38}H_{30}O$, (II), reported by Glidewell & Liles [*Acta Cryst.* (1978), B**34**, 696–698]. In (I), the two triphenylmethyl groups are interlocking propellers of different handedness and pitch. In (II), the two triphenylmethyl groups have different conformations, but neither of them is a propeller. In both structures, the central C–S and C–O bonds are stretched and the central C–S–C and C–O–C angles are increased from normal values. These distortions are greater for (I) than for (II). In both structures, the phenyl rings are compressed at the *ortho* positions so that the ring valence angle at the point of junction is less than 120°. With a molecular mechanics program, *MMPI*, three energy minima were found for (I), two of which were close to the observed conformation. The third conformation, which had the lowest calculated energy, was a non-propeller arrangement close to those observed and calculated for (II).

Introduction

Bis(triphenylmethyl) sulfide and ether, (I) and (II), are overcrowded molecules; molecular models cannot be constructed using the standard CPK components. (I) forms a stable crystalline solid, melting at 458 K, compared with $339 \cdot 7$ and $321 \cdot 7$ K for the comparable molecules $[(C_6H_5)_2CH]_2S$ and $[(C_6H_5)CH_2]_2S$, respectively (Tsurugi & Nakabayashi, 1959). (II) melts at 505 K (Gomberg, 1913).
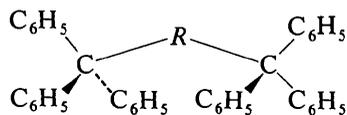
(I) $R = S$
(II) $R = O$

Since the phenyl rings of the triphenylmethyl groups cannot be coplanar, they will be inclined all in the same direction or in different directions. The former gives rise to propeller-like conformations such as observed in (I) and illustrated in Fig. 3(*a,b*). The latter is described as a non-propeller conformation, an example of which is found in (II) (Glidewell & Liles, 1978) and illustrated in Fig. 3(*c,d*).* Propeller conformations have been observed in triphenylmethane (Riche & Pascard-Billy, 1974), trimesitylmethane (Blount & Mislow, 1975), the cation of triphenylmethyl perchlorate (Gomes de Mesquita, MacGillavry & Eriks, 1965) and postulated for hexaphenylethane (Hounshell, Dougherty, Hummel & Mislow, 1977). Examples of non-propeller conformations are rare.

Apart from their instrinsic interest as examples of stable overcrowded molecules, these two structures provide a useful means of examining the predictive powers for molecules of this type of a well-known empirical force-field method, *MMPI* (Allinger, 1976).

Experimental

Compound (I) was prepared by condensation of equimolar quantities of chlorotriphenylmethane with triphenylmethanethiol in sodium ethoxide, as described in the original preparation (Vorlander & Mittag, 1919). After repeated decolorizing with charcoal and recrystallization in a 9:1 chloroform–ethanol mixture, slow evaporation at room temperature gave colorless crystals. The crystal and diffraction data for (I) are given in Table 1. The structure was solved by locating the S–S vectors on an E^2 Patterson synthesis. A heavy-atom Fourier synthesis based on the position of the sulfur atom revealed all 38 carbon atoms. The refinement was full-matrix anisotropic using a local modification of *ORFLS* (Busing, Martin & Levy, 1962), in two blocks, each consisting of the sulfur atom

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* A table of the atomic coordinates of (II), converted to the notation used in this paper, has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35172 (40 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Crystal and experimental diffraction data for bis(triphenylmethyl) sulfide*

$[(C_6H_5)_3C]_2S$, $M_r = 518 \cdot 7$, m.p. $= 458$ K

Crystal data
  Space group $P\bar{1}$
  $a = 8 \cdot 831$ (1), $b = 9 \cdot 474$ (1), $c = 17 \cdot 590$ (2) Å
  $\alpha = 90 \cdot 146$ (5), $\beta = 92 \cdot 584$ (4), $\gamma = 106 \cdot 580$ (4)$^\circ$
  $V = 1409$ Å^3; $D_m = 1 \cdot 212$, $D_x = 1 \cdot 277$ Mg m^{-3}
Intensity data
  Crystal dimensions $0 \cdot 36 \times 0 \cdot 24 \times 0 \cdot 11$ mm
  CAD-4 diffractometer with graphite-monochromated Cu $K\alpha$ radiation ($\lambda = 1 \cdot 5418$ Å) to $2\theta = 150^\circ$
  6548 intensity measurements gave 5757 independent $|F_o|$'s, of which 4791 had $I_o > 2\sigma$. Standard reflections 006, $\bar{6}40$ and 608 varied less than 5% during data collection at 298 K
Absorption corrections ($\mu_{CuK\alpha} = 1 \cdot 16$ mm^{-1}) were applied by means of the program ABL (Craven, 1976). The maximum correction factor was $1 \cdot 128$
Refinement data
  Refinement on $(\omega|F_o| - k|F_c|)^2$, where $\omega = (\sigma_c)^{-2}$ from counting statistics
  $R(F)$ and $R_w(F) = 0 \cdot 035, 0 \cdot 049$ for all observed reflections
  • $0 \cdot 049, 0 \cdot 050$ for all measured reflections
  Goodness of fit $S = 1 \cdot 28$

Table 2. *Fractional atomic coordinates for bis(triphenylmethyl) sulfide*

Values are $\times 10^5$ for sulfur, $\times 10^4$ for carbon and $\times 10^3$ for hydrogen atoms.

	x	y	z	B_{eq} or B_{iso} (Å^2)
S	20148 (4)	−20809 (3)	22559 (2)	2·65
C(M1)	999 (1)	−1212 (1)	1478 (1)	2·45
C(1A)	1540 (1)	478 (1)	1569 (1)	2·68
C(2A)	492 (2)	1312 (2)	1437 (1)	3·85
C(3A)	993 (2)	2837 (2)	1490 (1)	4·95
C(4A)	2548 (2)	3572 (2)	1667 (1)	4·62
C(5A)	3617 (2)	2762 (2)	1786 (1)	4·25
C(6A)	3125 (2)	1240 (2)	1737 (1)	3·50
C(1B)	−810 (1)	−1809 (1)	1418 (1)	2·80
C(2B)	−1619 (2)	−2411 (2)	743 (1)	3·70
C(3B)	−3267 (2)	−2861 (2)	686 (1)	5·21
C(4B)	−4130 (2)	−2707 (2)	1298 (1)	5·60
O(5B)	−3350 (2)	−2093 (3)	1963 (1)	5·93
C(6B)	−1702 (2)	−1640 (2)	2020 (1)	4·73
C(1C)	1737 (1)	−1723 (1)	788 (1)	2·63
C(2C)	2574 (2)	−749 (2)	262 (1)	3·35
C(3C)	3188 (2)	−1256 (2)	−364 (1)	4·49
C(4C)	2982 (2)	−2738 (2)	−472 (1)	4·78
C(5C)	2129 (2)	−3733 (2)	40 (1)	4·19
C(6C)	1521 (2)	−3226 (2)	660 (1)	3·22
C(M2)	1268 (1)	−2251 (1)	3252 (1)	2·65
C(1D)	986 (2)	−803 (2)	3522 (1)	3·13
C(2D)	−424 (2)	−737 (2)	3820 (1)	4·39
C(3D)	−614 (3)	632 (3)	4029 (1)	5·98
C(4D)	571 (3)	1909 (2)	3951 (1)	6·46
C(5D)	1977 (3)	1851 (2)	3664 (1)	5·37
C(6D)	2182 (2)	512 (2)	3453 (1)	3·88
C(1E)	−133 (2)	−3631 (1)	3349 (1)	2·93
C(2E)	−602 (2)	−4025 (2)	4088 (1)	3·78
C(3E)	−1792 (2)	−5288 (2)	4220 (1)	4·55

Table 2 *(cont.)*

	x	y	z	B_{eq} or B_{iso} (Å^2)
C(4E)	−2540 (2)	−6213 (2)	3626 (1)	4·95
C(5E)	−2076 (2)	−5856 (2)	2894 (1)	4·96
C(6E)	−891 (2)	−4570 (2)	2757 (1)	3·83
C(1F)	2707 (1)	−2549 (1)	3686 (1)	2·71
C(2F)	3463 (2)	−1727 (2)	4323 (1)	3·39
C(3F)	4752 (2)	−2037 (2)	4697 (1)	4·16
C(4F)	5308 (2)	−3162 (2)	4443 (1)	4·33
C(5F)	4545 (2)	−4009 (2)	3823 (1)	4·33
C(6F)	3248 (2)	−3724 (2)	3458 (1)	3·57
H(2A)	−67 (2)	77 (2)	132 (1)	4·6 (4)
H(3A)	25 (2)	340 (2)	140 (1)	5·9 (4)
H(4A)	297 (2)	471 (2)	170 (1)	6·3 (4)
H(5A)	472 (2)	333 (2)	191 (1)	4·7 (3)
H(6A)	389 (2)	70 (2)	183 (1)	4·1 (4)
H(2B)	106 (2)	−251 (2)	30 (1)	4·7 (4)
H(3B)	−384 (2)	−329 (2)	19 (1)	6·5 (3)
H(4B)	−530 (3)	−299 (2)	126 (1)	7·2 (5)
H(5B)	−396 (2)	−201 (2)	241 (1)	7·0 (5)
H(6B)	−114 (2)	−113 (2)	251 (1)	5·8 (5)
H(2C)	271 (2)	34 (2)	32 (1)	3·9 (3)
H(3C)	374 (2)	−58 (2)	−72 (1)	5·4 (4)
H(4C)	343 (2)	−308 (2)	−91 (1)	5·9 (4)
H(5C)	200 (2)	−480 (2)	−6 (1)	5·6 (4)
H(6C)	97 (2)	−388 (2)	101 (1)	3·8 (3)
H(2D)	−134 (2)	−162 (2)	388 (1)	4·5 (4)
H(3D)	−161 (2)	52 (2)	418 (1)	6·9 (5)
H(4D)	53 (2)	294 (2)	404 (1)	7·1 (5)
H(5D)	294 (2)	282 (2)	359 (1)	6·2 (5)
H(6D)	326 (2)	51 (2)	324 (1)	4·1 (3)
H(2E)	−1 (2)	−337 (2)	451 (1)	4·4 (4)
H(3E)	−204 (2)	−559 (2)	474 (1)	5·6 (4)
H(4E)	−339 (2)	−712 (2)	370 (1)	5·3 (4)
H(5E)	−255 (2)	−652 (2)	242 (1)	5·8 (4)
H(6E)	−54 (2)	−436 (2)	222 (1)	4·0 (4)
H(2F)	300 (2)	−97 (2)	450 (1)	4·0 (3)
H(3F)	529 (2)	−151 (2)	514 (1)	5·5 (4)
H(4F)	623 (2)	−338 (2)	474 (1)	5·1 (4)
H(5F)	495 (2)	−478 (2)	363 (1)	5·0 (4)
H(6F)	268 (2)	−438 (2)	305 (1)	4·8 (4)

and one of the triphenylmethyl groups. The hydrogen atoms were placed at $1 \cdot 07$ Å from the carbon atoms to which they were attached, with equal C—C—H valence angles. Their coordinates were refined with isotropic temperature factors. The sulfur atomic scattering factors were corrected for anomalous dispersion.

The final atomic parameters are given in Table 2.* A rigid-body thermal-motion analysis (Schomaker & Trueblood, 1968) gave a fit of r.m.s. $\Delta U_{ij} = 0 \cdot 0084$ Å^2 for the whole-molecule rigid-body model; a model consisting of two separate triphenylmethyl groups gave values of $0 \cdot 0075$ and $0 \cdot 0044$ Å^2 for each half. These values suggest that the thermal motion of the molecule is more complex than represented by either of these models.

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* Tables of observed and calculated structure factors, anisotropic thermal parameters and results of a rigid-body thermal-motion analysis have been deposited. See previous footnote.
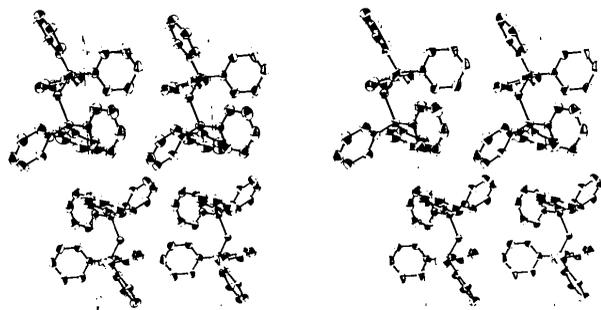
Fig. 1. Stereoview of the crystal structure of bis(triphenylmethyl) sulfide. The thermal ellipsoids are at 50% probability.
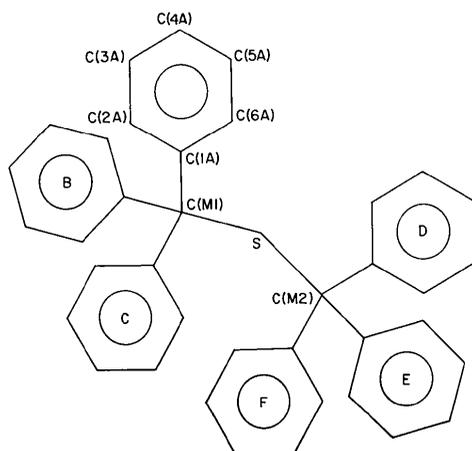
Fig. 2. Key to the atomic notation used for the molecule of bis(triphenylmethyl) sulfide.

A stereoview of the crystal structure of (I) is shown in Fig. 1. The key to the atomic notation is given in Fig. 2. The hydrogen atoms are labelled to correspond to the carbon atoms to which they are attached.

Discussion

In the reference molecule of the enantiomeric pair in the triclinic centrosymmetric crystal structure (the atomic coordinates of which are given in Table 2), the triphenylmethyl propeller, $C(M1)–C(1,A,B,C)$ has a left-handed twist (λ) and that of $C(M2)–C(1,D,E,F)$ has a right-handed twist (Δ). The propeller on $C(M1)$ is closer to having a threefold axis of symmetry than that on $C(M2)$, as shown by the angles between the best planes of the phenyl rings: A and B, $72 \cdot 5$ $(1)°$; A and C, $70 \cdot 6$ $(1)°$; B and C, $70 \cdot 7$ $(1)°$; in contrast to those between D and E, $62 \cdot 3$ $(1)°$; D and F, $62 \cdot 9$ $(1)°$; E and F, $91 \cdot 8$ $(1)°$.

Since there is no reason why the preparation of (I) should be stereospecific, three propeller-type atropo-isomers are expected in the reaction product, i.e. $\lambda\Delta$, $\Delta\Delta$ and $\lambda\lambda$. These could result in the crystallization of five polymorphs, i.e. the observed centrosymmetrical $\Delta\lambda,\lambda\Delta$ racemic mixture, a $\Delta\Delta,\lambda\lambda$ racemic mixture and non-centric crystals of $\Delta\lambda$, $\Delta\Delta$ or $\lambda\lambda$. In addition, there could be an indefinite number of conformational polymorphs in which one or both of the triphenyl-methyl groups are not propellers.

The principal torsion angles of the molecule are given in Table 3. Those which define the overall conformation are of the type $C(M1)–S–C(M2)–C(1D)$. Those which define the conforma-

Table 3. *Principal torsion angles* (°) *in bis(triphenylmethyl) sulfide and ether*

| | (I) $X = S$ | | | | (II) $X = O$ | | |
| | | Calculated by *MMPI* | | | | Calculated by *MMPI* | |
	Observed molecule	min. 1	min. 2	min. 3	Observed molecule	min. 1	min. 2
$X–C(M1)–C(1A)–C(2A)$	−141·8 (1)	−128·2	−142·2	−173·9	1·2	−175·4	−173·4
$X–C(M1)–C(1B)–C(2B)$	−123·6 (1)	−128·3	−103·3	−68·4	−76·9	−77·9	−78·4
$X–C(M1)–C(1C)–C(2C)$	−124·2 (1)	−131·7	−145·0	138·7	151·5	149·9	151·6
$X–C(M2)–C(1D)–C(2D)$	128·6 (1)	130·6	127·0	−72·2	−61·1	−61·4	−61·0
$X–C(M2)–C(1E)–C(2E)$	168·5 (1)	166·2	175·0	26·0	16·6	9·2	14·7
$X–C(M2)–C(1F)–C(2F)$	127·2 (1)	126·2	129·7	148·2	147·2	147·5	152·7
$C(M1)–X–C(M2)–C(1D)$	−46·4 (1)	−48·9	−57·0	−52·4	−53·8	−48·5	−53·6
$C(M1)–X–C(M2)–C(1E)$	83·9 (1)	83·4	75·7	79·8	78·0	88·5	85·2
$C(M1)–X–C(M2)–C(1F)$	−164·1 (1)	−167·9	−175·1	−170·2	−171·8	−165·1	−168·0
$C(M2)–X–C(M1)–C(1A)$	78·2 (1)	77·6	80·1	89·0	121·4	119·9	121·0
$C(M2)–X–C(M1)–C(1B)$	−48·5 (1)	−51·0	−46·7	−40·9	−2·8	−8·7	−8·3
$C(M2)–X–C(M1)–C(1C)$	−165·8 (1)	−166·1	−165·9	−161·0	−127·0	−134·6	−133·2
Calculated strain energy (kJ mol⁻¹)		274·2	270·3	262·8		273·0	273·9
Angle $C–X–C$ (°)	119·8 (1)	122·7	120·9	119·5	127·8	125·0	123·9

Table 4. *Bond lengths (Å) and selected valence angles (°) in bis(triphenylmethyl) sulfide*

E.s.d.'s given in parentheses refer to the least significant figure.

C—S—C geometry

S—C($M1$)	1·916 (1)	C($M1$)—C(1C)	1·543 (2)	C($M1$)—S—C($M2$)	119·8 (1)	C(1A)—C($M1$)—C(1B)	111·4 (1)
S—C($M2$)	1·892 (1)	C($M2$)—C(1D)	1·537 (2)	S—C($M1$)—C(1A)	110·0 (1)	C(1A)—C($M1$)—C(1C)	111·3 (1)
C($M1$)—C(1A)	1·540 (2)	C($M2$)—C(1E)	1·539 (2)	S—C($M1$)—C(1B)	114·9 (1)	C(1B)—C($M1$)—C(1C)	110·8 (1)
C($M1$)—C(1B)	1·533 (2)	C($M2$)—C(1F)	1·549 (2)	S—C($M1$)—C(1C)	97·6 (1)	C(1D)—C($M2$)—C(1E)	114·5 (1)
				S—C($M2$)—C(1D)	111·1 (1)	C(1D)—C($M2$)—C(1F)	111·7 (1)
				S—C($M2$)—C(1E)	112·9 (1)	C(1E)—C($M2$)—C(1F)	106·2 (1)
				S—C($M2$)—C(1F)	99·3 (1)		

Phenyl C—C bond distances   Ring notation

	Mean	A	B	C	D	E	F
C(1)—C(2)	1·3920 (2)	1·390	1·391	1·390	1·390	1·400	1·393
C(2)—C(3)	1·3927 (2)	1·387	1·394	1·392	1·404	1·378	1·392
C(3)—C(4)	1·3775 (3)	1·372	1·377	1·374	1·368	1·378	1·376
C(4)—C(5)	1·3775 (3)	1·386	1·370	1·387	1·376	1·384	1·382
C(5)—C(6)	1·3842 (3)	1·383	1·393	1·381	1·384	1·391	1·382
C(6)—C(1)	1·3935 (2)	1·398	1·384	1·398	1·394	1·385	1·395
Mean		1·3860 (3)	1·3848 (3)	1·3870 (3)	1·3860 (3)	1·3860 (3)	1·3875 (3)

tion of the triphenylmethyl groups relative to each other are of the type S—C($M1$)—C(1A)—C(2A). The relative conformation of the two triphenylmethyl groups is illustrated in stereo in Fig. 3(b), which shows the view in the direction of C($M1$)---C($M2$).

The bond lengths and valence angles are reported in Table 4. The two most unusual features are the long C—S bonds, 1·916 (1) and 1·892 (1) Å, which differ significantly in length by 20σ, and the C—S—C valence angle of 120°. These are the longest C—S bonds and the largest C—S—C valence angle that have been observed in an organic sulfide. An extraordinarily long C—C bond of 1·64 Å was predicted for hexaphenylethane (Hounshell, Dougherty, Hummel & Mislow, 1977). Comparable C—S bond lengths and C—S—C bond angles are: 1·847 (2) Å, 76·8 (3)° in trimethylene sulfide (Karakido & Kuchitsu, 1975), 1·844 (12) Å in dibenzyl disulfide (Van Dyk & Visser, 1971), 1·819 (2) Å in 1,2-ethanedithiol (Hargitten & Schultz, 1972), 1·806 (2) Å in dimethyl disulfide (Beagley & McAloon, 1971), 1·807 (2) Å, 99·05 (4)° in dimethyl sulfide (Iijima, Tsuchiya & Kimura, 1977), 1·788 (3) Å in diphenyl disulfide (Sacerdoti, Gilli & Domiano, 1975), 1·785 (2) Å in di-2-pyridyl disulfide (Raghavan & Seff, 1977), 1·776 (6) Å, 103° in di-o-tosyl sulfide (Sarcerdoti, Bertolasi & Gilli, 1976).

The effect of steric strain is also observed in the distortion of the S—C—C valence angles, with the result that the axes of the triphenylmethyl propellers do not coincide with the C—S bonds. If the axes of the propellers are defined by the normals to the plane C(1A)—C(1B)—C(1C) passing through C($M1$) and to the plane C(1D)—C(1E)—C(1F) passing through

C($M2$), these axes are inclined at 138·0°, and fail to intersect by 0·10 Å. The differences in the angles C(M)—C(1)—C(2) and C(M)—C(1)—C(6) are +0·1 (1), −1·0 (1), −5·1 (1)° for rings A,B,C and −4·3 (1), −5·7 (1), −3·1 (1)° for rings D,E,F, respectively.

Each of the phenyl rings is close to planar, having deviations from the best least-squares planes of less than 0·011 (2) Å, except for ring F, where C(1F) and C(6F) are 0·018 (2) and 0·017 (2) Å out of the plane. The C(M) atoms are both significantly out of the phenyl planes, by 0·054 (2), 0·087 (2) and 0·029 (2) Å for C($M1$) out of rings A, B, and C, respectively, and by 0·052 (2), 0·089 (2) and 0·022 (2) Å for C($M2$) out of rings D, E, and F, respectively. The C($M1$)—C(1) and C($M2$)—C(1) bonds are not collinear with the C(1)---C(4) diameters of the benzene rings. A table giving the equation to and the deviations from the phenyl planes has been deposited.*

There is no significant stretching of the C—C single bonds. The largest deviation (0·007 Å) from the mean value of 1·5402 Å is marginally significant. The mean values for the aromatic C—C bond lengths for each ring agree very closely, within 0·003 Å, but there are significant differences in the means of the individual bond lengths around the rings. The same is true of the phenyl-ring valence angles. Within the experimental errors, the data for the phenyl rings are consistent with mm symmetry about the C(1)---C(4) axes. The mean dimensions of the phenyl rings averaged over all six rings and the mm symmetry are shown below in (I). A

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* See first footnote.

very similar distribution of bond lengths and valence angles was observed in bis(triphenylmethyl) ether, (II) (Glidewell & Liles, 1978), tetraphenylmethane, (III) (Robbins, Jeffrey, Chesick, Donohue, Cotton, Frenz & Murillo, 1975), and tetraphenylbutadiene, (IV) (Berkovitch-Yellin & Leiserowitz, 1977). Ring deformation in substituted benzene derivatives is well known (Domenicano & Vaciago, 1975), and a linear correlation between the phenyl valence angle at the position of substitution and the electronegativity of the substituent has prompted electronic interpretations (Domenicano, Vaciago & Coulson, 1975). However, the similarity of the results in (I)–(IV) indicates that this deformation either is a molecular characteristic of the methane phenyl group or is caused by the steric interactions in these overcrowded molecules. All the non-vicinal intramolecular non-bonding distances less than 0·9 times the sum of the Pauling van der Waals radii involve the *ortho* carbon atoms or the hydrogens attached thereto. A table of the shorter intramolecular distances less than the sum of the van der Waals radii has been deposited.*
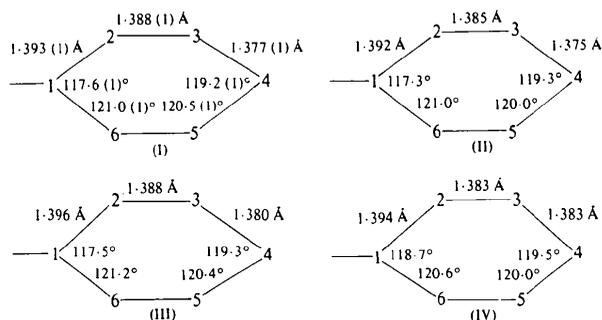
The differences between the bond lengths and valence angles in the phenyl groups are correlated due to the constraints for deformation of planar six-membered rings as described by Britton (1977). Mirror symmetry about C(1)–C(4), for example, requires that $\beta_1 = -\frac{1}{2}\beta_2 - \frac{1}{2}\beta_3 + \sqrt{\frac{3}{2}}(-\varepsilon_{12} + \varepsilon_{34})$, where the β's are deviations in ring valence angles from 2·094 rad, the ε's are deviations from the mean C–C bond length in Å and the subscripts 1 to 4 correspond to sequential numbering around the ring.

The structure of bis(triphenylmethyl) ether

In contrast to (I), the two triphenylmethyl groups in (II) have non-propeller conformations (Glidewell & Liles, 1978). A comparison of the relevant torsion angles is given in Table 3. The C–O bond lengths of 1·454 (2), 1·465 (2) Å are significantly greater than those generally observed in uncrowded ethers, e.g. 1·429 (5) Å in diethyl ether (André, Fourme & Zechmeister, 1972), but comparable bond lengths have

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* See first footnote.

been reported, for example for the ring C–O bonds in some pyranosyl halides (Jeffrey & Yates, 1979). The C–O–C angle is expanded beyond the normal angle of about 110 to 127·9 (1)°. Neither of these distortions is as large as in (I). The C(Ph)–C–C(Ph) angles lie between 103·4 and 115·9°, which is a larger range than for (I). The C–C bond lengths are uniform. As described in the earlier section, the dimensions of the phenyl rings are in agreement with those of the thio compound, within experimental error.

Empirical force-field calculations

The empirical force-field caculations were carried out on both (I) and (II) using the Allinger (1976) *MMPI* program, redimensioned and implemented on a DEC KI-10 computer. The only program changes made were an increase of the criterion for energy convergence from 0·022 to 0·105 kJ mol⁻¹ when using the torsion-angle-drive option. No changes were made in the empirical parameters as described in Program No. 318 of the Quantum Chemistry Program Exchange (Indiana University, Bloomington, Indiana, USA).

For molecule (I), three energy minima were obtained by using different starting coordinates. These are as follows.

Minimum 1, at $E = 274·2$ kJ mol⁻¹, was obtained with an idealized molecule with standard bond lengths and valence angles (as defined by *MMPI*), except for a C–S–C valence angle of 150°, with the torsion angles of the observed molecule. The 'standard' C–S–C valence angle of 94·3° gave unreasonable interpenetration of the phenyl van der Waals radii; with 150°, normal van der Waals separations were possible. The resulting conformation is very close to that observed in the crystal structure, as shown by the torsion angles in Table 3. A least-squares best molecular fit (Nyburg, 1974) gave mean and maximum differences of 0·16 and 0·41 Å respectively between the observed and calculated atomic positions. The largest difference in the conformational torsion angles was 10·5° in S–C(*M*1)–C(1*A*)–C(2*A*). The C–S–C valence angle was 122·7°; the C–S bond lengths did not expand more than 0·01 Å, and remained close to the assumed standard value of 1·816 Å.

Minimum 2, at $E = 270·3$ kJ mol⁻¹, was obtained by starting with the observed atomic coordinates. This gave a conformation of lower energy which was, surprisingly, further from the observed conformation than that of minimum 1. The mean and maximum differences of the best molecular fit were larger, 0·34 and 1·07 Å, respectively. The largest difference in the conformational torsion angle was 20·3° for S–C(*M*1)–C(1*B*)–C(2*B*), making the more symmetrical triphenylmethyl group less so. The C–S–C valence angle was 120·9° and the C–S bond lengths contracted away from the observed values towards the

standard values used in the program, *i.e.* 1·829 and 1·824 Å.

Minimum 3, at $E = 262·8$ kJ mol^{-1}, was obtained by starting with an idealized molecule with standard bond lengths and valence angles, a C—S—C valence angle of 150°, and the torsion angles of the observed molecule, except that those of the type S—C(M2)—C(1)—C(2) had reversed signs. The driver option of *MMPI* was then used to seek an energy minimum. The pathway of the minimization included a reversal of the twist angle of four of the phenyl groups and, consequently, the adoption of a non-propeller conformation for both triphenylmethyl groups. Although this was the lowest-energy conformation found, the fit with the observed molecule was poorest, with mean and maximum deviations from the best molecular fit of 0·89 and 2·67 Å.

For molecule (II), the calculations started with the crystal-structure coordinates and gave a minimum at 273·0 kJ mol^{-1} with a good least-squares best molecular fit to the observed structure of 0·18 Å for the mean and 0·38 Å for the maximum differences. The greatest difference was 10° in the C(M1)—O—C(M2)—C(1E) torsion angle. The conformations of the triphenyl-methyl groups resembled those of minimum 3 of (I). The principal difference was a rotation of about 30° around the O—C(M1) bond. Because of this similarity, another set of starting coordinates for (II) was derived by substituting C—O bond lengths for C—S bond lengths in the minimum 3 data and adding oxygen lone pairs. The torsion-angle-driver option was then used to locate another minimum, at 273·9 kJ mol^{-1}. This had the same general conformation as the previous mini-mum, but was not as close to the observed structure. The mean and maximum differences of the least-squares fit were 0·21 and 0·31 Å. The atomic parameters of the three calculated minima for (I) and the two for (II) have been deposited.* Stereoviews of the observed and calculated molecules are shown in Fig. 3.

Summary

The conformations of the closely related bis(triphenyl-methyl) sulfide and ether molecules in their crystal structures differ markedly in that the former has propeller-like triphenylmethyl groups, whereas the latter does not. In (I), there is significant stretching of the central C—S bonds which are unequal in length. The stretching of the C—O bonds in (II) is much smaller and an observed difference in lengths is marginally significant. The sulfur and oxygen valence angles are opened and there are distortions of some of the carbon valence angles. Both the bond-length and valence-angle distortions are greater for the sulfur than for the oxygen atoms. The phenyl rings show very characteristic distortions in both structures, involving significant differences in bond lengths and closure of the ring angle at the point of junction to the rest of the molecule. The application of the molecular-mechanics calculation *MMPI* suggests that both the propeller and non-propeller conformations correspond to energy minima of comparable stability. The fact that the observed conformations are so different in these two related molecules may be fortuitous, or due to some unknown factors in the nucleation and crystallization processes.

Only when starting parameters close to the observed molecular structure were used did *MMPI* predict the observed conformation for these two molecules. The long C—S bond lengths were not predicted, either because the assumed stretching force constants were too large or because some of the non-bonding repulsion terms were inappropriate for use with overcrowded molecules of this type.
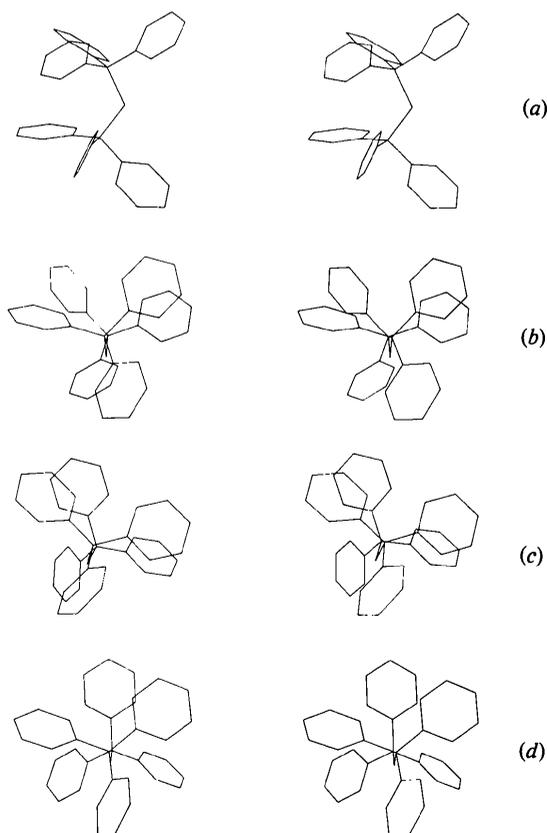
Fig. 3. Stereoviews of the X—[C—(C$_6$H$_5$)$_3$]$_2$ conformations. (*a*) $X = $ S, observed molecule, viewed normal to C—S—C bonds, (*b*) $X = $ S, observed molecule, viewed in direction of C(M1)···C(M2), (*c*) $X = $ S, calculated molecule, minimum-energy model 3, viewed in same direction as (*b*), (*d*) $X = $ O, observed molecule, viewed in same direction as (*b*).

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Studies of Ribonuclease-A by X-ray and Neutron Diffraction

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Abstract

The structure of monoclinic bovine ribonuclease-A [$P2_1$, $a = 30.18$ (12), $b = 38.4$ (10), $c = 53.32$ (15) Å, $\beta = 105.85$ (8)°] has been studied by a combination of X-ray and neutron diffraction techniques. A model based on X-ray data to 2.5 Å resolution has been refined by restrained least squares, with a final $R = 25.2\%$ for 951 non-hydrogen atoms and one phosphate molecule. Partially refined coordinates of ribonuclease-S were initially used. A good fit between the model and difference Fourier maps was obtained. Several maps based on neutron diffraction intensities at 2.8 Å resolution and various phasing schemes were calculated and they are discussed in terms of their usefulness in further refinement of the structure.

Introduction

Bovine pancreatic ribonuclease is one of the enzymes whose structure has been extensively studied by a variety of physicochemical techniques. Both the native enzyme and its modification, ribonuclease-S (product of cleavage by subtilisin of a peptide bond between residues 20 and 21), have been studied by X-ray diffraction techniques. The structure of monoclinic ribonuclease-A has been reported at 5.5 Å resolution by Avey, Boles, Carlisle, Evans, Morris, Palmer, Woolhouse & Shall (1967) and later at 2.5 Å by Carlisle, Palmer, Mazumdar, Gorinsky & Yeates (1974). The structure has been independently solved at 2 Å by Kartha, Bello & Harker (1967). The structure of trigonal ribonuclease-S has been reported by