Structure and Conformation of β-Thiodan in the Solid State and in Solution. Application of the Infrared–*X*-Ray Method

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We have determined the structure of the β isomer (m.p. 208—210 °C) of the commercial insecticide thiodan by single-crystal *X*-ray techniques and determined its solution conformation by the i.r.–*X*-ray method. β-Thiodan, 6,7,8,9,10,10-hexachloro-1,2,2a,4,4a,5-hexahydro-6,9-methano-2,4,3-benzodioxathiepin-3-oxide, crystallizes in space group $P2_1/c$ with a = 8.244(2), b = 10.104(3), c = 17.32(1) Å, β = 95.48(3)°, and Z = 4. The structure was solved by direct methods and refined to R 0.074. The structure is consistent with the assignment based on n.m.r. and stability considerations and inconsistent with that assigned based on dipole-moment measurements.

I.r. spectra were used to compare the solid-state and solution conformation. The solid-state and solution i.r. spectra showed almost identical absorption maxima, but the i.r. difference spectra had substantially different intensities of the absorptions in these two states. Thus β-thiodan was probably in the same conformation in the solid state and in solution and care must be taken in interpreting i.r. difference spectra.

Dihedral angles for thiodan indicated a Lambert R value of 2.17 while the observed R value was *ca.* 1.0 based on the reported ratio of *trans* and *cis* vicinal coupling constants, indicating that this method does not apply to such systems.

The results of the i.r., dipole-moment, and R value studies indicate the necessity of using several methods when comparing solid-state and solution conformations.

CRYSTALLOGRAPHIC studies of thiodan were carried out to resolve an interesting structural problem. In addition, i.r. spectroscopy was used to compare the solid and solution conformations and thus provide another test of the applicability of the i.r.–*X*-ray method for the determination of solution conformation.

The commercial insecticide thiodan (I) crystallizes in two stereoisomers α-thiodan (m.p. 108—110 °C) and β-thiodan (m.p. 208—210 °C). Twenty-four configurational and conformational isomers of thiodan can be drawn: however, chemical degradation and n.m.r. spectral studies led to the elimination of sixteen of these.[1]

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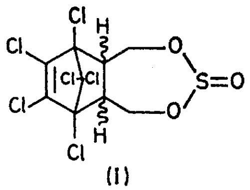
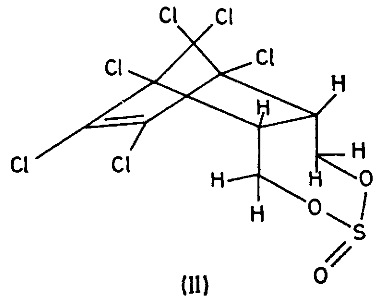
[1] S. E. Forman, A. J. Durbetaki, M. V. Cohen, and R. A. Olofson, *J. Org. Chem.*, 1965, **30**, 169.

Further examination of the n.m.r. spectra and application of the Karplus equation led to the assignment of structure

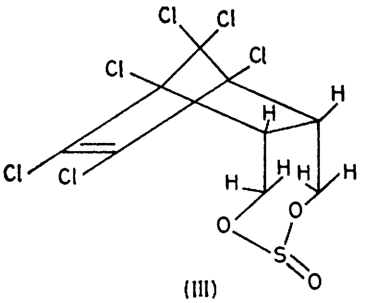


(I)

(II) to α-thiodan. Ring-stability considerations as well as the presumed structure of α-thiodan were used to assign structure (III) to β-thiodan.[1] The structures



(II)



(III)

assigned to α- and β-thiodan were exactly the reverse of those made by Riemschneider on the basis of dipole-moment measurements and calculations.[2] Furthermore, Forman *et al.*[1] measured dipole moments of 1.02 D for α-thiodan and 3.18 D for β-thiodan while Riemschneider obtained values of 1.63 and 2.31 D. The dipole-moment values obtained by Forman *et al.*[1] did not agree with those calculated by Riemschneider for any of the possible *endo*-isomers.

We have recently developed and tested the i.r.–*X*-ray method for the determination of solution conformation based on *X*-ray crystallographic data.[3] Our studies showed that this method could be applied to choline and several antihistamines. The combined crystallographic [4,5] and i.r. studies of trimethylene sulphites [6] constitute an early application of this method and suggested that it could successfully be applied to sulphites included in a seven-membered ring, *e.g.* thiodan.

We have also compared the structural parameters of the sulphite group and the hexachloronorbornene group in thiodan with those reported previously.

EXPERIMENTAL

Least-squares analysis of the positions of 14 independent reflections gave unit-cell parameters.

Crystal Data.—$C_9H_6Cl_6O_3S$, $M = 407$. Monoclinic, $a = 8.244(2)$, $b = 10.104(3)$, $c = 17.32(1)$ Å, $\beta = 95.48(3)°$, $U = 1\,436.12$ Å^3, $Z = 4$, $D_c = 1.89$ g cm^{-3}. Cu-K_α radiation, $\lambda = 1.541\,8$ Å; μ(Cu-K_α) $= 124.1$ cm^{-1}. Systematic absences: $h0l$, $l = 2n + 1$ and $0k0$, $k = 2n + 1$, space group $= P2_1/c$.

Data Collection.—A crystal $0.32 \times 0.18 \times 0.32$ mm, obtained by slow evaporation of a hexane solution, was mounted on a glass fibre and aligned with the *b* axis parallel to the ϕ axis of the diffractometer. Data were collected on a card-driven Picker four-angle diffractometer by use of β-filtered Cu-K_α radiation and a scintillation detector. A θ—2θ scan of 3° was applied with scan speed 30 s per degree. Backgrounds were counted for 20 s at each end of the scan range. The reciprocal region $h\overline{kl}$ and $\overline{hk}l$ was explored to a $2\theta_{max.}$ 134.5°. Of 2 502 independent reflections 2 408 satisfied the conditions $F_o \geqslant 3\,\sigma(F_o)$ and were considered observed. The intensities of two standard reflections measured every 60 reflections remained essentially constant during data collection. No absorption or extinction correction was made.

Structure Determination.—The structure was determined by direct methods. An *E* map based on the phases obtained from the programs Singen and Phase [7] revealed the positions of all non-hydrogen atoms. Refinement of these atomic positions first with isotropic then anisotropic temperature factors proceeded smoothly to *R* 0.079. A difference map revealed four peaks of 1.0—1.1 eA^{-3}; however, none of these were in positions expected for the hydrogen atoms or any other recognizable molecular fragment. The appearance of these peaks may be connected with the fact that no absorption or extinction corrections were made. The positions of the hydrogen atoms were calculated assuming tetrahedral geometry and C–H 1.02, and the final *R* of 0.074 and atom parameters were obtained after one cycle of anisotropic least-squares refinement of non-hydrogen atoms only. Final atomic positions are listed in Table 1. Final observed and calculated structure factors and anisotropic thermal parameters are deposited in Supplementary Publication No. SUP 21845 (4 pp., 1 microfiche).*

Powder Diffraction of β-Thiodan.—The powder diffraction pattern was measured by use of a Debye–Scherrer powder

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1975, Index issue.

[2] R. Riemschneider and J. C. Hilscher, *Z. Naturforsch.*, 1960, **15b**, 809; R. Riemschneider, *ibid.*, 1962, **17b**, 723; R. Riemschneider and V. Wuscherpfennig, *ibid.*, p. 585; *Naturwiss.*, 1960, **48**, 130; *Z. Chem.*, 1963, **87**, 387.

[3] S. R. Byrn, C. W. Graber, and S. L. Midland, *J. Org. Chem.*, 1976, **42**, 2283.

[4] W. L. VanOwen, R. C. D. E. Hasekamp, G. C. Verschoor, and C. Romers, *Acta Cryst.*, 1968, **B24**, 147.

[5] C. Altona, H. J. Geise, and C. Romers, *Rec. Trav. chim.*, 1966, **85**, 1197.

[6] H. F. Van Woerden and E. Havinga, *Rec. Trav. chim.*, 1967, **86**, 341.

[7] '*X*-Ray' program system, version of June 1972, updated, April 1974. Technical Report TR 192, Computer Science Center, University of Maryland.

camera and Ni-filtered Cu-K_α radiation. The expected powder pattern was calculated from the atomic parameters and the program POWD 5.[8] The 12 most intense calculated peaks corresponded to 11 of the 13 most intense observed peaks. Only the peak with a calculated 2θ of 21.56° was absent from the 13 most intense observed bands.

TABLE 1

Final atomic positions (× 10^4) for β-thiodan, with standard deviations in parentheses

	x	y	z
Cl(1)	−299(2)	184(2)	1 191(1)
Cl(2)	3 271(3)	400(2)	506(1)
Cl(3)	6 024(2)	8 580(2)	1 640(2)
Cl(4)	4 182(3)	7 305(2)	3 075(1)
Cl(5)	2 467(3)	368(2)	2 804(1)
Cl(6)	107(3)	8 326(2)	2 881(1)
S	3 250(4)	6 210(3)	−38(1)
O(1)	4 000(8)	6 145(6)	858(4)
O(2)	2 018(9)	7 460(7)	4(4)
O(3)	2 243(11)	5 044(7)	−183(5)
C(1)	2 007(10)	6 753(7)	1 788(5)
C(2)	2 978(13)	5 673(9)	1 430(6)
C(4)	558(11)	7 273(9)	372(5)
C(5)	755(9)	7 579(8)	1 247(5)
C(6)	1 233(9)	9 033(7)	1 472(4)
C(7)	2 902(9)	9 330(7)	1 227(5)
C(8)	3 990(9)	8 631(7)	1 672(4)
C(9)	3 050(9)	7 856(7)	2 233(4)
C(10)	1 701(9)	8 912(7)	2 358(5)

Solid-state and Solution I.r. Spectra of β-Thiodan.—The spectra of Nujol mulls and chloroform solutions of thiodan were measured on a Beckman IR 4230 spectrometer.

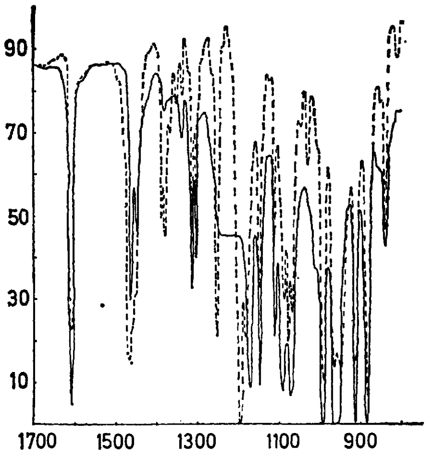

FIGURE 1 I.r. spectra of Nujol mull (dashed line) and $CHCl_3$ (full line) solution of β-thiodan

Difference i.r. spectra were recorded as before[3] by subtracting the spectrum of a $CHCl_3$ solution from that of a mull. A nearly perfect concentration match was obtained by successively diluting the $CHCl_3$ solution. Figure 1 shows the i.r. spectra of β-thiodan in a Nujol mull and in

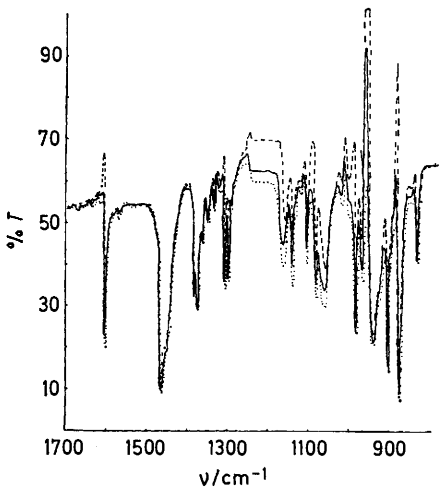

FIGURE 2 I.r. difference spectra between a Nujol mull and a $CHCl_3$ solution of β-thiodan. The spectrum with nearly equal concentrations of thiodan in the solid state and solution lies between those denoted by the dashed and full line. The concentration of β-thiodan in the mull is greater than that in solution for the spectrum denoted by the dotted line

TABLE 2

I.r. absorptions of a Nujol mull and $CHCl_3$ solution of β-thiodan

Nujol	$CHCl_3$
2 960—2 905	2 950
	2 908
2 850	2 878 *
1 609	1 609
1 468 (N) †	1 464
1 450 (SH)	1 448
1 388	
1 380 (N) †	1 380 *
1 360 *	
1 350 *	
1 338 *	1 338 *
1 312 †	1 312
1 302	1 302
1 251 1 195	1 250—1 185 ($CHCl_3$)
1 182	
	1 170
1 145	1 145
1 111	1 109 †
1 088	1 090
1 078 1 068	1 072
1 029 *	
	1 010 (SH) †
991	992 †
965 951	970—950
912 †	912
881 †	885 †
841	838
810 * 710 * 742 698—688 672 635 620	$CHCl_3$ Absorptions

* Peak with $\%T > 50$. † Peaks deviating by >10% T from the centre line of the i.r. difference spectra.

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[8] Program POWD 5, C. M. Clark, D. K. Smith, and G. G. Johnson, Pennsylvania State University, University Park, Pennsylvania.

$CHCl_3$ solution and Figure 2 shows the difference spectra. Table 2 compares the absorptions of the Nujol mull and $CHCl_3$ solution.

RESULTS AND DISCUSSION

Structural Features.—Bond lengths and angles are summarized in Tables 3 and 4, and Figure 3 shows a stereoview of the molecule. The structure is consistent with that assigned by use of n.m.r. spectra and stability arguments [1] and inconsistent with that assigned on the basis of observed and calculated dipole-moments.[2]

TABLE 3

Bond lengths (Å) of β-thiodan, with standard deviations in parentheses

S–O(1)	1.616(7)	Cl(1)–C(6)	1.751(7)
S–O(2)	1.626(7)	Cl(4)–C(2)	1.745(8)
S–O(3)	1.449(8)	Cl(2)–C(7)	1.702(8)
		Cl(3)–C(8)	1.684(8)
C(1)–C(2)	1.52(1)	Cl(5)–C(10)	1.751(8)
C(1)–C(5)	1.57(1)	Cl(6)–C(10)	1.768(8)
C(1)–C(9)	1.57(1)		
C(4)–C(5)	1.54(1)		
C(5)–C(6)	1.56(1)		
C(6)–C(7)	1.51(1)		
C(8)–C(9)	1.52(1)		
C(6)–C(10)	1.55(1)		
C(9)–C(10)	1.57(1)		
C(7)–C(8)	1.33(1)		
O(1)–C(2)	1.44(1)		
O(2)–C(4)	1.43(1)		

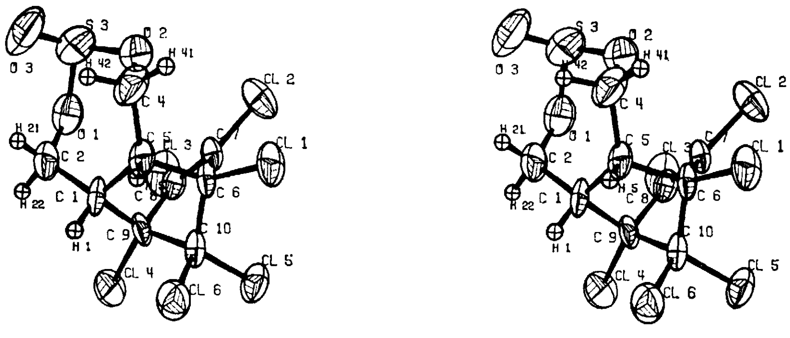

FIGURE 3 Stereoview of the crystal structure. Hydrogen atoms were placed in calculated positions assuming tetrahedral geometry

The hexachloronorbornene group resembles that of endrin and aldrin.[9] The olefinic C–Cl distances are 1.702(8) and 1.684(8) Å compared to 1.694, 1.695, 1.706, and 1.703 Å in endrin and aldrin.[9] The C–C bonds adjacent to the olefin are slightly shortened [1.51(1) and 1.52(1)] as were those in aldrin [1.52 and 1.54 Å] and endrin [1.48 and 1.54 Å]. The long C(9)–C(10) [1.57(1) Å] bond is consistent with one of the bridge methylene bonds in endrin [1.57(1)].[9]

The bond angles about the C(7)–C(8) double bond are significantly distorted. Those involving the chlorine atoms range from 124.4 to 128.1° while the C(6)–C(7)–C(8) and C(7)–C(8)–C(9) angles are 108.3(7) and 107.6(6) respectively. In endrin the corresponding angles involving chlorine atoms range from 124.3 to 129.4 and in aldrin from 124.3 to 128.4; corresponding angles at the olefinic carbon atoms are 106.2 and 108.5, and 107.9 and 108.3°. Best planes analysis indicated that the olefin carbon atoms and their four substituents were essentially planar although not statistically (see Table 5). A much better plane contained only the four carbon atoms C(6)—(9) with Cl(2) 0.030 and Cl(3) −0.014 Å out of this plane. The dihedral angles (see Table 6) involving the olefin group are consistent with the carbon atoms being in a plane with the chlorine atoms deviating slightly from this plane.

TABLE 4

Bond angles (°) in β-thiodan, with the standard deviations in parentheses

C(5)–C(6)–Cl(1)	113.4(5)		
C(7)–C(6)–Cl(1)	116.3(5)	C(2)–C(1)–C(9)	115.2(7)
C(10)–C(6)–Cl(1)	115.6(6)	C(5)–C(1)–C(9)	102.4(6)
C(1)–C(9)–Cl(4)	114.2(5)	C(1)–C(5)–C(4)	118.9(7)
C(8)–C(9)–Cl(4)	115.7(5)	C(1)–C(5)–C(6)	102.5(6)
C(10)–C(9)–Cl(4)	115.6(5)	C(4)–C(5)–C(6)	115.8(7)
C(6)–C(10)–Cl(6)	114.0(5)	C(5)–C(6)–C(7)	109.4(6)
C(9)–C(10)–Cl(6)	114.4(5)	C(5)–C(6)–C(10)	101.8(6)
C(6)–C(10)–Cl(5)	114.5(5)	C(7)–C(6)–C(10)	98.5(6)
C(9)–C(10)–Cl(5)	113.6(5)	C(1)–C(9)–C(8)	109.9(6)
		C(1)–C(9)–C(10)	100.9(6)
Cl(5)–C(10)–Cl(6)	108.0(4)	C(8)–C(9)–C(10)	98.6(6)
		C(6)–C(10)–C(9)	91.8(6)
O(1)–C(2)–C(1)	114.1(7)	C(2)–C(1)–C(5)	118.8(7)
O(2)–C(4)–C(5)	113.5(7)		
O(1)–S–O(2)	99.9(3)	C(6)–C(7)–C(8)	108.3(7)
O(1)–S–O(3)	107.1(4)	C(7)–C(8)–C(9)	106.7(6)
O(2)–S–O(3)	106.8(4)		
		C(6)–C(7)–Cl(2)	124.4(5)
S–O(1)–C(2)	118.6(6)	C(8)–C(7)–Cl(2)	127.2(6)
S–O(1)–C(4)	118.3(6)	C(7)–C(8)–Cl(3)	128.1(6)
		C(9)–C(8)–Cl(3)	125.2(6)

The C(6)–C(10)–C(9) angle of 91.8° deviates significantly from tetrahedral geometry. The corresponding angle is 92.1 in endrin and 93.2° in aldrin.

Bond lengths and angles involving the sulphite group are quite similar to those of trimethylene sulphite (IV) [4] and 1,1-dichlorotrimethylene sulphite (V).[5] The S=O bond length [1.433(8) Å] compares favourably with that of (IV) [1.45(1) Å] and (V) [1.442(6) Å] as do the S–O bond lengths [1.626(7) and 1.616(7)], [1.59(1) and 1.60(2) in (IV), and 1.608(6) and 1.623(6) Å in (V)].

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[9] T. D. DeLacy and C. H. L. Kennard, *J.C.S. Perkin II*, 1972, 2153.

The O–S–O bond angles [107.1(4), 106.8(4), and 99.3(3)°] also compare favourably with those in (IV) [105.6(6), 103.1(6), and 100.3(6)°] and (V) [107.8(3), 97.8(3), and 107.4(3)°]. The S–O–C angles [118.3(6) and 118.6(6)°] are larger than those observed in the sulphites (IV) and (V) [115.5(1.0) and 116.1(1.0) in (IV) and 115.8(5) and 116.6(5)° in (V)]. These differences are probably due to different ring geometries since in our study the sulphite is included in a seven rather than a six-membered ring. All S–O–C bond angles are significantly greater than the accepted values of 109—110°.[5]

TABLE 5

Details of the best planes of β-thiodan *

Cl(3)	−7	−14	−2
Cl(2)	10	30	2
C(9)	12	2	23
C(8)	0	−3	5
C(7)	−5	3	−5
C(6)	−10	−17	−16
χ^2 †	9.58	0.35	1.75
P	0.025	0.50	0.50

* Distance from the plane in Å × 103. The distances for atoms included in the plane calculation are underlined. † The results of a χ^2 significance test with the probability (P) of a planar set of atoms having such a χ^2 value. Table IV of W. C. Hamilton, 'Statistics in Physical Science,' Ronald Press, New York, 1964, p. 207 was used for the probability values.

TABLE 6

Summary of dihedral angles (°) in β-thiodan

Atoms	Angle
C(6)–C(7)–C(8)–C(9)	−0.5(8)°
Cl(2)–C(7)–C(8)–Cl(3)	−1.3(1.2)
C(1)–C(5)–C(4)–O(2)	−60.9(1.0)
C(5)–C(1)–C(2)–O(1)	61.0(1.0)

Crystal Packing.—Figure 4 shows a stereoscopic packing diagram of the contents of the unit cell. Table 7 lists all close intermolecular contacts involving non-hydrogen atoms. The packing is dominated by Cl · · · Cl and Cl · · · O contacts; however, none of these contacts is significantly shorter than the sum of the van der Waals radii of the atoms involved.[10]

TABLE 7

Intermolecular distances of <3.70 Å involving heavy atoms

Cl(3) · · · Cl(1^{I})	3.59	Cl(5) · · · Cl(3^{VI})	3.58
Cl(2) · · · Cl(2^{II})	3.58	Cl(2) · · · Cl(4^{VI})	3.63
S · · · O(1^{III})	3.66		
O(1) · · · O(3^{III})	3.62	Cl(5) · · · O(1^{VI})	3.63
Cl(2) · · · Cl(1^{IV})	3.64	Cl(1) · · · Cl(6^{VII})	3.56
Cl(1) · · · O(2^{IV})	3.38	Cl(5) · · · O(3^{VIII})	3.53
C(4) · · · O(3^{V})	3.28		

Roman numerals as superscripts refer to molecules related to the one at the origin by the following symmetry operations:

I, $x + 1, y, z$; II, $-x + 1, -y + 2, -z$; III, $-x + 1, -y + 1, -z$; IV, $-x, -y + 2, -z$; V, $-x, 1 - y, -z$; VI, $-x + 1, y + \frac{1}{2}, z + \frac{1}{2}$; VII, $-x, y + \frac{1}{2}, -z + \frac{1}{2}$; VIII, $x, -y + 1.5, z + \frac{1}{2}$.

Conformation in the Solid State and in Solution.—The hexachloronorbornene group is rigid and probably has the same conformation in the solid state and in solution. N.m.r. and i.r. studies are equivocal but suggest that the seven-membered sulphite ring adopted a solution conformation which is similar to that of the solid state.

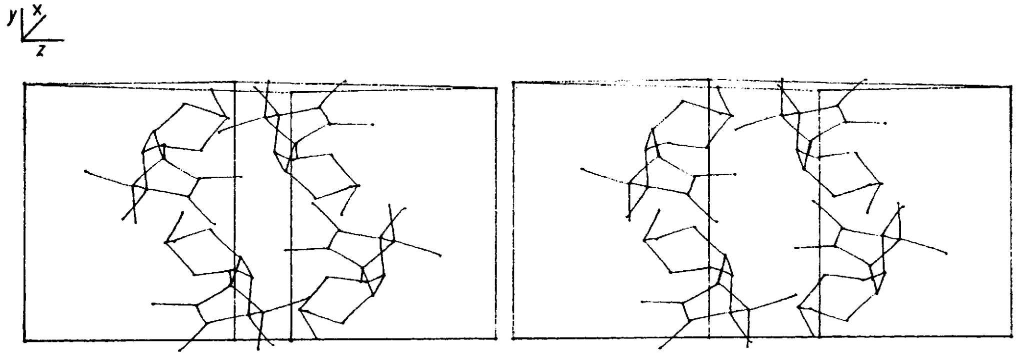

FIGURE 4 Stereoview of the crystal packing of β-thiodan

Recently, we have introduced the i.r.–X-ray method for determining the solution conformation of biologically important ethylene derivatives.[3] This method involved three steps: (1) determination of the crystal structure, (2) use of powder X-ray diffraction to establish that grinding did not induce a crystalline phase transformation, and (3) comparison of the i.r. spectra of the powder (Nujol mull) and solution. Studies on model compounds suggested that it could be used to determine unequivocally the conformation in solution if it was identical to that of the solid state.

Powder diffraction studies showed that no phase transformation occurred upon grinding β-thiodan. Comparison of the wavelengths of absorption of the powder

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[10] A. I. Kitaigordskii, 'Organic Chemical Crystallography,' Consultants Bureau, New Jersey, New York, 1961, p. 7; F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' Interscience, New York, 1972, p. 103.

and solution of β-thiodan (Table 2 and Figure 1) showed that the spectra were only slightly different with only one difference in intense peaks occurring at 1 182 *vs.* 1 170 cm^{-1}. From our earlier studies it was therefore indicated that the solid-state and solution conformations were similar. Unexpectedly, the difference spectra (Figure 2) between powder and solution showed nine differences of $>10\% T$ (Table 2), which reflect differences in intensity between the solid state and solution spectra rather than the appearance or disappearance of bands. This observation illustrates the dangers involved in using only i.r. difference spectra to compare the solid-state and solution conformation of a compound. I.r. spectra should be compared visually, in tabulated form and with difference spectra in order to avoid such dangers.

Lambert introduced the *R* value method for comparing the dihedral angles in six-membered rings with the *J*(H–H) vicinal coupling constants.[11] The C(9)–C(5)–C(4)–O(2) and C(5)–C(1)–C(2)–O(1) dihedral angles (−60.9 and 61.0°) require an *R* value ($R = J_{trans}/J_{cis}$) of 2.7. The observed *R* value was *ca.* 1.0.[1] An *R* value of 1.0 requires a dihedral angle of 45° which would require sterically unfavourable C(5)–O(1) and C(1)–O(2) interactions and would place O(1) and O(2) extremely close to each other. The O(1) · · · O(2) intramolecular contact was 2.482(9) Å in β-thiodan. Thus the *R* value method does not give structurally reasonable conformational information in the case of this seven-membered sulphite ring.

The foregoing data illustrate the limits of the *R* value and the published data illustrate the limits of dipole-moment studies in unequivocally establishing the relationship between solution and solid-state conformations. Our studies suggest that in the future combinations of these methods and the i.r.–*X*-ray method should be used for such studies.

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[5/2528 *Received*, 29*th December*, 1975]

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[11] J. B. Lambert, *Accounts Chem. Res.*, 1971, **4**, 87.