

PTCH-2, where the dihedral angles ranged from 47.0 to 50.5° [Table 6(b)]. The same phenomenon has also been found for bicyclohexylidene (Sasvári & Löw, 1965) with almost the same dihedral angles (49.4 and 51.1°) and also for the free cyclohexane molecule (Wohl, 1964). In the present case the largest dihedral angle belongs to the very end of the molecule. Thus the flattening is more apparent within the linear molecular chain.

All C–C bonds of the molecule are single bonds of sp^3 -hybridized C atoms and their lengths vary from 1.473 to 1.565 Å with a mean value of 1.527 Å (Table 7). Although the maximum deviation of 0.054 Å from the mean value is rather significant, it is within 3σ of the C–C bond lengths and can be attributed to the fact that only a restricted number of intensities were used for the accurate refinement. The average value of the bond lengths (1.527 Å) is in good agreement with the values of 1.524 and 1.523 Å found in PTCH-2 and bicyclohexylidene (Sasvári & Löw, 1965) respectively.

The spatial packing of the molecules conforms to molecular close packing in both isomeric forms and the molecules, in both cases, are held together by van der Waals forces. The shortest intermolecular H–H distances (six in PTCH-1 and 15 in PTCH-2) range from 2.42 to 2.71 Å (average 2.60 Å) and from 2.44 to 2.69 Å (average 2.59 Å) in PTCH-1 and PTCH-2 respectively, and the averages compare with the van

der Waals distances (2.54 Å). Stereographic projections of both isomeric forms are given in Fig. 5(a) and (b) (ORTEP; Johnson, 1965).

References

- DAVIS, M. & HASSEL, O. (1963). *Acta Chem. Scand.* **17**, 1181–1181.
 HEIDT, J., KISS, I., JÄGER, S. & BENKE, B. (1965). Hungarian Patent MA-1344/b.
 HEIDT, J., NESZMÉLYI, A., IMRE, L. & KISS, I. (1967). *Magy. Kém. Folyóirat*, **73**, 95–98.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
 JOHNSON, C. K. (1965). ORTEP. Oak Ridge National Laboratory Report ORNL-3794.
 KARLE, I. L. & KARLE, J. (1971). *Acta Cryst.* **B27**, 1891–1898.
 LINDQVIST, O. & WENGELIN, F. (1968). *Ark. Kem.* **28**, 179–188.
 MAIN, P., WOOLFSON, M. M. & GERMAIN, G. (1968). *LSAM System of Computer Programs for the Automatic Solution of Centrosymmetric Structures by the Logical Symbolic Addition Method*, Univ. of York, York, England.
 SASVÁRI, K. (1972). *Cryst. Struct. Commun.* **1**, 163–166.
 SASVÁRI, K. & LÖW, M. (1965). *Acta Cryst.* **19**, 840–848.
 SASVÁRI, K., SIMON, K., BOGNÁR, R. & MAKLEIT, S. (1974). *Acta Cryst.* **B30**, 634–641.
 SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
 WOHL, R. A. (1964). *Chimia*, **18**, 219–221.

Acta Cryst. (1976). **B32**, 1065

The Crystal and Molecular Structure of 2,6-Diphenyl-3-benzyl-2*H*-thiopyran-5-carboxaldehyde

BY S. A. CHAWDHURY*

Physics Department, University of York, York YO1 5DD, England

(Received 12 June 1975; accepted 8 July 1975)

Crystals of 2,6-diphenyl-3-benzyl-2*H*-thiopyran-5-carboxaldehyde are monoclinic, space group $P2_1/c$ with four molecules in a unit cell of dimensions $a = 10.871$, $b = 10.956$, $c = 18.904$ Å, $\beta = 118.39^\circ$. The structure has been refined with a full-matrix least-squares technique to a final R index of 0.053 for 1623 observed reflexions. The thiopyran ring is non-planar. One of the C–C bonds of 1.455 (6) Å in the thiopyran ring is a shortened single bond. One of the S–C distances of 1.712 (5) Å indicates a partial double bond.

Introduction

An X-ray examination of the crystal structure of 2,6-diphenyl-3-benzyl-2*H*-thiopyran-5-carboxaldehyde, $C_{25}H_{20}OS$, was undertaken to study the nature of the heterocyclic ring. Since the exact conformation of the

thiopyran ring is the most interesting feature of the compound, its atomic parameters have been determined very precisely and the details of its geometry have been investigated. After the structure was determined and refined it was discovered that it had already been investigated (Haque & Caughlan, 1967). Since the present analysis is based on full three-dimensional diffractometer data and the results differ significantly from those obtained by Haque & Caughlan, a brief account of the new analysis seems desirable.

* Present address: Physics Department, Rajshahi University, Rajshahi, Bangladesh.

Experimental

The compound, $C_{25}H_{20}OS$, m.p. 153°C was synthesized by Latif, Razzaq, Adhikari & Eunos (1959) and recrystallized from acetone as yellow well-developed needles elongated along the monoclinic b axis. Cell dimensions with standard deviations calculated by a least-squares fit to 20 reflexions measured on the diffractometer are: $a=10.871$ (4), $b=10.956$ (5), $c=18.904$ (7) Å, $\beta=118.39$ (1)°. $D_m=1.22$, $D_c=1.233$ g cm $^{-3}$ with four molecules in the unit cell. Systematic absences for reflexions $h0l$ with l odd and $0k0$ with k odd fix the space group as $P2_1/c$.

The intensities of 2708 unique reflexions, 1185 of which were regarded as unobserved ($I < 2.5\sigma$), were measured on a computer-controlled Hilger and Watts four-circle diffractometer. As the crystal specimen used for intensity measurements was very small, no correction was made for absorption in data reduction.

Determination and refinement of the structure

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971). 220 E^3 's and 2000 \sum_2 relationships were used to develop eight sets of phases. The E map calculated from the set of phases with the highest combined figure of merit (2.94) showed 25 out of 27 non-hydrogen atoms.

Refinement began with a residual, R , of 0.23 for the 1623 observed reflexions (0.32 for the total 2708 reflexions). Two cycles of full matrix least-squares isotropic refinement reduced R to 0.11 for the observed reflexions. At this stage a weighting scheme after

Table 1. Fractional positional parameters of non-hydrogen atoms and their estimated standard deviations ($\times 10^4$)

	x	y	z
S	5515 (2)	4409 (1)	3178 (1)
O	1853 (4)	7554 (4)	1530 (3)
C(1)	6529 (5)	5364 (5)	2866 (3)
C(2)	5611 (5)	5932 (5)	2048 (3)
C(3)	4281 (6)	6274 (5)	1799 (4)
C(4)	3537 (5)	6026 (5)	2252 (3)
C(5)	3951 (5)	5155 (4)	2835 (3)
C(6)	3037 (6)	4660 (5)	3156 (3)
C(7)	1672 (6)	4308 (6)	2623 (4)
C(8)	811 (7)	3855 (7)	2919 (5)
C(9)	1316 (9)	3711 (6)	3726 (5)
C(10)	2660 (9)	4021 (6)	4256 (5)
C(11)	3547 (7)	4505 (6)	3978 (4)
C(12)	7426 (5)	6301 (5)	3499 (3)
C(13)	6874 (6)	7400 (5)	3557 (4)
C(14)	7712 (7)	8221 (6)	4160 (4)
C(15)	9071 (7)	7936 (6)	4696 (4)
C(16)	9610 (6)	6859 (7)	4632 (4)
C(17)	8803 (6)	6017 (6)	4043 (4)
C(18)	6313 (7)	6175 (5)	1528 (4)
C(19)	6687 (6)	5033 (5)	1219 (3)
C(20)	5959 (8)	3968 (6)	1099 (5)
C(21)	6285 (9)	2952 (7)	788 (5)
C(22)	7320 (9)	2982 (8)	595 (5)
C(23)	8038 (9)	4044 (9)	695 (5)
C(24)	7718 (8)	5068 (7)	1003 (5)
C(25)	2299 (6)	6774 (5)	2054 (4)

Cruickshank (1965) and anisotropic temperature factors for the non-hydrogen atoms were introduced. R fell to 0.074 in three more cycles. H atoms located from the difference Fourier map were then assigned isotropic temperature factors and included in the calculations. The refinement continued until the shifts in the parameters were less than one-quarter of their standard deviations. The final R indices were 0.053 for the observed reflexions and 0.078 for the total number of reflexions.

Table 2. Anisotropic temperature factors, U_{ij} , in the form $\exp(-2\pi^2 \sum U_{ij} h_i h_j a_i^* a_j^*)$ with standard deviations ($\times 10^3 \text{ \AA}^2$)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S	57 (1)	40 (1)	69 (1)	1 (1)	31 (1)	7 (1)
O	59 (3)	85 (3)	85 (3)	14 (2)	27 (3)	30 (3)
C(1)	55 (3)	34 (3)	66 (4)	5 (3)	34 (3)	3 (3)
C(2)	63 (4)	38 (3)	63 (4)	-1 (3)	39 (3)	-2 (3)
C(3)	63 (4)	38 (3)	56 (4)	-4 (3)	30 (3)	3 (3)
C(4)	51 (3)	46 (4)	49 (4)	-3 (3)	24 (3)	0 (3)
C(5)	57 (3)	31 (3)	55 (4)	-1 (3)	31 (3)	3 (3)
C(6)	57 (4)	46 (4)	60 (4)	-3 (3)	33 (3)	4 (3)
C(7)	67 (4)	72 (4)	88 (4)	-6 (4)	46 (4)	10 (4)
C(8)	73 (5)	83 (5)	115 (6)	6 (4)	52 (5)	22 (5)
C(9)	105 (6)	73 (5)	111 (7)	7 (4)	74 (6)	21 (5)
C(10)	121 (6)	75 (5)	80 (6)	0 (4)	64 (5)	12 (4)
C(11)	85 (5)	68 (4)	67 (4)	-7 (4)	44 (4)	6 (4)
C(12)	41 (3)	47 (4)	60 (4)	3 (3)	28 (3)	8 (3)
C(13)	63 (4)	54 (4)	62 (4)	4 (3)	25 (3)	-3 (3)
C(14)	79 (5)	55 (4)	63 (4)	-1 (4)	26 (4)	-3 (4)
C(15)	72 (4)	73 (5)	56 (4)	-13 (4)	32 (4)	3 (4)
C(16)	50 (4)	90 (5)	83 (6)	-7 (4)	26 (4)	6 (5)
C(17)	49 (4)	74 (4)	80 (4)	10 (3)	32 (3)	12 (4)
C(18)	68 (4)	56 (4)	73 (4)	-2 (3)	48 (3)	-1 (3)
C(19)	59 (2)	57 (4)	59 (4)	1 (3)	37 (3)	7 (3)
C(20)	115 (5)	65 (4)	118 (6)	-18 (4)	85 (5)	-18 (5)
C(21)	124 (6)	73 (5)	119 (7)	-5 (5)	81 (6)	-28 (5)
C(22)	124 (6)	92 (6)	101 (6)	24 (5)	64 (6)	-15 (5)
C(23)	117 (6)	124 (7)	144 (8)	23 (6)	99 (6)	-12 (6)
C(24)	93 (5)	95 (5)	109 (6)	-4 (4)	68 (5)	-11 (5)
C(25)	61 (4)	54 (4)	63 (4)	2 (3)	27 (3)	6 (4)

Table 3. Final coordinates ($\times 10^3$) and isotropic temperature factors ($\text{\AA}^2 \times 10^2$) of hydrogen atoms

	x	y	z	U_{iso}
H(1)	717 (6)	474 (5)	279 (4)	514
H(2)	378 (6)	674 (6)	125 (4)	576
H(3)	133 (7)	441 (6)	203 (4)	665
H(4)	-12 (8)	362 (6)	248 (4)	671
H(5)	76 (7)	335 (5)	401 (4)	685
H(6)	305 (7)	398 (7)	481 (4)	672
H(7)	455 (7)	468 (6)	436 (4)	624
H(8)	594 (7)	764 (6)	315 (4)	581
H(9)	728 (6)	903 (5)	418 (3)	408
H(10)	958 (6)	857 (5)	516 (4)	486
H(11)	1050 (7)	663 (6)	493 (4)	566
H(12)	923 (6)	528 (5)	393 (3)	415
H(13)	561 (7)	665 (6)	106 (4)	615
H(14)	721 (6)	668 (6)	185 (4)	528
H(15)	535 (6)	393 (6)	131 (4)	637
H(16)	571 (7)	215 (6)	68 (4)	681
H(17)	755 (6)	225 (5)	31 (4)	698
H(18)	873 (6)	414 (6)	49 (4)	713
H(19)	827 (6)	580 (5)	114 (4)	676
H(20)	186 (7)	665 (6)	245 (4)	681

Estimated standard deviations are in parentheses.

Results and discussion

The final positional and thermal parameters of the non-hydrogen atoms are given in Tables 1 and 2, the parameters of the H atoms in Table 3.*

Fig. 1 shows the dimensions of the molecule calculated from the final coordinates. The estimated standard deviations were calculated with the formula of Darlow (1960). Since the thiopyran ring is the most interesting feature of the structure, the bond distances and angles of the ring are given separately in Table 4 and compared with the results obtained by Smith, Kalish & Smutny (1972) for 2*H*-thiopyran *p*-bromobenzyl ester. The results of Haque & Caughlan (1967) are also shown in Table 4. The bond distances C(2)–C(3) and C(4)–C(5), 1.343 (8) and 1.363 (6) Å respectively, indicate clearly that they are double bonds. The observed C(3)–C(4) distance of 1.455 (6) Å indicates

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31249 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

a shortened single bond. The approximate planarity of C(1), C(2), C(3), C(18), H(2) and S, C(4), C(5), C(6), C(25) and the fact that bond angles C(3)–C(2)–C(18), C(3)–C(2)–C(1), C(2)–C(3)–H(2), C(2)–C(3)–C(4) and C(3)–

Table 4. Bond lengths (Å) and angles (°) of the thiopyran ring

	Smith <i>et al.</i> (1972)	Haque & Caughlan (1967)
S—C(1)	1.810 (5)	1.827 (13)
S—C(5)	1.712 (5)	1.759 (17)
C(1)–C(2)	1.519 (6)	1.509 (18)
C(2)–C(3)	1.343 (8)	1.364 (17)
C(3)–C(4)	1.455 (6)	1.417 (20)
C(4)–C(5)	1.363 (6)	1.369 (23)
C(1)–S—C(5)	104.5 (0.2)	100.4 (0.7)
S—C(1)–C(2)	111.2 (0.3)	109.4 (0.8)
C(1)–C(2)–C(3)	123.2 (0.3)	122.8 (1.1)
C(2)–C(3)–C(4)	123.2 (0.4)	124.5 (1.2)
C(3)–C(4)–C(5)	123.0 (0.4)	121.3 (1.4)
C(4)–C(5)–S	121.7 (0.3)	121.7 (1.1)
		106.3†
		107.8
		123.6
		128.4
		117.7
		123.6

* Standard deviations are 0.03–0.06 Å.

† Standard deviations are ~1°.

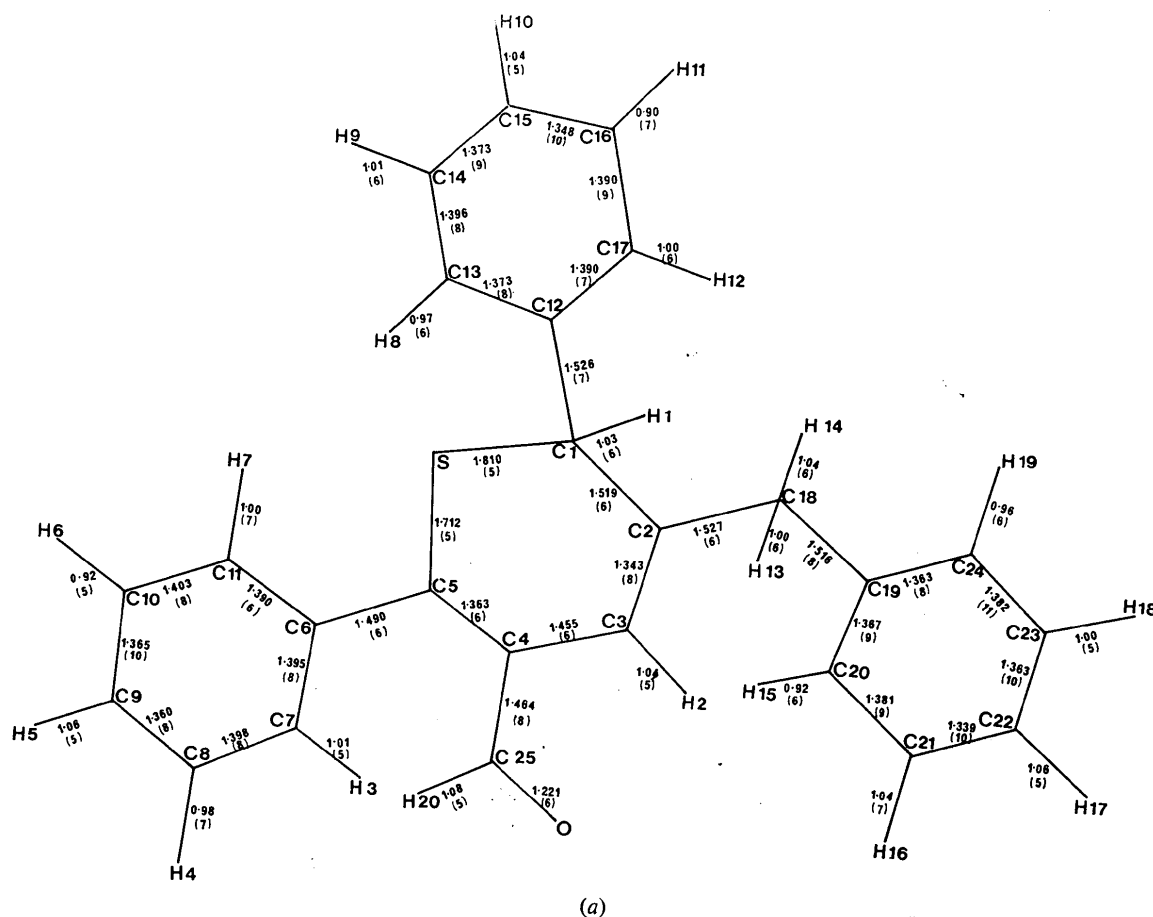


Fig. 1. Dimensions of 2,6-diphenyl-3-benzyl-2*H*-thiopyran-5-carboxaldehyde. (a) Numbering of atoms with bond lengths and standard deviations (Å).

C(4)–C(5), C(3)–C(4)–C(25), S–C(5)–C(4), C(6)–C(5)–C(4) are close to 120° indicate sp^2 bonding for C(2), C(3), C(4) and C(5). The S–C(1) bond length is normal but S–C(5) is a partial double bond. These results agree quite well with those obtained by Smith *et al.* (1972) for their thiopyran compound.

The non-planarity of the thiopyran ring is evident from Table 5 where the results of the best least-squares planes passing through the atoms in the thiopyran ring are given. The thiopyran ring has an almost 'boat shaped' conformation in which C(1) and C(4) are the out-of-the-plane atoms, being 0.523 and 0.119 Å respectively from the least-squares plane passing through C(2), C(3), C(5) and S.

The three aromatic rings are all planar and the bond

lengths and angles are normal. The dihedral angles of the phenyl rings at C(1) and C(5) and of the benzyl ring at C(2) are 87.9°, 47.0° and 64.9° respectively to plane III of Table 5.

The structure of the molecule with its environment when viewed along [100] is shown in Fig. 2. All the intermolecular distances are normal.

The author is grateful to Dr K. A. Latif of the University of Rajshahi, Bangladesh for providing the crystal and suggesting the project. The author is also indebted to Professor M. M. Woolfson for his keen interest during the progress of the work.

References

Table 5. Displacements (Å) of atoms of the thiopyran ring from the least-squares best planes

	Plane I through	Plane II through	Plane III through
	C(1)C(2)C(3)C(4)C(5)S	C(2)C(3)C(4)C(5)	C(2)C(3)C(5)S
C(1)	0.2706	0.4655	0.5234
C(2)	-0.1254	0.0366	0.0555
C(3)	-0.1140	-0.0745	-0.0606
C(4)	0.1476	0.0738	0.1188
C(5)	0.0354	-0.0360	0.0483
S	-0.2141	-0.1425	-0.0431

- CRUICKSHANK, D. W. J. (1965). *Computing Methods in Crystallography*, edited by J. S. ROLLETT, pp. 112–116. New York: Pergamon Press.
- DARLOW, S. F. (1960). *Acta Cryst.* **13**, 683.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
- HAQUE, M. & CAUGHLAN, C. N. (1967). *J. Org. Chem.* **32**, 3017–3021.
- LATIF, K. A., RAZZAQ, M. A., ADHIKARI, S. K. & EUNUS, M. M. (1959). *J. Ind. Chem. Soc.* **36**, 209–211.
- SMITH, A. E., KALISH, R. & SMUTNY, E. J. (1972). *Acta Cryst.* **B28**, 3494–3501.

Acta Cryst. (1976). **B32**, 1069

The Crystal and Molecular Structure of 2,4,6-Trimethyldiphenyl Sulphone (Phenyl Mesityl Sulphone)

BY S. A. CHAUDHURY*

Physics Department, University of York, Heslington, York YO1 5DD, England

(Received 3 June 1975; accepted 18 July 1975)

Crystals of 2,4,6-trimethyldiphenyl sulphone are orthorhombic, space group $Pn2_1a$, with eight molecules in the unit cell of dimensions $a=16.103$, $b=21.164$, $c=7.937$ Å. The structure was solved by direct methods using 2186 independent reflexions collected on a computer-controlled, four-circle Hilger and Watts diffractometer. It was refined by full-matrix least-squares calculations to a final R index of 0.046 for 1467 observed reflexions and 0.051 (weighted) for all the reflexions. Both molecules in the asymmetric unit are related by an almost exact centre of symmetry which does not coincide with any crystallographic centre of symmetry. Steric interactions between the sulphone and methyl groups lead to some abnormal bond lengths and angles.

Introduction

2,4,6-Trimethyldiphenyl sulphone, $C_6H_5 \cdot C_6H_2(CH_3)_3 \cdot SO_2$, usually called phenyl mesityl

sulphone, is a very unstable compound chemically (Holt & Pagdin, 1961). This chemical instability is no doubt closely linked to strain in the molecule caused by steric interactions between the sulphone and methyl groups. The crystal structure analysis has been carried out to investigate the nature of these strains. An X-ray examination of a similar unstable compound, dimesityl

* Present address: Physics Department, University of Rajshahi, Rajshahi, Bangladesh.