Table 3. ^{13}C *NMR data of the ketone and the alcohol*

Chemical shifts in p.p.m., TMS as internal standard

	C(1),C(5)	C(2),C(4)	C(6),C(8)
Ketone	65·6	82·8	65·8
Alcohol	52·2	82·3	60·7

0·005, and 0·001 *M*). At high concentrations a broadened signal at 3540 cm^{-1} is observed. Upon dilution this broadened absorption band disappears in favour of a sharp band appearing at 3640 cm^{-1} indicating a free OH group (Aaron, 1979). The results in CS_2 are similar. From this observation, it can be concluded that the alcohol exhibits an intermolecular hydrogen-bonded OH group in highly concentrated solutions.

This communication is dedicated to the memory of Professor Dr R. Haller who died on 6 April 1987 and who initiated the research on this class of compounds and gave various and valuable stimulations to this work.

Parts of the structure determination were performed in the course of a workshop in Göttingen, 1987, arranged by Professor G. M. Sheldrick. Further thanks are due to K.-F. Hesse for collecting the intensities, and to Mrs U. Bennewitz for retouching the drawings.

References

AARON, H. S. (1979). *Topics in Stereochemistry*, Vol. 11, edited by N. L. ALLINGER & E. L. ELIEL, pp. 1–52. New York: John Wiley.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE*. Report ORNL-TM-306. Oak Ridge National Laboratory, Tennessee, USA.

CASY, A. F. & PARFITT, R. T. (1986). *Opioid Analgesics – Chemistry and Receptors*. New York: Plenum.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

HALLER, R. & ASHAUER, U. (1985). *Arch. Pharm (Weinheim)*, **318**, 700–707.

HALLER, R. & UNHOLZER, H. (1971). *Arch. Pharm. (Weinheim)*, **304**, 855–863.

JEYARAMAN, R., JAWAHARSINGH, C. B., AVILA, S., GANAPATHY, K., ELIEL, E. L., MANOHARAN, M. & MORRIS-NATSCHKE, S. (1982). *J. Heterocycl. Chem.* **19**, 449–558.

JOHNSON, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

KÜPPERS, H., HESSE, K.-F., ASHAUER-HOLZGRABE, U., HALLER, R. & BOESE, R. (1987). *Z. Naturforsch. Teil B*, **42**, 221–228.

KÜPPERS, H., SAMHAMMER, A. & HALLER, R. (1987). *Acta Cryst.* C**43**, 1974–1976.

MANNICH, C. & MÜCK, M.-W. (1930). *Ber. Dtsch. Chem. Ges.* **63**, 604–608.

SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

SHELDRICK, G. M. (1986). *SHELXS*86. Program for the solution of crystal structures from diffraction data. Univ. of Göttingen, Federal Republic of Germany.

SPEK, A. L. (1987). *PLATON*87. Univ. of Utrecht, The Netherlands.

Acta Cryst. (1988). C**44**, 1754–1757

Structure of *O,S*-Dibenzoylthiamin

BY WHANCHUL SHIN

Department of Chemistry, College of Natural Sciences, Seoul National University, Seoul 151, *Korea*

(*Received* 1 *February* 1988; *accepted* 15 *March* 1988)

Abstract. 4-{*N*-[(4-Amino-2-methyl-5-pyrimidinyl)-methyl]formamido}-3-benzoylthio-3-penten-1-yl benzoate, $C_{26}H_{26}N_4O_4S$, $M_r = 490{\cdot}6$, triclinic, $P\bar{1}$, $a = 8{\cdot}139$ (1), $b = 14{\cdot}903$ (2), $c = 12{\cdot}107$ (1) Å, $\alpha = 109{\cdot}63$ (1), $\beta = 107{\cdot}87$ (1), $\gamma = 66{\cdot}19$ (1)°, $V = 1240$ Å^3, $Z = 2$, $D_x = 1{\cdot}284$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 13{\cdot}87$ cm^{-1}, $F(000) = 516$, $T = 295$ K, $R = 0{\cdot}055$ for 2368 reflections with $I > 3\sigma(I)$. The *N*-formyl and ethylenic planes are nearly perpendicular to each other and the N(3)—C(4) bond retains single-bond character as observed characteristically in other ring-opened disulfide derivatives of thiamin. However, there is no intramolecular N(4′α)—H···O(2α) hydrogen bond which has been observed in the disulfide derivatives. The molecules related by a centre of symmetry form a dimer *via* N(4′α)—H···N(3′) hydrogen bonds [2·999 (5) Å]. Two *S*-benzoyl groups intercalate between the pyrimidine base-pair planes without any strong stacking interactions.

Introduction. Thiamin (vitamin B_1) is labile against acid, alkali and heat (Dwidevi & Arnold, 1973). The thiazolium ring in thiamin is easily hydrolyzed in mildly alkaline solution to give various thiol or disulfide derivatives which, in turn, can be easily converted to thiamin upon acidification (Hopmann, 1982). Some of the ring-opened disulfide derivatives have been used either as prodrugs or as starting materials for other thiamin derivatives. The crystal structures of three thiamin disulfide derivatives have been determined. These include thiamin propyl disulfide (TPD; Nishikawa, Kamiya, Asahi & Matsumura, 1969), thiamin tetrahydrofurfuryl disulfide (TTFD; Shin & Kim, 1986*a*) and thiamin disulfide dinitrate (TDD; Shin &

0108-2701/88/101754-04$03.00

Table 1. *Atomic coordinates* ($\times 10^4$) *and thermal factors* ($Å^2 \times 10^3$) *of DBT*

	x	y	z	U_{eq}*
N(1')	−781 (4)	3895 (2)	1254 (3)	57
C(2')	−1233 (5)	4604 (3)	2242 (3)	52
N(3')	−413 (4)	4550 (2)	3356 (2)	51
C(4')	1014 (5)	3731 (3)	3543 (3)	47
C(5')	1606 (4)	2921 (2)	2554 (3)	43
C(6')	644 (5)	3078 (3)	1460 (3)	51
C(2'α)	−2826 (8)	5530 (4)	2064 (6)	79
N(4'α)	1893 (6)	3707 (3)	4665 (3)	67
C(35')	3174 (5)	1981 (3)	2713 (4)	52
S(1)	333 (1)	1796 (1)	4926 (1)	53
C(2)	3983 (5)	1038 (3)	4223 (3)	55
N(3)	2801 (4)	1353 (2)	3252 (2)	43
C(4)	1224 (4)	1051 (2)	2728 (3)	43
C(5)	22 (5)	1210 (3)	3367 (3)	48
O(2α)	5282 (4)	1312 (3)	4789 (2)	81
C(4α)	1035 (8)	554 (4)	1416 (3)	58
C(5α)	−1558 (5)	792 (3)	2878 (4)	55
C(5β)	−845 (6)	−297 (3)	2937 (4)	66
O(5γ)	−2331 (4)	−688 (2)	2645 (2)	63
C(6)	−1683 (6)	2888 (3)	4952 (3)	58
O(6)	−2750 (5)	3071 (2)	4051 (3)	90
C(A1)	−1885 (5)	3548 (3)	6171 (3)	57
C(A2)	−800 (7)	3280 (4)	7191 (4)	70
C(A3)	−1057 (9)	3932 (4)	8286 (4)	85
C(A4)	−2381 (9)	4851 (5)	8357 (6)	92
C(A5)	−3471 (11)	5130 (5)	7373 (6)	113
C(A6)	−3234 (9)	4500 (5)	6276 (6)	109
C(7)	−2953 (5)	−1038 (3)	1496 (3)	53
O(7)	−2435 (5)	−976 (3)	706 (3)	86
C(B1)	−4319 (5)	−1527 (3)	1306 (3)	48
C(B2)	−5088 (6)	−1917 (3)	148 (4)	61
C(B3)	−6328 (7)	−2412 (4)	−65 (5)	74
C(B4)	−6809 (6)	−2485 (3)	878 (4)	67
C(B5)	−6074 (6)	−2090 (3)	2025 (4)	63
C(B6)	−4807 (5)	−1604 (3)	2250 (4)	53

* $U_{eq} = \frac{1}{3}\sum_i\sum_j a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

Chun, 1987). We report in this paper the first crystal structure of a ring-opened thiol derivative of thiamin, *O,S*-dibenzoylthiamin (DBT).

Experimental. Colorless tabular crystals obtained from an ethanol solution of DBT (Tokyo Kasei) by slow evaporation at room temperature; crystal *ca* 0·2 × 0·3 × 0·5 mm, Rigaku AFC diffractometer, graphite-monochromated Cu $K\alpha$ radiation, $2\theta < 120°$, ω–2θ scan, scan speed 2° min^{-1} in 2θ, ω-scan width $(1{\cdot}2 + 0{\cdot}4\tan\theta)°$, background measured for 12 s on either side of the peak; cell parameters by least-squares fit to observed 2θ values for 24 centred reflections with $25 < 2\theta < 45°$; intensity checks for three standard reflections showed little (±1·2%) variation; 2889 independent reflections (h −8 to 8, k −14 to 14, l 0 to 12), 2368 (82·0%) observed with $I > 3\sigma(I)$ and used in refinement; Lp corrections, no absorption or extinction correction. Structure solved by direct methods and refined by full-matrix least squares on F with anisotropic thermal parameters using *SHELX*76 (Sheldrick, 1976); H atoms identified on a difference map and refined isotropically. $\sum w(|F_o| - |F_c|)^2$ minimized, with $w = k/[\sigma^2(F_o) + gF_o^2]$, $\sigma(F)$ from counting statistics, k and g optimized in the least-squares procedure (k = 1·00, g = 0·0109); wR = 0·0674 for 2368 observed reflections, 420 variables, R = 0·058 for all data, S = 0·914, $(\Delta/\sigma)_{max}$ = 0·404 (y coordinate of H) in final refinement cycle; max. and min. heights in final difference map 0·26 and −0·29 e $Å^{-3}$, respectively. All calculations performed with *SHELX*76 on a VAX 11/780. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Final atomic parameters are in Table 1.* A view of the DBT molecule with atomic numbering scheme is shown in Fig. 1. Bond lengths and angles are listed in Table 2.

The present structure is the most accurately determined of those of the ring-opened derivatives of thiamin studied thus far. It has been suggested from the structural studies of the various thiamin analogues that there is no long-range structural effect between the pyrimidine and thiazolium rings (Shin & Kim, 1986*b*). This notion is supported by the present study in which all of the bond lengths and angles of the unprotonated pyrimidine ring agree within 4σ with those of native thiamin (Cramer, Maynard & Ibers, 1981) without any significant trends. The other molecular dimensions agree within 2σ with those of the related compounds such as TTFD, TPD, TDD and *N*-(*p*-bromophenylcarbamoyl)thiamin anhydrides (Nakai & Koyama, 1971, 1972).

There are many planar groups in the DBT molecule. The C(4)=C(5) ethylenic double bond and the four atoms attached to it are planar with a maximum deviation of 0·068 (4) Å. The five atoms around N(3) including the formyl group are also planar with a maximum deviation of 0·053 (4) Å. N(3) is only 0·014 (3) Å from the plane formed by C(2), C(4) and C(35') and the sum of the valence angles around N(3) is 360·0°. These are indicative of near-sp^2 hybridization

* Lists of structure factors, anisotropic thermal parameters, coordinates of H atoms, bond distances and angles involving the H atoms and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44869 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

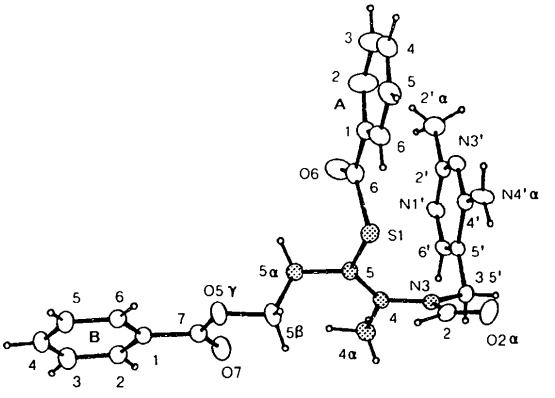

Fig. 1. An *ORTEP* (Johnson, 1976) view and atomic numbering scheme for *O,S*-dibenzoylthiamin. Atoms with dots are those in the ethylenic plane.

Table 2. *Bond lengths* (Å) *and angles* (°) *of DBT*

N(1′)–C(2′)	1·338 (5)	N(1′)–C(6′)	1·332 (5)
C(2′)–N(3′)	1·322 (5)	C(2′)–C(2′α)	1·489 (7)
N(3′)–C(4′)	1·330 (5)	C(4′)–C(5′)	1·427 (5)
C(4′)–N(4′α)	1·333 (6)	C(5′)–C(6′)	1·359 (5)
C(5′)–C(35′)	1·489 (5)	C(35′)–N(3)	1·467 (5)
S(1)–C(5)	1·779 (4)	S(1)–C(6)	1·784 (4)
C(2)–N(3)	1·356 (5)	C(2)–O(2α)	1·212 (5)
N(3)–C(4)	1·424 (4)	C(4)–C(5)	1·330 (5)
C(4)–C(4α)	1·498 (6)	C(5)–C(5α)	1·524 (6)
C(5α)–C(5β)	1·506 (6)	C(5β)–O(5γ)	1·448 (5)
O(5γ)–C(7)	1·326 (5)	C(6)–O(6)	1·203 (5)
C(6)–C(*A*1)	1·489 (6)	C(7)–O(7)	1·200 (5)
C(7)–C(*B*1)	1·484 (5)		
C(*A*1)–C(*A*2)	1·357 (7)	C(*A*1)–C(*A*6)	1·393 (8)
C(*A*2)–C(*A*3)	1·373 (8)	C(*A*3)–C(*A*4)	1·353 (9)
C(*A*4)–C(*A*5)	1·329 (10)	C(*A*5)–C(*A*6)	1·363 (10)
C(*B*1)–C(*B*2)	1·380 (6)	C(*B*1)–C(*B*6)	1·372 (6)
C(*B*2)–C(*B*3)	1·393 (7)	C(*B*3)–C(*B*4)	1·365 (7)
C(*B*4)–C(*B*5)	1·364 (6)	C(*B*5)–C(*B*6)	1·400 (6)
N(3′)–C(2′)–N(1′)	126·1 (3)	C(4′)–N(3′)–C(2′)	118·6 (3)
C(5′)–C(4′)–N(3′)	120·2 (3)	C(5′)–C(6′)–N(1′)	125·8 (3)
C(6′)–N(1′)–C(2′)	114·3 (3)	C(6′)–C(5′)–C(4′)	114·9 (3)
C(2′α)–C(2′)–N(1′)	116·6 (4)	C(2′α)–C(2′)–N(3′)	117·3 (4)
N(4′α)–C(4′)–N(3′)	118·2 (4)	N(4′α)–C(4′)–C(5′)	121·5 (4)
C(35′)–C(5′)–C(4′)	122·4 (3)	C(35′)–C(5′)–C(6′)	122·6 (3)
C(2)–N(3)–C(35′)	120·1 (3)	N(3)–C(35′)–C(5′)	113·4 (3)
C(4)–N(3)–C(35′)	119·6 (3)	C(4)–N(3)–C(2)	120·3 (3)
C(4)–C(5)–S(1)	121·3 (3)	C(5)–C(4)–N(3)	121·7 (3)
O(2α)–C(2)–N(3)	125·4 (4)	C(4α)–C(4)–N(3)	114·9 (3)
C(4α)–C(4)–C(5)	123·4 (3)	C(5α)–C(5)–S(1)	115·0 (3)
C(5α)–C(5)–C(4)	123·3 (3)	C(5β)–C(5α)–C(5)	108·9 (3)
O(5γ)–C(5β)–C(5α)	111·1 (3)	C(6)–S(1)–C(5)	100·2 (2)
O(6)–C(6)–S(1)	121·9 (3)	C(*A*1)–C(6)–S(1)	114·1 (3)
C(*A*1)–C(6)–O(6)	123·9 (4)	C(*A*2)–C(*A*1)–C(6)	123·5 (4)
C(*A*6)–C(*A*1)–C(6)	118·5 (4)	C(7)–O(5γ)–C(5β)	117·1 (3)
O(7)–C(7)–O(5γ)	123·0 (4)	C(*B*1)–C(7)–O(5γ)	112·5 (3)
C(*B*1)–C(7)–O(7)	124·4 (4)	C(*B*2)–C(*B*1)–C(7)	118·5 (4)
C(*B*6)–C(*B*1)–C(7)	121·5 (4)		
C(*A*3)–C(*A*2)–C(*A*1)	120·2 (5)	C(*A*4)–C(*A*3)–C(*A*2)	120·3 (6)
C(*A*5)–C(*A*4)–C(*A*3)	120·7 (6)	C(*A*5)–C(*A*6)–C(*A*1)	120·7 (6)
C(*A*6)–C(*A*5)–C(*A*4)	120·1 (7)	C(*A*6)–C(*A*1)–C(*A*2)	118·0 (4)
C(*B*3)–C(*B*2)–C(*B*1)	120·1 (4)	C(*B*4)–C(*B*3)–C(*B*2)	119·6 (5)
C(*B*5)–C(*B*4)–C(*B*3)	120·7 (4)	C(*B*5)–C(*B*6)–C(*B*1)	119·4 (4)
C(*B*6)–C(*B*5)–C(*B*4)	120·2 (4)	C(*B*6)–C(*B*1)–C(*B*2)	120·0 (4)

of N(3). The bond lengths around N(3) indicate that the lone-pair electrons of N(3) are delocalized mainly through the C(2)–N(3) [1·356 (5) Å] bond for conjugation with the formyl group, but only slightly through the N(3)–C(35′) [1·467 (5) Å] and N(3)–C(4) [1·424 (4) Å] bonds. The pyrimidine ring is planar with a maximum deviation of 0·010 (3) Å. The planarities of the phenyl rings are good with maximum deviations of 0·008 (7) and 0·008 (4) Å for rings *A* and *B*, respectively. The thiocarbonyl group is rotated by 9·5° with respect to ring *A*, while the ester group is nearly coplanar (dihedral angle 1·9°) with ring *B*.

The most important feature commonly observed in the conformations of the three disulfide derivatives is the nearly perpendicular arrangement of the *N*-formyl and ethylenic planes. The dihedral angles between the two planes are 117·0, 111·2 and 97·6° for TPD, TTFD and TDD, respectively. It has been suggested that the marked reactivity of the ring-opened disulfide derivatives of thiamin toward the formation of the thiazolium ring results from the preserved capability of easy rotation about the N(3)–C(4) single bond (Nishikawa, Kamiya, Asahi & Matsumura, 1969; Shin & Kim, 1986*a*). The N(3)–C(4) bond remains an easily rotatable single bond since the interaction between the lone-pair electrons of N(3) and the ethylenic π orbital is practically forbidden owing to the perpendicular arrangement of the two planar groups. This structural feature is more or less maintained in the thiol derivative DBT which shows a dihedral angle of 127·6°.

Another characteristic feature in the disulfide derivatives is the formation of an intramolecular N(4′α)–H···O(2α) hydrogen bond. Owing to this hydrogen bond, the pyrimidine ring becomes nearly perpendicular to both planar groups. However, there is no hydrogen-bonding interaction in DBT, although the mutually perpendicular arrangement between the three planar groups is maintained [N(4′α)···O(2α) = 3·539 (5), N(4′α)–H = 0·91 (4), H···O(2α) = 2·65 (4) Å, ∠N–H···O = 165 (4)°]. The absence of the hydrogen bond seems to be the result of the particular packing of DBT as discussed below.

Besides these conformational characteristics, the conformations of the substituents at S(1) and O(5γ) vary widely among the derivatives depending on the crystal packing. This can be seen in the comparison of selected torsion angles listed in Table 3.

Crystal packing is shown in Fig. 2. There is only one unique hydrogen bond in the crystal lattice [N(4′α)···N(3′)($-x$, $1-y$, $1-z$) = 2·999 (5), N(4′α)–H = 0·89 (4), H···N(3′) = 2·11 (4) Å, ∠N–H···N = 173 (4)°]. This hydrogen bond produces a molecular dimer around a centre of symmetry at $(0,\frac{1}{2},\frac{1}{2})$, forming a

Table 3. *Comparison of selected torsion angles* (°) *in related compounds*

	DBT	TTFD	TPD	TDD
C(4′)–C(5′)–C(35′)–N(3)	68·4 (4)	81·2	81·2	78·3
C(5′)–C(35′)–N(3)–C(4)	53·9 (3)	80·0	74·2	74·9
C(35′)–N(3)–C(4)–C(5)	−127·3 (4)	−113·0	−117·6	−96·9
N(3)–C(4)–C(5)–S(1)	−0·9 (2)	0·7	−1·4	2·1
C(4)–C(5)–S(1)–C(6)*	119·1 (3)	164·4	148·0	−122·6
C(5)–S(1)–C(6)*–C(*A*1)*	178·0 (3)	−72·5	−80·3	87·4
C(4)–C(5)–C(5α)–C(5β)	80·6 (4)	91·4	107·1	−94·2
C(5)–C(5α)–C(5β)–O(5γ)	171·7 (4)	175·2	−67·0	66·4

* C(6) and C(*A*1) in DBT correspond to S and C, respectively, in disulfide compounds.

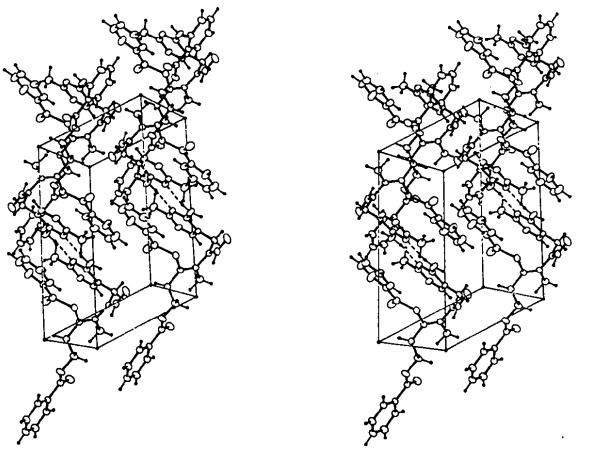

Fig. 2. Stereoscopic *ORTEP* (Johnson, 1976) packing drawing of *O,S*-dibenzoylthiamin. The dotted lines denote the hydrogen bonds. Origin lower left, *a* axis horizontal, *b* axis vertical.

pyrimidine base pair. This kind of base pairing is frequently observed in the crystal structures of thiamin and its derivatives (Shin & Lah, 1987). Two *S*-benzoyl groups intercalate between these planar base pairs. The dihedral angle between the pyrimidine and *S*-benzoyl planes is 1·9°. These groups form a continuous planar stack approximately parallel to the $(23\bar{1})$ plane. However, there is no strong stacking interaction; the average separation is *ca* 3·7 Å. This particular arrangement of the ring systems seems to prevent the formation of an intramolecular N—H···O hydrogen bond. There are no unusually short contacts in the structure. The packing mode of DBT is quite different from those of disulfide derivatives in which there are rather complicated hydrogen-bonding schemes. Therefore, the essential feature of the conformational property of the ring-opened derivatives of thiamin seems to be determined by the short-range intramolecular interactions.

We thank the Korea Science and Engineering Foundation for their support of this research.

References

CRAMER, R. E., MAYNARD, R. B. & IBERS, J. A. (1981). *J. Am. Chem. Soc.* **103**, 76–81.

DWIDEVI, B. K. & ARNOLD, R. G. (1973). *J. Agric. Food Chem.* **21**, 54–60.

HOPMANN, R. F. W. (1982). *Ann. NY Acad. Sci.* **378**, 32–50.

International Tables for X-ray Crystallography (1974). Vol. IV, p. 99. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

JOHNSON, C. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

NAKAI, N. & KOYAMA, H. (1971). *J. Chem. Soc. B*, **71**, 1525–1529.

NAKAI, N. & KOYAMA, H. (1972). *J. Chem. Soc. Perkin Trans.* 2, **3**, 248–252.

NISHIKAWA, M., KAMIYA, K., ASAHI, Y. & MATSUMURA, H. (1969). *Chem. Pharm. Bull.* **17**, 932–938.

SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

SHIN, W. & CHUN, K. S. (1987). *Acta Cryst.* C**43**, 2123–2125.

SHIN, W. & KIM, Y. C. (1986*a*). *Bull. Korean Chem. Soc.* **7**, 331–334.

SHIN, W. & KIM, Y. C. (1986*b*). *J. Am. Chem. Soc.* **108**, 7078–7082.

SHIN, W. & LAH, M. S. (1987). *Acta Cryst.* C**43**, 125–129.

Acta Cryst. (1988). C**44**, 1757–1759

Structure of Octamethylbiphenylene

BY J. BOWEN JONES, D. S. BROWN, K. A. HALES AND A. G. MASSEY

*Department of Chemistry, Loughborough University of Technology, Loughborough LE*11 3*TU, England*

(*Received* 25 *June* 1987; *accepted* 25 *May* 1988)

Abstract. $C_{20}H_{24}$, $M_r = 264{\cdot}412$, monoclinic, $P2_1/a$, $a = 17{\cdot}865\ (2)$, $b = 5{\cdot}40\ (1)$, $c = 7{\cdot}917\ (2)$ Å, $\beta = 91{\cdot}75\ (1)°$, $V = 763{\cdot}40$ Å^3, $Z = 2$, $D_m = 1{\cdot}129$, $D_x = 1{\cdot}151$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}32$ cm^{-1}, $F(000) = 288$, $T = 293$ K, final $R = 0{\cdot}061$ for 773 observed reflections with $I > 3\sigma(I)$. The molecule is centrosymmetric with a dihedral angle of 0·3 (2)° between the C_4 and C_6 rings. The methyl C atoms are displaced by no more than 0·045 (3) Å from the least-squares ring-plane to which they are attached. The molecule shows similar bond fixation in the benzenoid rings to that noted previously in biphenylene and octafluorobiphenylene.

Introduction. We recently described the structure of octafluorobiphenylene and compared it with that of biphenylene (Bowen Jones, Brown, Massey & Slater, 1986). Since subtle variations occurred in some of the bond lengths and angles of the two molecules, we decided to study octamethylbiphenylene since the substituent methyl groups are both relatively electron-releasing and sterically more demanding than either F or H atoms.

Experimental. Preparation by the method of Hart & Teuerstein (1979); D_m measured by flotation in an aqueous solution of sodium bromide; colourless, rectangular block-shaped crystals obtained from acetone; crystal, 0·58 × 0·31 × 0·06 mm, sealed in a Lindemann-glass capillary, mounted about **b**; preliminary lattice constants determined from oscillation and Weissenberg photographs; refined lattice constants from a Stoe Stadi-2 two-circle diffractometer using axial-row reflections (θ range 5–22°); no correction for absorption or extinction; $2\theta_{max} = 60°$; index range: $0 \le h \le 24$; $0 \le k \le 6$; $-10 \le l \le 10$; one standard reflection every 50 reflections, no significant change; 2252 reflections measured, 2188 being unique and 773 having $I > 3\sigma(I)$; C atoms located by direct methods and H atoms from successive ΔF syntheses; anisotropic refinement of C and isotropic refinement of H by full-matrix least squares on F with unit weights gave final $R = 0{\cdot}061$; $\Delta/\sigma < 0{\cdot}1$; $\Delta\rho$ excursions = +0·08 to −0·09 e Å^{-3}; scattering factors from Cromer & Mann (1968); calculations carried out with *SHELX*76 (Sheldrick, 1976) implemented at Loughborough University of Technology Computer Centre, and with *XRAY*72

0108-2701/88/101757-03$03.00