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 $1{\cdot}9^\circ$. 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* $3{\cdot}7$ 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.

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

Structure of Octamethylbiphenylene

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(*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, $\beta = 91{\cdot}75\,(1)^\circ$, $V = 763{\cdot}40$ Å^3, $Z = 2$, $D_m = 1{\cdot}129$, $D_x = 1{\cdot}151$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ 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 $0{\cdot}3\,(2)^\circ$ between the C_4 and C_6 rings. The methyl C atoms are displaced by no more than $0{\cdot}045\,(3)$ 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, $0{\cdot}58 \times 0{\cdot}31 \times 0{\cdot}06$ 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; $2\theta_{\max} = 60^\circ$; 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 $= +0{\cdot}08$ to $-0{\cdot}09$ 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

Table 1. *Atomic coordinates* ($\times 10^4$, H $\times 10^3$) *and isotropic thermal parameters* (Å^2)

$B_{eq} = \frac{1}{3}\sum_i B_{ii}$.

	x	y	z	B_{eq}	B_{iso}
C(1)	5419 (2)	11342 (7)	5134 (5)	3·0 (2)	
C(2)	5238 (2)	9578 (7)	3859 (5)	2·9 (2)	
C(3)	5645 (2)	9329 (7)	2428 (5)	3·2 (2)	
C(4)	6266 (2)	11003 (8)	2303 (5)	3·4 (2)	
C(5)	6435 (2)	12725 (8)	3564 (5)	3·3 (2)	
C(6)	6004 (2)	12937 (7)	5058 (5)	3·2 (2)	
C(7)	5454 (3)	7386 (10)	1121 (6)	4·3 (2)	
C(8)	6727 (4)	10836 (13)	732 (7)	5·2 (3)	
C(9)	7090 (3)	14482 (11)	3395 (8)	4·6 (3)	
C(10)	6194 (4)	14801 (11)	6415 (8)	4·6 (3)	
H(1)	585 (3)	636 (1)	87 (6)		7·4 (15)
H(2)	539 (3)	805 (10)	2 (7)		6·6 (14)
H(3)	494 (4)	650 (14)	129 (8)		11·3 (21)
H(4)	679 (4)	1237 (15)	14 (9)		11·3 (23)
H(5)	724 (4)	1053 (13)	98 (8)		10·8 (22)
H(6)	646 (4)	1002 (13)	−12 (9)		10·8 (24)
H(7)	691 (3)	1616 (12)	338 (7)		9·0 (18)
H(8)	745 (3)	1454 (10)	438 (7)		7·7 (16)
H(9)	738 (4)	1421 (13)	249 (8)		9·5 (20)
H(10)	592 (4)	1459 (12)	728 (8)		8·9 (20)
H(11)	671 (3)	1456 (11)	696 (6)		7·3 (15)
H(12)	623 (3)	1641 (11)	599 (6)		6·6 (14)

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

C(1)—C(2)	1·418 (5)	C(7)—H(1)	0·93 (6)
C(1)—C(2′)	1·522 (8)	C(7)—H(2)	0·94 (5)
C(2)—C(1′)	1·522 (8)	C(7)—H(3)	1·04 (8)
C(2)—C(3)	1·372 (5)	C(8)—H(4)	0·96 (8)
C(3)—C(4)	1·436 (5)	C(8)—H(5)	0·95 (7)
C(3)—C(7)	1·506 (6)	C(8)—H(6)	0·93 (7)
C(4)—C(5)	1·391 (6)	C(9)—H(7)	0·96 (7)
C(4)—C(8)	1·516 (6)	C(9)—H(8)	1·00 (5)
C(5)—C(6)	1·435 (5)	C(9)—H(9)	0·91 (7)
C(5)—C(9)	1·515 (9)	C(10)—H(10)	0·86 (7)
C(6)—C(1)	1·357 (5)	C(10)—H(11)	1·01 (5)
C(6)—C(10)	1·504 (6)	C(10)—H(12)	0·94 (6)

C(2)—C(1)—C(2′)	89·5 (3)	C(3)—C(4)—C(5)	121·5 (3)
C(2)—C(1)—C(6)	123·6 (4)	C(3)—C(4)—C(8)	117·4 (4)
C(2′)—C(1)—C(6)	146·9 (4)	C(5)—C(4)—C(8)	121·1 (4)
C(1)—C(2)—C(1′)	90·5 (3)	C(4)—C(5)—C(6)	122·3 (4)
C(1)—C(2)—C(3)	122·6 (4)	C(4)—C(5)—C(9)	120·4 (4)
C(1′)—C(2)—C(3)	146·9 (4)	C(6)—C(5)—C(9)	117·3 (4)
C(2)—C(3)—C(4)	115·2 (3)	C(1)—C(6)—C(5)	114·8 (4)
C(2)—C(3)—C(7)	121·4 (4)	C(1)—C(6)—C(10)	123·4 (4)
C(4)—C(3)—C(7)	123·4 (4)	C(5)—C(6)—C(10)	121·8 (4)

(Stewart, Kruger, Ammon, Dickinson & Hall, 1972) implemented at the University of Manchester Regional Computer Centre.*

Discussion. Final positional parameters are listed in Table 1, and bond lengths and angles in Table 2. The molecular structure, with atom numbering, is given in Fig. 1 and the **b**-projection of the cell contents is shown in Fig. 2. 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 skeletal dimensions of octamethylbiphenylene are very similar to those of biphenylene and again show the pronounced alternation in bond lengths round the two benzenoid rings.

When octafluorobiphenylene is compared with biphenylene and octamethylbiphenylene it is immediately obvious that the C—C bond lengths in $C_{12}F_8$, other than those in the C_4 ring, are short (*Molecular Structure by Diffraction Methods* 1, 1973; Meresse, Courseille & Nguyen Ba Chanh, 1974; Pappas, 1974). The inductive effect would be expected to reduce the π-electron density and so lengthen the C—C bonds. A possible explanation is that the positive charge on the C atoms bonded to F causes contraction of the sp^2-hybrid orbitals used in C—C bond formation, allowing better overlap. Significantly, the *a* bond (Fig. 1) is 1·417 (9) Å in $C_{12}F_8$, virtually equal to the 1·418 (5) Å in $C_{12}Me_8$; the C atoms comprising this bond carry no F atoms. The $2p_z$ orbitals of F have the same symmetry as the π^* anti-bonding orbitals of the benzenoid ring and interaction between them will *increase* the C—C bond lengths in $C_{12}F_8$; however, the large difference in energy between the two sets of orbitals will result in only a weak interaction and hence a very small effect on the C—C bond lengths.

The bond fixation noted in all three biphenylenes suggests a significant cyclobutane-like contribution to the electronic structure of the C_{12} skeleton. Molecular-orbital calculations (Ali & Coulson, 1960; Dewar & Gleicher, 1965; Randić & Maksić, 1971) support this assumption but the bond lengths calculated for *d* (Fig. 1) from the π bond orders are too long. This

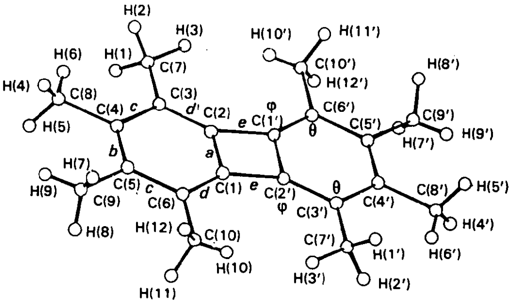

Fig. 1. *ORTEP* plot (Johnson, 1965) of the title compound, with atom labelling.

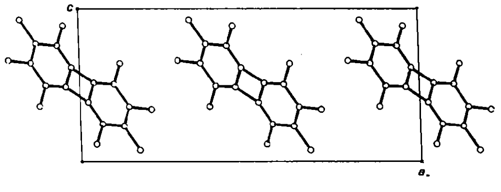

Fig. 2. Unit-cell contents projected down the *b* axis (H atoms omitted).

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* Lists of structure factors, anisotropic thermal parameters and bond angles at methyl C atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51059 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

discrepancy could arise because the π interaction in the d bonds is actually stronger than calculated, although the agreement for b in $C_{12}H_8$ and $C_{12}Me_8$ is excellent. Alternatively (Randić & Maksić, 1971), the 'shortness' of the d bonds could be due to the unusual hybridization of the C orbitals in the central four-membered ring. The rectangular shape of the central ring demands that the σ orbitals in the C_4 ring have a high p character consequently leading to an abnormally high s character in the d bonds; this would necessarily lead to some shortening of these bonds but would leave b unaffected, as found. The molecular-orbital calculations suggest a π contribution to the e bonds but in all three biphenylenes these bonds are longer than calculated. Although the high p character in e will lead to some increase in e relative to normal (*i.e.* sp^2-hybridized) C—C bond lengths, the very considerable difference between the calculated and observed values of e (*ca* 0·055–0·060 Å) makes one question the presence of any significant π interaction across the bridge bonds between the benzenoid rings. Other workers have suggested previously that conjugation across the C_4 ring in octafluorobiphenylene is best ignored.

As in $C_{12}H_8$ and $C_{12}F_8$, a notable feature in the structure of octamethylbiphenylene is the extremely small value [mean 115·0 (4)°] of the θ angles (Fig. 1); again this is no doubt due to the presence of the rectangular C_4 ring strongly dictating the values of the θ and φ angles. Methyl groups in adjacent positions in a benzenoid ring have their H atoms as far apart as possible when eclipsed, unlike the situation in sp^3-hybridized-C systems. Although the methyls on C(5) and C(6) are eclipsed (Fig. 1), surprisingly all the others are staggered. Steric interaction in this less favourable staggered conformation is reduced in the molecule by angles C(4)—C(3)—C(7), C(5)—C(4)—C(8) and C(4)—C(5)—C(9) all having values greater than 120°. The steric strain between the staggered methyls on C(3) and C(4) is further reduced by a comparatively long bond [1·436 (5) Å] between these two C atoms. The value of 121·4 (4)° for angle C(2)—C(3)—C(7) relative to 123·4 (4)° for angle C(1)—C(6)—C(10) [*cf.* average value of 124·7 (4)° for these angles in perfluorobiphenylene] may again reflect the larger steric strain between staggered, rather than eclipsed, methyl groups.

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Acta Cryst. (1988). C**44**, 1759–1762

Structural and Electronic Analysis of 7-Phenyltriazolo[4,3-*b*]pyridazine, a Benzodiazepine Receptor Ligand

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(*Received* 4 *December* 1987; *accepted* 23 *May* 1988)

Abstract. $C_{11}H_8N_4$, $M_r = 196·2$, monoclinic, $P2_1/c$, $a = 20·048$ (2), $b = 7·295$ (2), $c = 13·524$ (2) Å, $\beta = 107·42$ (4)°, $V = 1887·2$ Å^3, $Z = 8$, $D_x = 1·38$ g cm^{-3}, Cu $K\bar{\alpha}$, $\lambda = 1·54178$ Å, $\mu = 6·28$ cm^{-1}, $F(000) = 816$, $T = 293$ K, final $R = 0·046$ for 3003 observed reflections [$I \geq 2·5\sigma(I)$]. The electronic structure determined by non-empirical calculations is compared with those of pyridazine and aminopyridazine. Fusion of triazole with a pyridazine ring decreases the aromaticity of the latter.

Introduction. We report here the X-ray crystal structure of a substituted triazolopyridazine. This work is part of a structure–activity-relationship study on

0108-2701/88/101759-04$03.00