

- MATA, F., MARTIN, M. C. & SØRENSEN, G. O. (1978). *J. Mol. Struct.* **48**, 157–163.
- MELHUS, I. E. (1935). US Patent No. 2007433.
- MEUNIER, B. & PASCARD, C. (1980). *Cryst. Struct. Commun.* **9**, 121–128.
- RAVICHANDRAN, V. & CHACKO, K. K. (1985). *Acta Cryst.* **C41**, 1470–1473.
- SARKAR, P. B. & SEN GUPTA, S. P. (1980). *Cryst. Struct. Commun.* **9**, 925–932.
- SIKIRICA, M., GRDENIĆ, D. & CIMAŠ, Š. (1982). *Acta Cryst.* **B38**, 926–927.
- SRINIVASAN, R. & CHANDRASEKHARAN, R. (1986). *Acta Cryst.* **B24**, 1698–1700.
- STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. L., HECK, H. & FLACK, H. (1976). The *XRAY76* system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- TAYLOR, R. & KENNARD, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.
- TAYLOR, R., KENNARD, O. & VERSICHEL, W. (1983). *J. Am. Chem. Soc.* **105**, 5761–5766.
- TAYLOR, R., KENNARD, O. & VERSICHEL, W. (1984). *Acta Cryst.* **B40**, 280–288.
- VLAHOV, A. (1976). *Synthesis of Some N-Hydroxyalkyl- and N-Chloroalkylamides Derived from Thiobenzoic and 2-Furanthiocarboxylic Acids*. MSc Thesis, Univ. of Zagreb.
- VLAHOV, A. (1982). *The Effect of Newly Synthesized Derivatives of 2-Furancarboxylic Acid on Functional Capacity of Lymphohematopoietic Cells*. PhD Thesis, Univ. of Zagreb.
- VLAHOV, A. & VOLF, D. (1983). *Topics in Furan Chemistry*. Proc. Fourth Symp. Furan Chem., edited by J. KOVAC, pp. 237–239. Bratislava.

*Acta Cryst.* (1987). **C43**, 482–484

## Structure of 2,2',4,4',5,5'-Hexamethoxybiphenyl

BY D. CHATTOPADHYAY, T. BANERJEE AND S. K. MAJUMDAR

*Crystallography and Molecular Biology Division, Saha Institute of Nuclear Physics, Sector I, Block 'AF', Bidhannagar, Calcutta-700 064, India*

G. PODDER

*Department of Chemistry, School of Tropical Medicine, Calcutta, India*

AND S. KASHINO AND M. HAISA

*Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama 700, Japan*

(Received 25 June 1986; accepted 15 September 1986)

**Abstract.** C<sub>18</sub>H<sub>22</sub>O<sub>6</sub>, *M<sub>r</sub>* = 334.4, monoclinic, *C2/c*, *a* = 24.801 (3), *b* = 5.3654 (5), *c* = 15.428 (2) Å, β = 126.18 (1)°, *V* = 1657.1 (4) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.340, *D<sub>m</sub>* = 1.320 Mg m<sup>-3</sup>, λ(Cu *Kα*) = 1.5418 Å, μ(Cu *Kα*) = 0.79 mm<sup>-1</sup>, *F*(000) = 712, *T* = 293 K, *R* = 0.053 for 1168 observed reflections. The crystallographic diad coincides with the molecular diad with an inter-ring twist angle of 81.2 (1)°. The methoxy groups are coplanar with the phenyl ring and the crystal structure is stabilized by van der Waals interactions.

**Introduction.** Structure analyses of the biphenyl molecule in different states have revealed that interesting conformational changes in the molecule take place on crystallization. The inter-ring twist angle is 42° in the gas phase (Bastiansen & Trætteberg, 1962) whereas X-ray diffraction analysis (Trotter, 1961; Hargreaves & Rizvi, 1962; Charbonneau & Delugeard, 1976, 1977) has shown the molecule to be planar. We are interested in studying the molecular geometry and packing arrangements of substituted biphenyls. The

present work reports the crystal structure analysis of 2,2',4,4',5,5'-hexamethoxybiphenyl.

**Experimental.** Crystals from ethanol by slow evaporation; density measured by flotation in benzene–bromofrom mixture, crystal size 0.28 × 0.38 × 0.15 mm; intensity data collected on rotating-anode Rigaku AFC-5 four-circle diffractometer at 40 kV, 200 mA with Ni-filtered Cu *Kα* radiation; lattice parameters refined by the least-squares fit of the setting angles of 19 reflections in the range 17 < 2θ < 34°; 1324 independent reflections collected with 2θ<sub>max</sub> = 125.0° (*h* = -28→28, *k* = 0→6, *l* = 0→17); scan speed 4° min<sup>-1</sup> in ω, scan range (1.2° + 0.15° tanθ), background measured for 4 s on either side of the peak; three standard reflections (600, 111, 112) recorded after every 57 reflections to ensure stability of the crystal quality and position; variation in *I<sub>o</sub>* within 0.8%; data corrected for *L<sub>p</sub>* but not for absorption; intensity statistics and successful refinement confirmed space group *C2/c*, structure solved by direct methods (*MULTAN78*;

Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) with 148  $E$  values having  $E_{\min} = 1.507$ ; full-matrix least-squares refinement including all the non-hydrogen atoms with anisotropic thermal parameters and all the hydrogen atoms, located from  $\Delta F$  syntheses, with isotropic thermal parameters based on  $F_o$  with 1168 observed reflections [ $I \geq 2.5\sigma(I)$ ] (*SHELX76*; Sheldrick, 1976);  $R = 0.053$ ,  $wR = 0.071$ ,  $S = 1.96$ ,  $w = 1/[\sigma^2(|F_o|) + 0.01621|F_o|^2]$ ; residual  $\Delta\rho$  excursions  $-0.20$  to  $+0.26 \text{ e \AA}^{-3}$  in final  $\Delta F$  synthesis; average and maximum  $\Delta/\sigma$  in final refinement 0.2 and 0.6 respectively. Atomic scattering factors included in *SHELX76*.

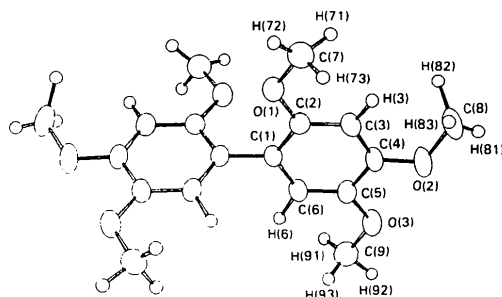


Fig. 1. View of the molecule with numbering of atoms.

Table 1. Fractional coordinates of the atoms and their isotropic temperature factors ( $\text{\AA}^2$ ) with *e.s.d.*'s in parentheses

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$
O(1)	0.0729 (1)	-0.5455 (3)	-0.2426 (1)	0.04
O(2)	0.2055 (1)	-0.1959 (3)	0.1183 (1)	0.06
O(3)	0.1119 (1)	0.1243 (3)	0.0626 (1)	0.05
C(1)	0.0318 (1)	-0.2193 (3)	-0.1952 (1)	0.03
C(2)	0.0835 (1)	-0.3828 (3)	-0.1648 (1)	0.03
C(3)	0.1422 (1)	-0.3781 (4)	-0.0613 (1)	0.04
C(4)	0.1505 (1)	-0.2089 (4)	0.0138 (2)	0.04
C(5)	0.0999 (1)	-0.0373 (3)	-0.0159 (1)	0.04
C(6)	0.0420 (1)	-0.0445 (3)	-0.1194 (1)	0.03
C(7)	0.1261 (1)	-0.7057 (4)	-0.2151 (2)	0.05
C(8)	0.2531 (1)	-0.3902 (6)	0.1574 (2)	0.06
C(9)	0.0610 (1)	0.3002 (4)	0.0342 (2)	0.05

Table 2. Bond distances ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) with *e.s.d.*'s in parentheses

C(1)—C(6)	1.401 (2)	C(2)—O(1)—C(7)	117.4 (1)
C(1)—C(2)	1.387 (3)	C(4)—O(2)—C(8)	117.8 (2)
C(2)—C(3)	1.387 (2)	C(5)—O(3)—C(9)	117.2 (1)
C(3)—C(4)	1.389 (3)	C(2)—C(1)—C(6)	117.8 (1)
C(4)—C(5)	1.397 (3)	O(1)—C(2)—C(1)	116.3 (1)
C(5)—C(6)	1.380 (2)	C(1)—C(2)—C(3)	120.7 (1)
C(2)—O(1)	1.378 (2)	O(1)—C(2)—C(3)	123.0 (2)
C(7)—O(1)	1.414 (3)	C(2)—C(3)—C(4)	120.7 (2)
C(4)—O(2)	1.365 (2)	O(2)—C(4)—C(3)	124.8 (2)
C(8)—O(2)	1.415 (3)	C(3)—C(4)—C(5)	119.6 (2)
C(5)—O(3)	1.372 (2)	O(2)—C(4)—C(5)	115.6 (2)
C(9)—O(3)	1.422 (3)	O(3)—C(5)—C(4)	116.2 (1)
C(1)—C(1')	1.483 (2)	C(4)—C(5)—C(6)	118.7 (2)
		O(3)—C(5)—C(6)	125.0 (2)
		C(1)—C(6)—C(5)	122.4 (2)
		C(2)—C(1)—C(1')	122.3 (1)
		C(6)—C(1)—C(1')	119.9 (2)

**Discussion.** The molecular conformation and the atomic labelling scheme are shown in Fig. 1 (*ORTEP* plot; Johnson, 1965). Symmetry-related atoms have been indicated by primes. The atomic parameters have been listed in Table 1.\* The molecular dimensions are given in Table 2.

An interesting feature of the crystal structure is the retention of the molecular diad symmetry in the crystal. The length of the bond C(1)—C(1') joining the two rings of the molecule is close to that in *2H*-nonafluorobiphenyl (Hamor & Hamor, 1978) and 4,4'-dichlorobiphenyl (Brock, Kuo Mei-Shiow & Levy, 1978) and slightly shorter than that in unsubstituted biphenyl (Trotter, 1961) and 2,3,5,6-tetrafluorobiphenyl (Goodhand & Hamor, 1978). The narrowing of the endocyclic angle at C(1) from the  $sp^2$  value indicates inter-ring conjugation to be small (Domenicano, Vaciago & Coulson, 1975).

The twist angle of  $81.1 (1)^\circ$  about the central bond between the two phenyl rings is large compared with those in other substituted biphenyls:  $59.6^\circ$  in *2H*-nonafluorobiphenyl (Hamor & Hamor, 1978),  $42^\circ$  in 4,4'-dichlorobiphenyl (Brock *et al.*, 1978),  $57.9^\circ$  in 2,3,5,6-tetrafluorobiphenyl (Goodhand & Hamor, 1978). In biphenyl this twist angle is  $0^\circ$  in the crystalline phase (Trotter, 1961; Hargreaves & Rizvi, 1962). The increased twist angle in the present structure minimizes the  $\text{OCH}_3 \cdots \text{OCH}_3$  interactions. The angular asymmetry observed in the exocyclic angles at C(1) results from the short contact between C(1) and O(1') [ $2.790 (3) \text{\AA}$ ].

The methoxy groups at C(2), C(4) and C(5) have coplanar arrangements with the phenyl ring,  $\text{C}(9)\text{—O}(3)\text{—C}(5)\text{—C}(6) = 1.0 (3)$ ,  $\text{C}(7)\text{—O}(1)\text{—C}(2)\text{—C}(3) = -2.8 (3)$ ,  $\text{C}(8)\text{—O}(2)\text{—C}(4)\text{—C}(3) = -9.8 (4)^\circ$ . This coplanarity of the methoxy groups gives rise to steric interactions between the methyl carbon and the ring carbon atoms,  $\text{C}(7) \cdots \text{C}(3) = 2.786 (3)$ ,  $\text{C}(8) \cdots \text{C}(3) = 2.827 (2)$ ,  $\text{C}(9) \cdots \text{C}(6) = 2.818 (3) \text{\AA}$ . Angular asymmetry in the exocyclic angles at C(2), C(4) and C(5), similar to that found in other methoxy-substituted phenyl rings (Eliopoulous, Sheldrick & Hamodrakas, 1983; Banerjee & Chaudhuri, 1986), relieves the steric strain. The small differences between the observed values of the endocyclic angles and the values calculated [ $\text{C}(2)\text{—C}(1)\text{—C}(6) = 117.1$ ,  $\text{C}(1)\text{—C}(2)\text{—C}(3) = 121.2$ ,  $\text{C}(2)\text{—C}(3)\text{—C}(4) = 122.1$ ,  $\text{C}(3)\text{—C}(4)\text{—C}(5) = 120.4$ ,  $\text{C}(4)\text{—C}(5)\text{—C}(6) = 118.9$ ,  $\text{C}(5)\text{—C}(6)\text{—C}(1) = 122.6^\circ$ ] by assuming the additivity of the

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond distances and angles involving H atoms, selected torsion angles, and deviations from least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43405 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

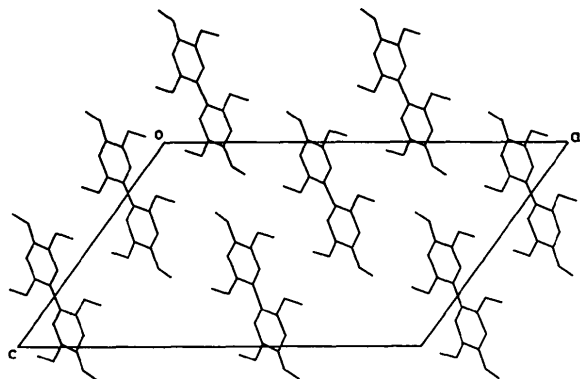


Fig. 2. View of the crystal structure.

effects of the methoxy groups (Domenicano & Murray-Rust, 1979) can be attributed to the +*R* effect of the methoxy group (Chattopadhyay, Banerjee, Mazumdar & Podder, 1985).

The molecular packing in the crystal is shown in Fig. 2. The molecules are stacked along *b* to form a column in which the interplanar distance between the phenyl rings is 3.487 (4) Å, the intermolecular H(6)⋯O(1) being 2.52 (3) Å. The columns related by a centre of symmetry at  $\frac{1}{2}, \frac{1}{2}, 0$  are held together by van der Waals interactions between the methoxyphenyl rings with an interplanar distance of 3.428 (4) Å to form a sheet in (101). The sheets related by a *c* glide plane are stacked along *c* to complete the whole structure, the shortest intermolecular distance being 2.69 (5) Å for H(92)⋯O(1).

*Acta Cryst.* (1987). C43, 484–488

### A Highly Potent Angiotensin Converting Enzyme Inhibitor: (*S,S,S*)-5-[*N*-(1-Carboxy-3-phenylpropyl)alanyl]-4,5,6,7-tetrahydrothieno[3,2-*c*]pyridine-4-carboxylic Acid Monohydrate, SBG 107

BY PETER LUGER

*Institut für Kristallographie, Freie Universität Berlin, Takustrasse 6, D-1000 Berlin 33, Federal Republic of Germany*

AND GERD SCHNORRENBURG

*Department of Medicinal Chemistry, Boehringer Ingelheim KG, D-6507 Ingelheim, Federal Republic of Germany*

(Received 23 June 1986; accepted 22 September 1986)

**Abstract.**  $C_{21}H_{24}N_2O_5S \cdot H_2O$ ,  $M_r = 434.51$ , orthorhombic,  $P2_12_12_1$ ,  $a = 18.192$  (3),  $b = 11.886$  (2),  $c = 10.088$  (2) Å,  $V = 2181$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.327$  (7),  $D_x = 1.323$  g cm<sup>-3</sup>,  $\lambda(\text{Cu K}\alpha) = 1.5418$  Å,

$\mu = 16.26$  cm<sup>-1</sup>,  $F(000) = 920$ ,  $T = 295$  K,  $R = 3.8\%$  for 1763 observed reflections. The molecule is present in its zwitterionic form in the crystal. In the non-protein C terminal amino acid the tetrahydrothienopyridine

The authors thank the Crystallographic Research Center, Institute for Protein Research, Osaka University, for the use of the facility, and Mr S. Chaudhuri of Bose Institute, Calcutta, for many useful discussions.

#### References

- BANERJEE, T. & CHAUDHURI, S. (1986). *Can. J. Chem.* In the press.  
 BASTIANSEN, O. & TRÆTTEBERG, M. (1962). *Tetrahedron*, **17**, 147–154.  
 BROCK, C. P., KUO MEI-SHIOW & LEVY, H. A. (1978). *Acta Cryst.* **B34**, 981–985.  
 CHARBONNEAU, G. P. & DELUGEARD, Y. (1976). *Acta Cryst.* **B32**, 1420–1423.  
 CHARBONNEAU, G. P. & DELUGEARD, Y. (1977). *Acta Cryst.* **B33**, 1586–1588.  
 CHATTOPADHYAY, D., BANERJEE, T., MAZUMDAR, S. K. & PODDER, G. (1985). *Acta Cryst.* **C41**, 287–289.  
 DOMENICANO, A. & MURRAY-RUST, P. (1979). *Tetrahedron Lett.* No. 24, pp. 2283–2286.  
 DOMENICANO, A., VACIAGO, A. & COULSON, C. A. (1975). *Acta Cryst.* **B31**, 221–234.  
 ELIOPOULOUS, E., SHELDRIK, B. & HAMODRAKAS, S. (1983). *Acta Cryst.* **C39**, 1693–1695.  
 GOODHAND, N. & HAMOR, T. A. (1978). *Acta Cryst.* **B34**, 1644–1647.  
 HAMOR, M. J. & HAMOR, T. A. (1978). *Acta Cryst.* **B34**, 863–866.  
 HARGREAVES, A. & RIZVI, S. H. (1962). *Acta Cryst.* **15**, 365–373.  
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.  
 MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.  
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination, Univ. of Cambridge, England.  
 TROTTER, J. (1961). *Acta Cryst.* **14**, 1135–1140.