group whereas the cyclopropane derivatives, both binaphthyl and biphenyl, crystallize in centro-symmetric space groups could be a result of the larger asymmetric part of the molecule (Fig. 2), which influences the packing in the crystal.

The shortest intermolecular distances are 2·44 Å for H···H, 2·83 Å for C···H and 2·68 Å for O···H.

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Structure of 3,3'-Spirobi[3H-2,4-dihydrobenzo[1,4]dioxepin]

BY KATARZYNA STADNICKA AND ŁUKASZ LEBIODA

Institute of Chemistry, Jagiellonian University, ul. Karasia 3, 30-060 Kraków, Poland

AND JACEK GROCHOWSKI

Regional Laboratory of Physicochemical Analysis and Structural Research, Kraków, Poland and Georgetown University, Department of Chemistry, Washington DC 20057, USA

Abstract. $C_{17}H_{16}O_4$, $M_r = 284·3$, $P2_1/c$, $a = 6·165$ (1), $b = 7·147$ (1), $c = 15·992$ (2) Å, $\beta = 104·04$ (2)°, $U = 683·6$ Å^3, $D_m = 1·38$, $D_x = 1·38$ Mg m^{-3}, $Z = 2$. The structure was solved by direct methods and refined to $R = 0·057$ for 1207 unique reflections. The molecules are randomly distributed in special positions giving an effective centre of symmetry to the structure. The conformation of the seven-membered ring has near C_2 symmetry. The separation between the planes of the benzo moieties, equivalent by the centre of symmetry, is 0·15 Å.

Introduction. The object of this study was to compare the conformation of molecule (I) with that found in the naphtho counterpart 3,3'-spirobi[3H-2,4-dihydro-naphtho[2,3-b][1,4]dioxepin] (SND) (Stadnicka & Lebioda, 1979).

(I)
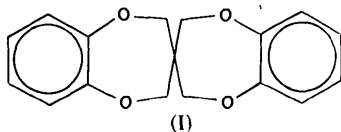
The compound obtained by Smoliński & Kubaszek (1968) was recrystallized by slow evaporation of a dioxane solution at room temperature. A crystal of dimensions 0·2 × 0·3 × 0·1 mm was used for data collection with graphite-monochromated Cu $K\alpha$ radiation on a CAD-4 diffractometer. The cell parameters were obtained from a least-squares fit of the setting angles of 15 reflections. 1326 reflections were measured by the ω–2θ scan with a scan range of (0·65 + 0·20 tan θ)° up to $\theta = 71°$. The intensities were corrected for Lorentz and polarization factors but not for absorption [μ(Cu $K\alpha$) = 0·714 mm^{-1}]. The structure was solved by direct methods and refined with 1207 reflections, $|F_o| \geq 2\sigma(F_o)$. In space group $P2_1/c$, $Z = 2$ implies that the position of the molecule is at a centre of symmetry, which is inconsistent with the tetrahedral binding around the spiro atom. The apparent centre of symmetry of the molecule is a result of a random arrangement of enantiomeric molecules. Thus for the C atoms bonded to the spiro atom, site-occupancy factors of 0·5 were used. Long-exposure Weissenberg photographs showed systematic absences

consistent with the space group $P2_1/c$. A search was made for any diffuse scattering, but it was not as obvious as in SND. Inspection of the anisotropic thermal parameters (Fig. 1) showed that for the other atoms separation of the disordered positions is not necessary. All H atoms were found on Fourier difference maps. The non-hydrogen and H-atom parameters were refined anisotropically and isotropically respectively using weights derived from counting statistics $\{w = [\sigma^2(F_o)]^{-1}\}$. The final $R = \sum \|F_o| - |F_c\|/\sum |F_o|$ and $R_G = [\sum w(|F_o| - |F_c|)^2/ \sum w|F_o|^2]^{1/2}$ were 0·057 and 0·053 respectively. The final Fourier difference map was featureless with a highest peak of 0·16 e Å^{-3}. Calculations were performed with the SHELX 76 system of programs
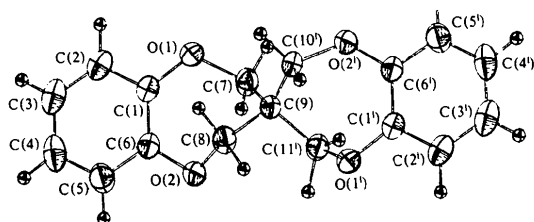

Fig. 1. Thermal-ellipsoid plot of the molecule (Johnson, 1965); the 50% probability ellipsoids are used for C and O atoms. Positions denoted (i) are related to those given in Table 1 by the operation $2 - x, -y, 1 - z$.

Table 1. The final atomic coordinates ($\times 10^4$ for non-hydrogen atoms and $\times 10^3$ for hydrogen) with their estimated standard deviations in parentheses

	x	y	z
C(1)	8741 (3)	3392 (3)	3679 (1)
C(2)	8748 (4)	4681 (3)	3031 (1)
C(3)	7043 (4)	5966 (4)	2789 (2)
C(4)	5314 (4)	5980 (3)	3198 (2)
C(5)	5293 (4)	4710 (3)	3851 (2)
C(6)	6988 (3)	3405 (3)	4089 (1)
C(7)*	9708 (9)	181 (6)	4050 (3)
C(8)*	9091 (8)	1776 (6)	5360 (3)
C(9)	10000	0	5000
C(10)*	7521 (7)	159 (6)	4508 (3)
C(11)*	11256 (7)	1720 (6)	4807 (3)
O(1)	10489 (2)	2133 (2)	3869 (1)
O(2)	6830 (2)	2155 (2)	4733 (1)
H(2)	1006 (4)	466 (4)	276 (2)
H(3)	702 (4)	679 (4)	230 (2)
H(4)	404 (5)	681 (4)	302 (2)
H(5)	406 (4)	468 (3)	412 (2)
H(71)*	814 (8)	−4 (6)	371 (3)
H(72)*	1084 (10)	−58 (9)	379 (4)
H(81)*	1026 (7)	281 (5)	532 (2)
H(82)*	877 (10)	143 (9)	596 (4)
H(101)*	679 (9)	−86 (8)	483 (4)
H(102)*	724 (7)	−5 (6)	382 (3)
H(111)*	1320 (15)	170 (11)	491 (5)
H(112)*	1131 (12)	270 (9)	510 (5)

* Position with site-occupancy factor $K = 0·5$.

(Sheldrick, 1976). The final atomic coordinates are in Table 1.*

Discussion. Bond lengths and angles together with torsion angles are given in Fig. 2. The best planes through the centrosymmetrically related benzo rings are 0·15 Å apart. The equation of the plane in the crystal-axis system is $2·1979x + 4·5972y + 9·1296z = 6·8389$; the value of the r.m.s.d. of the atoms is 0·003 Å. The exact parallelism of the benzo units is implied by an apparent centre of symmetry; however, the deviations of the atoms from the average plane are small, as can be inferred from the U_{ij} values.*

The structure can be described as basically 'spiro-coplanar' as in SND (Stadnicka & Lebioda, 1979) but here we can estimate better the deviations of the atoms from coplanarity. In SND the exact coplanarity was a result of averaging in the crystal structure of molecules in four positions which were equivalent not only by an inversion centre, as here, but also by a mirror plane corresponding to the observed plane of the molecule.

C(7)C(9)C(11¹)   109·6(2)
C(8)C(9)C(10¹)   105·8(2)

O(1)C(7)C(9)	107·9(3)	C(9)C(10¹)O(2¹)	104·0(3)
H(71)C(7)H(72)	110(4)	H(101¹)C(10¹)H(102¹)	115(4)
O(2)C(8)C(9)	104·8(3)	C(9)C(11¹)O(1¹)	108·1(3)
H(81)C(8)H(82)	121(4)	H(111¹)C(11¹)H(112¹)	92(5)

(b)
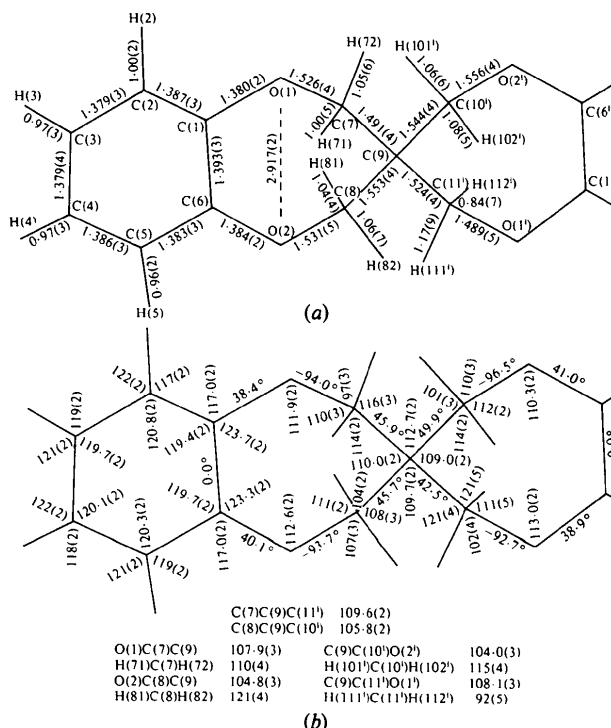
Fig. 2. (a) Bond lengths (Å) and (b) valence angles (°) and torsion angles (°). Estimated standard deviations are in parentheses, except for torsion angles for which the average value of the standard deviation is 0·5°. The positions denoted (i) are related to those given in Table 1 by the operation $2 - x, -y, 1 - z$.
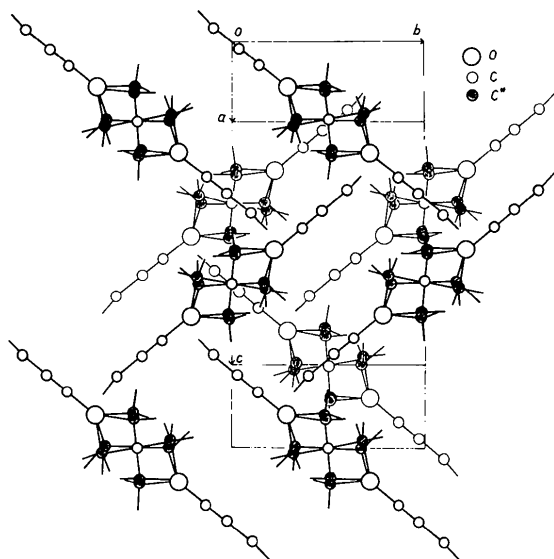
Fig. 3. Packing in the structure viewed approximately along [40Ī].
Partially occupied positions of C atoms are hatched.

The conformation of the seven-membered ring has C_2 symmetry within the limits of error, in agreement with the suggestion of Archer, Claret & Hayman (1971) based on UV spectra; the whole molecule has near D_2 symmetry. Values of the torsion angles for the seven-membered rings are similar to those in SND.

The packing in the structure is shown in Fig. 3. As in the case of SND, the disordered atoms are not in close contact, and interact primarily with the planar parts of neighbouring molecules so that the environments of the partially occupied positions are very similar. It seems worth noting that this type of disorder is the second observation of enantiomeric molecules being randomly located at a crystal site (De Camp, 1978). The shortest intermolecular approach distance is 2·41 Å for H(72) to H(2) in position $(2 - x, \frac{1}{2} + y, \frac{1}{2} - z)$. All other H···H distances are greater than 2·5 Å.

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Biphenyl–Perfluorobiphenyl; 1:1 Molecular Complex

By Douglas G. Naae

Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506, USA

Abstract. $C_{12}H_{10} \cdot C_{12}F_{10}$, monoclinic, $C2/c$, $a = 21·995$ (32), $b = 7·570$ (8), $c = 12·828$ (6) Å, $\beta = 112·33$ (7)°, $Z = 4$, $D_c = 1·64$, $D_m = 1·60$ (1) Mg m^{-3}. The perfluorobiphenyl and biphenyl molecules are packed alternately in infinite columns. The C_6F_5 and C_6H_5 rings of each molecule are inclined 25·4 and 18·3° respectively to the stack axis. The mean distance from each C_6H_5 ring to the plane of the C_6F_5 ring is 3·41 Å. The packing is very similar to that found in 2,3,4,5,6-pentafluorobiphenyl.

Introduction. Previously, we had reported that the crystalline, 1:1 molecular complex between biphenyl

$(C_{12}H_{10})$ and perfluorobiphenyl $(C_{12}F_{10})$ exhibits very low reactivity with gaseous methylamine (Lin & Naae, 1978). This low reactivity was also observed for 2,3,4,5,6-pentafluorobiphenyl $(C_{12}H_5F_5)$ and was attributed to the packing in the crystal. Due to their similar lack of solid-state reactivity and also to their similar elevated melting points (388–390 K for the 1:1 complex and 383–385 K for $C_{12}H_5F_5$ – relative to $C_{12}H_{10}$, 343–344 K, and $C_{12}F_{10}$, 340–341 K), we felt that a comparison of the two crystal structures would be informative regarding the similarity of the intermolecular interactions. In addition, the interactions present in the complex were expected to resemble those