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3,3′-Spirobi(3*H*-2,4-dihydronaphtho[2,3-*b*][1,4]dioxepin)

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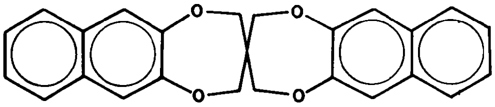
Abstract. $C_{25}H_{20}O_4$, orthorhombic, space group *Abam*, $a = 24{\cdot}926$ (3), $b = 6{\cdot}825$ (1), $c = 11{\cdot}187$ (2) Å, $Z = 4$, $D_m = 1{\cdot}342$ (3), $D_x = 1{\cdot}342$ Mg m^{-3}. The centre of symmetry is a result of statistical disorder in the structure. The conformation of the molecule is 'spirocoplanar', *i.e.* both naphthyl systems lie in one plane. The seven-membered ring has a pseudo-C_2 symmetry.

Introduction. Compound (I) is a symmetric oxaspiran (Smolinski & Malata, 1969). The hyperchromism observed in UV spectra indicates that the naphthyl systems are parallel. A study of Dreiding models suggested that they are coplanar (Smolinski, Nowicka, Mokrosz, Jamrozik, Jaworski & Wiekiera, 1977). The aim of this study was to verify this hypothesis.



(I)

A crystal of dimensions 0·10 × 0·08 × 0·18 mm was used to collect intensity data with an Enraf–Nonius CAD-4 diffractometer. The cell parameters were obtained from the least-squares fit of the φ, χ, ω and 2θ values for 15 reflections. The intensities were measured up to 70° with graphite-monochromated Cu *Kα* radiation. A $\theta/2\theta$ scan was used with scan range varying as 0·80° + 0·30° tan θ. Deviations in the intensities of three standard reflections were less than 3%. The intensities were corrected for Lorentz and polarization factors but not for absorption [μ(Cu *Kα*) = 0·322 mm^{-1}]. From 1514 measured reflections 870 unique $|F_o|$ values were obtained in a merging procedure giving an internal discrepancy factor of 3%. The structure was solved by direct methods. In the *Abam* centrosymmetric space group, $Z = 4$ implies the $2/m$ point symmetry of the molecule which is inconsistent with tetrahedral binding around the spiro atom. The centre of symmetry, however, can be the result of statistical disorder. Diffuse scattering is observed on Laue photographs and suggests that there is a short-range order of statistically distributed atoms.

The refinement was carried out in both centrosymmetric (*Abam*) and non-centrosymmetric (*Aba*2) space groups. In the latter, peaks corresponding to the statistical distribution of the neighbours of the spiro atom were also observed on Fourier maps. Strong correlations suggesting higher symmetry of the molecule and the deviations of the bond lengths from the expected values, obtained during the least-squares refinement, indicated the centrosymmetric space group. The fully occupied positions of the H atoms were found on a difference Fourier map; those partially occupied were obtained from the geometry of the molecule. Full-matrix least-squares refinement was carried out using 711 reflections with $|F_o| > 2\sigma(F_o)$ and with the weighting scheme $w = k[\sigma(F_o) + 0{\cdot}0002F_o^2]^{-1}$. This converged to $k = 2{\cdot}189$, $R = 0{\cdot}095$, $R_G = 0{\cdot}066$ and $S = 1{\cdot}31$, where $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_G = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ and S was the goodness-of-fit parameter. The maximum e.s.d. to shift ratio was less than 0·2 for nonhydrogen atoms and 0·3 for H atoms. The final Fourier difference map was featureless with a maximum peak of 0·3 e Å^{-3}.

The calculations were carried out with the *SHELX*76 (Sheldrick, 1976) and *XANADU* (Roberts & Sheldrick, 1972) programs. The final atomic posi-

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

	x	*y*	*z*
C(1)	4165 (1)	1608 (5)	626 (3)
C(2)	3856 (1)	284 (6)	1225 (4)
C(3)	3525 (1)	−1064 (5)	632 (3)
C(4)	3190 (2)	−2428 (8)	1233 (6)
C(5)	2880 (2)	−3730 (6)	612 (5)
C(6)*	5022 (3)	3136 (10)	793 (7)
C(7)*	4497 (3)	4943 (11)	−742 (7)
C(8)	5000	5000	0
O	4470 (1)	2872 (3)	1300 (2)
H(2)	390 (1)	32 (4)	209 (2)
H(4)	318 (1)	−235 (7)	204 (3)
H(5)	261 (2)	−467 (6)	105 (3)
H(61)*	516 (2)	199 (7)	36 (5)
H(62)*	533 (2)	352 (8)	143 (5)
H(71)*	415 (2)	522 (6)	−32 (5)
H(72)*	444 (3)	570 (13)	−147 (7)

* Position with site occupancy factor $K = 0{\cdot}5$.

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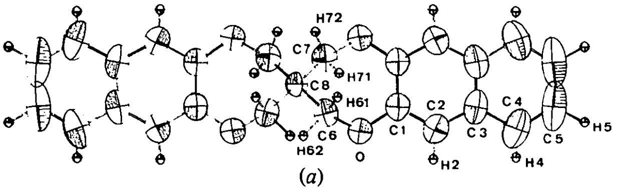
tional coordinates and their standard deviations are given in Table 1.*

Discussion. The molecule is shown in Fig. 1 with bond lengths and bond angles. Both naphthyl systems are coplanar; the deviations of the atoms from the best plane are given in Table 2. This exact coplanarity of both naphthyl systems is probably a result of disorder. The statistical centre of symmetry implies only parallelism of the naphthyl systems and not coplanarity. The coplanarity may be a result of averaging in the crystal lattice of molecules in four positions equivalent by the centre of inversion and also by the mirror plane, corresponding to the final plane of the molecule. Inspection of thermal parameters shows, however, that the deviations of the molecules from the mirror plane are small. In the structure of the benzene counterpart of this spiran, 3,3′-spirobi(3H-2,4-dihydrobenzo[1,4]-dioxepin) (Stadnicka, Lebioda & Grochowski, 1979), where disorder was found of inversion-centre-related molecules but not mirror-plane-related ones, the planes of the symmetric benzene groups were 0·14 Å distant. The 'spirocoplanarity' of the molecule is connected with the pseudo-C_2 conformation observed for the seven-membered ring. The asymmetry parameter (Duax & Norton, 1975) is 2·8°. The torsion angles obtained for this ring are closer to the values found from empirical force-field calculations for cycloheptene by Favini, Buemi & Raimondi (1968) (F, B & R) than to those given by Ermer & Lifson (1973) (E & L), as shown in Table 3. Although the calculations and empirical evidence quoted in the papers mentioned above indicate that the C_s conformation is more stable for cycloheptene, the energetic differences between C_s and C_2 conformations are small. The observed C_2 conformation is probably stabilized by the presence of the hetero-atoms in the ring and by the influence of the conjugated naphthyl system. The point symmetry of



(a)

Fig. 1. (a) Thermal ellipsoid plot of the molecule (Johnson, 1965); 50% probability ellipsoids are used for C and O atoms.

Table 2. *The deviations (in* Å) *of the symmetry-independent atoms from the best plane of both naphthyl systems*

The equation of the plane is

$$(18\cdot6333)x + (-4\cdot5329)y + (0\cdot0005)z = (7\cdot0502).$$

C(1)*	−0·018 (3)		
C(2)*	0·006 (4)	H(2)	0·066 (26)
C(3)*	0·000 (3)		
C(4)*	−0·006 (5)	H(4)	−0·068 (37)
C(5)*	0·007 (4)	H(5)	−0·069 (46)
O	−0·023 (2)		
C(6)	0·886 (7)	H(61)	1·666 (53)
		H(62)	1·284 (52)
C(7)	−0·912 (7)	H(71)	−1·694 (46)
		H(72)	−1·367 (81)
C(8)	0·000		

* Atom used in the plane calculation.

Table 3. *Torsion angles* (°) *for the seven-membered ring*

	This work	F, B & R	E & L
OC(6)C(8)C(7)	−44·2 (0·9)	−46·0	−43·1
C(1)OC(6)C(8)	94·9 (1·0)	91·3	77·9
C(1^i)C(1)OC(6)	−41·1 (1·8)	−37·6	−27·9
OC(1)C(1^i)O^i	0·0 (1·7)	0·0	−7·8
C(1)C(1^i)O^{i}C(7)	−37·6 (1·8)	−37·6	−27·9
C(1^i)O^{i}C(7)C(8)	94·4 (1·0)	91·3	77·9
O^{i}C(7)C(8)C(6)	−47·9 (1·0)	−46·0	−43·1

Symmetry code: (i) $x,y,-z$.

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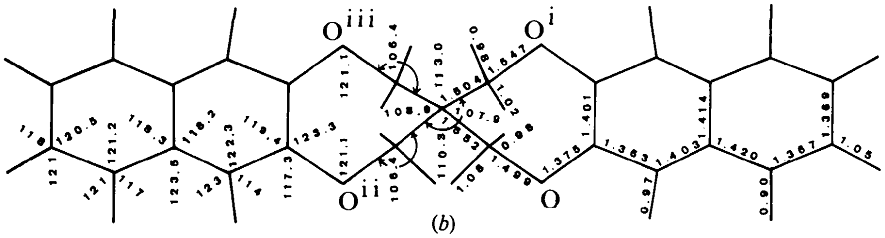
* Lists of structure factors, thermal parameters and intermolecular distances are available from the authors on request and have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34205 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.



(b)

Fig. 1 (*cont.*). (*b*) Bond lengths (Å) and bond angles (°). Average standard deviations are 0·006 Å and 0·5° for bonds involving C and O atoms, 0·05 Å and 3° for bonds involving H atoms. Symmetry code: (i) $x,y,-z$, (ii) $-x,-y,z$, (iii) $-x,-y,-z$. The angles not marked in the figure are OC(6)H(61) 114, OC(6)H(62) 115, C(8)C(6)H(61) 113, C(8)C(6)H(62) 102, H(61)C(6)H(62) 106, O^{i}C(7)H(71) 109, O^{i}C(7)H(72) 98, C(8)C(7)H(71) 117, C(8)C(7)H(72) 125, H(71)C(7)H(72) 99°.

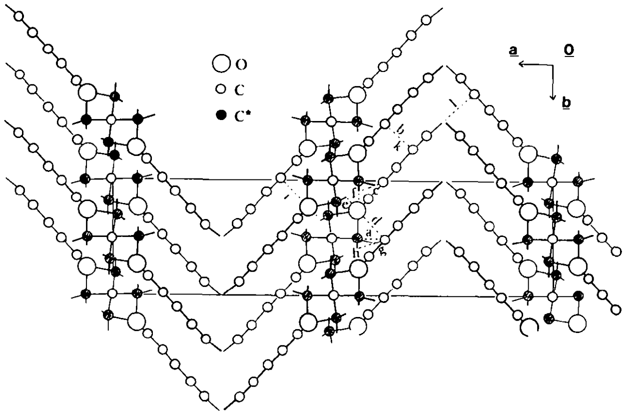


Fig. 2. Packing in the structure viewed along **c**. Partially occupied positions of C(6) and C(7) which coincide in this projection are hatched (C*).

the molecule in the structure together with the pseudo-C_2 conformation of the seven-membered rings joined by the spiro atom results in the pseudo-D_2 symmetry of the whole molecule.

The molecular structure observed is more consistent with the name 'spiran' (meaning pretzel in Latin) than the orthogonal conformations found in other structures such as N,N-dimethylspiro[5H-dibenzo[a,d]cycloheptene-5,1'-cyclohexane]-4'-amine (Rodgers, Kennard & Sheldrick, 1976) and (±)-2,2'-spirobi(indan)-1,1'-dione (Petersen & Danielsen, 1974).

The packing in the structure given in Fig. 2 shows that the disordered atoms are not in close contact. They interact primarily with the planar part of the neighbouring molecules so that the environment of the partially occupied positions is the same. The shortest intermolecular approach is H(72) to H(2) in $(x, \frac{1}{2}+y, -\frac{1}{2}+z)$ at 2·11 Å. All other H···H distances are greater than 2·59 Å.

We are greatly indebted to Professor Smolinski for suggesting the problem and providing the crystals.

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Bis(p-nitrophenyl)butadiyne

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Abstract. $C_{16}H_8N_2O_4$, M_r = 292·24, tetragonal, $I4_1/amd$, a = 7·088 (1), c = 26·785 (5) Å, Z = 4, D_c = 1·44, D_o = 1·44 (1) Mg m^{-3}. The phenyl rings on opposite ends of the molecules are mutually perpendicular. The packing arrangement is one of interpenetrating stacks of molecules arrayed along a and b in a manner that renders the molecules inert to solid-state polymerization.

Introduction. The solid-state polymerization of diacetylenes has been of considerable interest recently. This reaction, extensively studied by Wegner (1977) and co-workers, is illustrated in Fig. 1. Since this polymerization is often a single-crystal to single-crystal transformation, it readily lends itself to crystallographic analysis. We have taken advantage of this and studied several unreactive diacetylene monomers

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