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## Structure of Spiro[3,4-dihydro-2*H*-1,5-dioxadinaphtho[2,1-*f*:1,2-*h*]cyclononene-3,1'-cyclopentane]

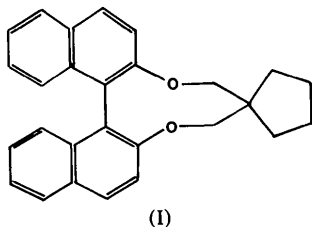
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**Abstract.** C<sub>25</sub>H<sub>20</sub>O<sub>2</sub>, *M<sub>r</sub>* = 380.5, tetragonal, crystal faces: {101}, {101}, {100}, space group *P4*<sub>1</sub>(*P4*<sub>3</sub>), *a* = 11.243 (5), *c* = 16.346 (6) Å, *V* = 2066 Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.184 Mg m<sup>-3</sup>, μ(Cu *Kα*) = 0.515 mm<sup>-1</sup>. The structure was solved by direct methods and refined by full-matrix least squares to a final *R* value of 0.054 for 1328 reflections. The molecule is asymmetric. There is little influence of strain in the small ring on the conformation of the nine-membered ring when compared with the cyclopropane counterpart.

**Introduction.** The structure of spiro[3,4-dihydro-2*H*-1,5-dioxadinaphtho[2,1-*f*:1,2-*h*]cyclononene-3,1'-cyclopentane] (I) (SNPE) was investigated in order to compare it with that of spiro[3,4-dihydro-2*H*-1,5-dioxadinaphtho[2,1-*f*:1,2-*h*]cyclononene-3,1'-cyclopropane] (SNPR) (Stadnicka, 1979) and to find any effect of the strain in the small ring on the conformation of the dioxacyclononene ring. The effects of the conjugated systems can be analysed by comparison of the SNPE and SNPR structures with the structure of spiro[3,4-dihydro-2*H*-1,5-dioxadibenzol[*f*,*h*]cyclononene-3,1'-cyclopropane] (SBPR) (Grochowski & Karle, 1978).



Transparent crystals of SNPE were synthesized by Smoliński & Paluchowska (1979). A crystal of

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approximate dimensions 0.2 × 0.2 × 0.3 mm was used to collect intensity data up to  $\theta = 55^\circ$  using an Enraf-Nonius CAD-4 diffractometer and graphite-monochromated Cu *Kα* radiation in the  $\omega/2\theta$  scan mode and  $(0.7 + 0.2 \tan \theta)^\circ$  scan range. The unit-cell parameters were obtained by least-squares refinement from the setting angles of 15 reflections used in the auto-indexing procedure. The fluctuation of intensity for two standard reflections was less than 5%. The intensities were corrected for geometrical factors but not for absorption. Of the 2765 reflections measured, 1336 unique values were obtained in a sort-merge procedure giving an internal *R* = 0.028. Eight reflections with  $|F_o| \leq \sigma(F_o)$  were treated as unobserved.

The structure was solved using the tangent formula on six selected initial phases. The *E* maps were calculated from 244 reflections (*E* > 1.2) and the solution with the best figure of merit revealed the positions of 27 non-hydrogen atoms. The two missing atoms of the cyclopentane ring were found in a Fourier difference map. Anisotropic full-matrix least-squares refinement and subsequent difference maps yielded positions of all the H atoms except H(221), H(241) and H(252), which were calculated instead. All H atoms were included in the refinement with isotropic thermal factors. The calculations were terminated when all the shifts were less than 0.2 of the e.s.d. and the discrepancy factors defined as  $R = \sum |\Delta F| / \sum |F_o|$ ,  $R_w = \sum w^{1/2} |\Delta F| / \sum w^{1/2} |F_o|$  and  $R_G = [\sum w (\Delta F)^2 / \sum w F_o^2]^{1/2}$  were 0.054, 0.042 and 0.038 respectively. The goodness-of-fit parameter *S* was 0.69. The peaks on the final Fourier difference map were less than 0.15 e Å<sup>-3</sup>. The weighting scheme was  $w = [\sigma(F_o)]^{-1}$  where  $\sigma(F_o)$  is the standard deviation in the observed  $|F(hkl)|$  values derived from counting statistics. The final

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fractional atomic coordinates are given in Table 1.\* The *SHELX 76* system of crystallographic programs (Sheldrick, 1976) was used for the calculations.

\* Lists of structure factors, thermal parameters and the results of a rigid-body analysis are available from the authors on request and have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34579 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ( $\times 10^4$ ; for hydrogen atoms  $\times 10^3$ ) with estimated standard deviations in parentheses

	x	y	z
C(1)	3393 (5)	1216 (5)	3261 (3)
C(2)	3982 (6)	97 (6)	3313 (5)
C(3)	3794 (7)	-611 (6)	3952 (5)
C(4)	3009 (6)	-295 (5)	4588 (5)
C(5)	2746 (7)	-1040 (6)	5272 (5)
C(6)	1960 (8)	-738 (7)	5839 (5)
C(7)	1360 (7)	367 (6)	5815 (4)
C(8)	1591 (5)	1132 (5)	5173 (4)
C(9)	2409 (5)	846 (4)	4553 (4)
C(10)	2660 (5)	1595 (5)	3867 (4)
C(11)	2110 (4)	2802 (4)	3810 (3)
C(12)	2440 (4)	3747 (4)	4351 (3)
C(13)	3266 (5)	3590 (5)	4989 (4)
C(14)	3543 (6)	4514 (5)	5496 (4)
C(15)	3047 (6)	5619 (5)	5386 (4)
C(16)	2264 (5)	5814 (5)	4775 (5)
C(17)	1935 (5)	4889 (5)	4236 (4)
C(18)	1120 (5)	5075 (6)	3580 (4)
C(19)	840 (5)	4183 (6)	3074 (4)
C(20)	1336 (5)	3049 (5)	3175 (3)
O(1)	3621 (3)	1963 (3)	2625 (2)
O(2)	1028 (3)	2095 (3)	2689 (2)
C(21)	3237 (7)	1599 (6)	1810 (4)
C(22)	1070 (6)	2277 (5)	1800 (4)
C(23)	2306 (6)	2472 (5)	1476
C(24)	2264 (8)	2277 (7)	511 (4)
C(25)	3150 (12)	3160 (11)	176 (7)
C(26)	3635 (8)	3898 (8)	848 (6)
C(27)	2762 (7)	3768 (6)	1532 (4)
H(2)	451 (4)	-6 (4)	279 (3)
H(3)	443 (5)	-140 (5)	410 (3)
H(5)	333 (4)	-189 (4)	526 (3)
H(6)	172 (5)	-132 (5)	633 (4)
H(7)	66 (6)	65 (6)	629 (5)
H(8)	108 (3)	191 (3)	516 (2)
H(13)	364 (3)	283 (3)	507 (3)
H(14)	413 (4)	436 (4)	586 (3)
H(15)	319 (4)	622 (4)	575 (3)
H(16)	190 (4)	659 (3)	473 (3)
H(18)	73 (4)	591 (4)	359 (2)
H(19)	17 (5)	434 (4)	267 (4)
H(211)	283 (3)	74 (4)	184 (2)
H(212)	400 (4)	157 (4)	142 (3)
H(221)	54 (8)	307 (8)	165 (5)
H(222)	67 (4)	135 (4)	155 (3)
H(241)	137 (8)	251 (8)	28 (5)
H(242)	248 (6)	130 (5)	43 (4)
H(251)	293 (7)	335 (7)	-33 (5)
H(252)	391 (8)	262 (8)	-8 (5)
H(261)	393 (5)	470 (5)	70 (3)
H(262)	465 (6)	380 (6)	117 (4)
H(271)	308 (4)	393 (4)	207 (3)
H(272)	206 (5)	438 (5)	140 (4)

**Discussion.** The conformation of the molecule and the atom numbering are shown in Fig. 1. The thermal parameters of the atoms were analysed in terms of rigid-body motion by the method of Schomaker & Trueblood (1968), with the program *THMB* (Huber-Buser, 1977, as revised by K. N. Trueblood). Two models were used: one treated the whole molecule as a rigid body and in the second C(24), C(25), C(26) and C(27) were deleted. The values of  $\langle (\Delta U_{ij})^2 \rangle^{1/2} = [\sum (\Delta U_{ij})^2 / (N_{\text{obs}} - N_{\text{par}})]^{1/2}$  were 0.0091 and 0.0061, respectively, while  $\langle \sigma^2(U_{ij}) \rangle^{1/2}$  were 0.0050 and 0.0044. These suggest some disorder or internal flapping motion of the cyclopentane ring. Bond lengths and valence angles are given in Fig. 2. The cyclopentane ring is close to an envelope form with an approximate mirror plane passing through C(27). The torsion angles of the cyclopentane are given in Fig. 2(b), and the asymmetry parameter (Duax & Norton, 1975) is 3.6°.

The geometry of both naphthyl systems is similar and corresponds to that found by Cruickshank (1957). The length of the linking single bond in the binaphthyl system is 1.493 (5) Å, which agrees with the 1.49 Å found in 2,2'-dihydroxy-1,1'-binaphthalene-3,3'-dicarboxylic acid dimethyl ester (Akimoto & Iitaka, 1969) and with values cited for biphenyls by Goodhand & Hamor (1978).

The torsion angles for the nine-membered ring are given in Table 2 together with those found in SNPR (Stadnicka, 1979) and SBPR (Grochowski & Karle, 1978). The conformation of the nine-membered ring in these three molecules is basically the same. The mean-square differences of torsion angles defined as  $\Delta =$

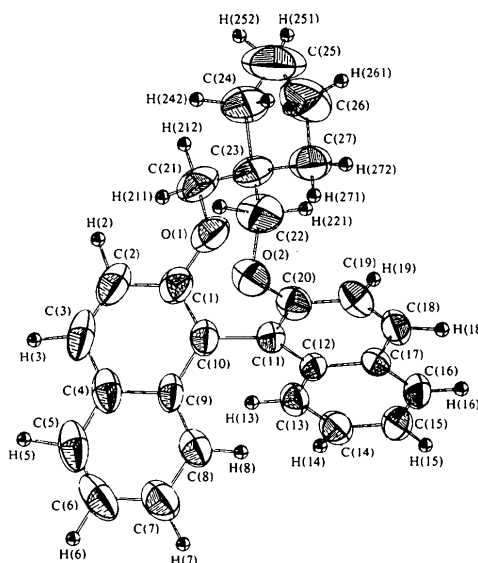


Fig. 1. Spiro[3,4-dihydro-2H-1,5-dioxadinaphtho[2,1-f':1,2-h]cyclopentane-3,1'-cyclopentane]. For non-hydrogen atoms the thermal ellipsoids are at 50% probability (Johnson, 1965). The temperature factors for the H atoms are set at an arbitrary level.



group whereas the cyclopropane derivatives, both binaphthyl and biphenyl, crystallize in centrosymmetric 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]

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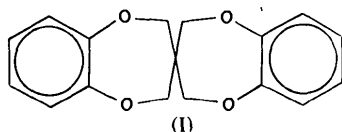
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**Abstract.** C<sub>17</sub>H<sub>16</sub>O<sub>4</sub>, *M<sub>r</sub>* = 284.3, *P2<sub>1</sub>/c*, *a* = 6.165 (1), *b* = 7.147 (1), *c* = 15.992 (2) Å, β = 104.04 (2)°, *U* = 683.6 Å<sup>3</sup>, *D<sub>m</sub>* = 1.38, *D<sub>x</sub>* = 1.38 Mg m<sup>-3</sup>, *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<sub>2</sub>* 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).



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*α 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 θ = 71°. The intensities were corrected for Lorentz and polarization factors but not for absorption [*μ*(Cu *K*α) = 0.714 mm<sup>-1</sup>]. The structure was solved by direct methods and refined with 1207 reflections, |*F<sub>o</sub>*| ≥ 2σ(*F<sub>o</sub>*). In space group *P2<sub>1</sub>/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