

6-Methoxy-8,10-dimethyl-1,14-dioxo-2,13-diaza[4]metacyclo[4](3,5)pyridinophane-2-Propanol (2:1)

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Abstract. $C_{20}H_{23}N_3O_3 \cdot \frac{1}{2}C_3H_8O$, $M_r = 383.5$, monoclinic, $P2_1/n$, $a = 17.699(2)$, $b = 21.05(1)$, $c = 11.062(1)$ Å, $\beta = 104.31(1)^\circ$, $V = 3993(3)$ Å³, $Z = 8$, $D_x = 1.28$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 6.71$ cm⁻¹, $F(000) = 1640$, room temperature, $R = 0.065$ for 3291 observed reflexions. The two molecules in the asymmetric unit have practically identical conformations, with one amide group in the *syn* and the other in the *anti* conformation. The two amide groups are not planar but show twist angles of 16 and 10° respectively. The rings are slightly boat-shaped.

Introduction. The title compound has been synthesized by Dr F. Rob in the course of a study of diastereodifferentiation in the hydride transfer to bridged NAD(H) models (Rob, 1983; Rob, Van Ramesdonk, Van Gerresheim, Bosma, Scheele & Verhoeven, 1984). The NMR spectra of the compound in solution were interpreted as resulting from two conformations, a major 'asymmetric' one in which the protons at C(2) and C(6) are magnetically different and a minor 'symmetric' one in which the two protons are equivalent. In order to obtain direct information about the conformations a crystal-structure determination was undertaken.

Experimental. D_m not measured. 18 reflexions (2θ 81–83°) used to measure lattice parameters; $2\theta_{\max} = 110^\circ$, $h - 18$ to 18, $k 0$ to 22, $l 0$ to 11; one standard reflexion, no systematic variation; 5004 unique reflections, 1713 with $I < 2.5\sigma(I)$; Nonius CAD-4 diffractometer with graphite-monochromatized Cu $K\alpha$ radiation; no absorption correction, crystal dimensions 0.35 × 0.21 × 0.14 mm. Structure solved by means of the symbolic addition program-set SIMPEL (Overbeek & Schenk, 1978). A ΔF synthesis revealed one molecule of 2-propanol, the O atom of which showed disorder. After anisotropic block-diagonal least-squares refinement of C, N and O, all H atoms were located in a ΔF synthesis and included in the refinement with isotropic thermal parameters. A weighting scheme $w = 1/(2.6 +$

Table 1. Positional parameters and equivalent isotropic thermal parameters with e.s.d.'s in parentheses

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

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} (Å ²)
N(1A)	0.5553 (3)	0.0907 (2)	0.0311 (4)	0.051 (2)
C(2A)	0.4871 (3)	0.1096 (3)	-0.0481 (5)	0.046 (2)
C(3A)	0.4703 (3)	0.1721 (2)	-0.0791 (4)	0.037 (2)
C(4A)	0.5243 (3)	0.2196 (3)	-0.0288 (4)	0.037 (2)
C(5A)	0.5939 (3)	0.2012 (3)	0.0539 (4)	0.035 (2)
C(6A)	0.6056 (3)	0.1368 (3)	0.0803 (5)	0.046 (2)
C(7A)	0.3933 (3)	0.1901 (3)	-0.1673 (4)	0.039 (2)
N(8A)	0.3447 (2)	0.2284 (2)	-0.1274 (4)	0.042 (2)
C(9A)	0.3496 (3)	0.2496 (3)	0.0011 (4)	0.037 (2)
C(10A)	0.3413 (3)	0.3217 (3)	0.0107 (5)	0.042 (2)
C(11A)	0.4098 (3)	0.3595 (2)	-0.0080 (4)	0.038 (2)
C(12A)	0.4788 (3)	0.3647 (2)	0.0879 (4)	0.035 (2)
C(13A)	0.5421 (3)	0.3992 (3)	0.0703 (4)	0.040 (2)
C(14A)	0.5368 (3)	0.4311 (3)	-0.0419 (5)	0.043 (2)
C(15A)	0.4685 (3)	0.4274 (3)	-0.1360 (5)	0.049 (2)
C(16A)	0.4059 (3)	0.3915 (3)	-0.1211 (5)	0.042 (2)
C(17A)	0.6200 (3)	0.4011 (3)	0.1671 (5)	0.047 (2)
C(18A)	0.6838 (3)	0.3627 (3)	0.1292 (6)	0.051 (2)
N(19A)	0.6536 (2)	0.3032 (2)	0.0665 (4)	0.042 (2)
C(20A)	0.6494 (3)	0.2491 (2)	0.1254 (4)	0.038 (2)
O(21A)	0.3777 (2)	0.1691 (2)	-0.2757 (3)	0.054 (1)
O(22A)	0.6849 (2)	0.2383 (2)	0.2342 (3)	0.052 (1)
C(23A)	0.4856 (3)	0.3317 (3)	0.2125 (5)	0.047 (2)
O(24A)	0.6038 (3)	0.4635 (2)	-0.0489 (4)	0.062 (2)
C(25A)	0.6069 (4)	0.4905 (3)	-0.1642 (6)	0.071 (2)
C(26A)	0.3340 (4)	0.3896 (4)	-0.2277 (6)	0.070 (2)
N(1B)	-0.0864 (2)	0.1065 (2)	-0.0145 (4)	0.049 (2)
C(2B)	-0.0186 (3)	0.1254 (2)	0.0639 (5)	0.041 (2)
C(3B)	-0.0008 (3)	0.1886 (2)	0.0937 (4)	0.034 (2)
C(4B)	-0.0554 (3)	0.2351 (3)	0.0427 (4)	0.036 (2)
C(5B)	-0.1245 (3)	0.2158 (2)	-0.0400 (4)	0.035 (2)
C(6B)	-0.1363 (3)	0.1525 (3)	-0.0642 (5)	0.047 (2)
C(7B)	0.0760 (3)	0.2055 (3)	0.1818 (4)	0.035 (2)
N(8B)	0.1241 (2)	0.2439 (2)	0.1411 (4)	0.038 (1)
C(9B)	0.1203 (3)	0.2646 (2)	0.0138 (5)	0.037 (2)
C(10B)	0.1272 (3)	0.3365 (3)	0.0025 (5)	0.045 (2)
C(11B)	0.0583 (3)	0.3747 (2)	0.0181 (5)	0.036 (2)
C(12B)	-0.0106 (3)	0.3786 (3)	-0.0793 (4)	0.035 (2)
C(13B)	-0.0745 (3)	0.4131 (2)	-0.0655 (4)	0.034 (2)
C(14B)	-0.0699 (3)	0.4453 (2)	0.0456 (5)	0.043 (2)
C(15B)	-0.0025 (3)	0.4428 (3)	0.1405 (5)	0.046 (2)
C(16B)	0.0601 (3)	0.4071 (2)	0.1296 (5)	0.042 (2)
C(17B)	-0.1524 (3)	0.4137 (3)	-0.1647 (5)	0.048 (2)
C(18B)	-0.2164 (3)	0.3770 (3)	-0.1237 (5)	0.051 (2)
N(19B)	-0.1865 (3)	0.3188 (2)	-0.0564 (4)	0.040 (1)
C(20B)	-0.1803 (2)	0.2641 (3)	-0.1127 (4)	0.041 (2)
O(21B)	0.0916 (2)	0.1833 (2)	0.2883 (3)	0.052 (1)
O(22B)	-0.2135 (2)	0.2522 (2)	-0.2232 (3)	0.053 (1)
C(23B)	-0.0150 (3)	0.3442 (3)	-0.2024 (5)	0.048 (2)
O(24B)	-0.1364 (2)	0.4789 (2)	0.0502 (4)	0.062 (2)
C(25B)	-0.1390 (4)	0.5063 (3)	0.1659 (6)	0.077 (3)
C(26B)	0.1315 (4)	0.4042 (3)	0.2376 (6)	0.064 (2)
C(27)	0.2379 (4)	0.5035 (4)	0.5175 (6)	0.098 (3)
C(28)	0.3022 (5)	0.5373 (3)	0.4919 (8)	0.104 (3)
C(29)	0.2963 (5)	0.6091 (3)	0.4890 (7)	0.100 (3)
O(301)*	0.3719 (5)	0.5256 (4)	0.5150 (9)	0.089 (3)
O(302)*	0.3440 (7)	0.5159 (4)	0.4165 (7)	0.102 (3)

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* Population parameter 0.5.

Table 2. Bond distances (Å) and angles (°) with e.s.d.'s in parentheses

	Molecule A	Molecule B		Molecule A	Molecule B		Molecule A	Molecule B
N(1)—C(2)	1.364 (7)	1.355 (6)	C(9)—C(10)	1.531 (9)	1.526 (8)	C(16)—C(26)	1.507 (8)	1.511 (8)
N(1)—C(6)	1.338 (8)	1.334 (7)	C(10)—C(11)	1.507 (8)	1.506 (8)	C(17)—C(18)	1.529 (9)	1.530 (9)
C(2)—C(3)	1.374 (8)	1.388 (6)	C(11)—C(12)	1.410 (6)	1.416 (6)	C(18)—N(19)	1.467 (7)	1.463 (8)
C(3)—C(4)	1.400 (7)	1.393 (7)	C(11)—C(16)	1.408 (8)	1.403 (8)	N(19)—C(20)	1.323 (6)	1.327 (8)
C(3)—C(7)	1.515 (7)	1.506 (7)	C(12)—C(13)	1.389 (9)	1.384 (8)	C(20)—O(22)	1.233 (6)	1.244 (5)
C(4)—C(5)	1.396 (7)	1.395 (7)	C(12)—C(23)	1.521 (8)	1.527 (8)	O(24)—C(25)	1.410 (8)	1.415 (8)
C(5)—C(6)	1.391 (9)	1.365 (8)	C(13)—C(14)	1.394 (8)	1.388 (7)	C(27)—C(28)		1.43 (1)
C(5)—C(20)	1.491 (7)	1.504 (7)	C(13)—C(17)	1.523 (7)	1.535 (7)	C(28)—C(29)		1.51 (1)
C(7)—N(8)	1.331 (8)	1.331 (8)	C(14)—C(15)	1.389 (7)	1.382 (7)	C(28)—O(301)		1.22 (1)
C(7)—O(21)	1.243 (6)	1.234 (6)	C(14)—O(24)	1.387 (8)	1.385 (7)	C(28)—O(302)		1.32 (2)
N(8)—C(9)	1.472 (7)	1.460 (8)	C(15)—C(16)	1.384 (9)	1.369 (8)			
C(2)—N(1)—C(6)	116.4 (5)	116.2 (5)	N(8)—C(9)—C(10)	112.6 (5)	112.9 (4)	C(15)—C(14)—O(24)	125.7 (5)	125.0 (5)
N(1)—C(2)—C(3)	122.8 (5)	123.1 (5)	C(9)—C(10)—C(11)	114.8 (5)	115.9 (5)	C(14)—C(15)—C(16)	121.0 (6)	121.3 (5)
C(2)—C(3)—C(4)	120.0 (4)	118.9 (4)	C(10)—C(11)—C(12)	121.0 (5)	120.9 (5)	C(11)—C(16)—C(15)	120.2 (5)	120.1 (4)
C(2)—C(3)—C(7)	120.3 (5)	119.7 (4)	C(10)—C(11)—C(16)	120.7 (4)	121.2 (5)	C(11)—C(16)—C(26)	122.0 (6)	120.6 (5)
C(4)—C(3)—C(7)	119.6 (5)	121.4 (4)	C(12)—C(11)—C(16)	118.3 (5)	118.0 (5)	C(15)—C(16)—C(26)	117.9 (6)	119.3 (5)
C(3)—C(4)—C(5)	117.9 (5)	118.0 (5)	C(11)—C(12)—C(13)	120.9 (4)	121.3 (5)	C(13)—C(17)—C(18)	113.3 (5)	112.6 (5)
C(4)—C(5)—C(6)	118.0 (5)	118.7 (5)	C(11)—C(12)—C(23)	120.4 (5)	119.7 (5)	C(17)—C(18)—N(19)	111.9 (5)	111.9 (5)
C(4)—C(5)—C(20)	121.3 (6)	120.5 (5)	C(13)—C(12)—C(23)	118.7 (4)	119.0 (4)	C(18)—N(19)—C(20)	124.1 (5)	123.3 (5)
C(6)—C(5)—C(20)	120.2 (4)	120.4 (4)	C(12)—C(13)—C(14)	119.9 (5)	118.9 (4)	C(5)—C(20)—N(19)	115.5 (4)	117.1 (4)
N(1)—C(6)—C(5)	124.9 (5)	125.0 (5)	C(12)—C(13)—C(17)	122.5 (5)	122.6 (5)	C(5)—C(20)—O(22)	120.2 (4)	118.5 (5)
C(3)—C(7)—N(8)	119.3 (4)	118.4 (4)	C(14)—C(13)—C(17)	117.6 (5)	118.3 (5)	N(19)—C(20)—O(22)	124.2 (4)	124.2 (5)
C(3)—C(7)—O(21)	118.8 (5)	118.8 (6)	C(13)—C(14)—C(15)	119.7 (6)	120.3 (5)	C(14)—O(24)—C(25)	118.3 (5)	117.3 (5)
N(8)—C(7)—O(21)	121.8 (5)	122.8 (5)	C(13)—C(14)—O(24)	114.6 (4)	114.7 (4)	C(27)—C(28)—C(29)		116.6 (8)
C(7)—N(8)—C(9)	128.0 (4)	128.8 (4)						

$F_o + 0.013F_o^2$) was employed. The final R was 0.065 ($wR = 0.093$). Max. shift/e.s.d. = 0.4; max./min. difference Fourier map peaks were $\pm 0.4 e \text{ \AA}^{-3}$. Scattering factors were taken from Cromer & Mann (1968). The calculations, except for the symbolic addition, were performed with the *XRAY76* system (Stewart, 1976).

Discussion. The final atomic parameters are given in Table 1.* The molecular shape and the atomic numbering are given in Fig. 1. The two molecules in the asymmetric unit are almost identical down to the smallest details. Numbers will be quoted in pairs, the first referring to molecule *A* and the second to molecule *B*. The bond distances (Table 2) and angles have normal values. The rings show small but systematic deviations from planarity such that they are slightly boat-shaped. The two ring-connecting chains are quite different, the amide group in the chain C(7)—C(10) having the *anti* conformation and the other amide group the *syn* conformation. In the corresponding paracyclophane (Van Herk, Goubitz, Overbeek & Stam, 1982) both amide groups are in the *syn* conformation. The amide groups are not planar but show twist angles of 10 (10) and 16 (16)° respectively. The difference between the two chains is also reflected in the deviations from the ring planes of the chain atoms attached to the rings. C(7) and C(10) have small deviations of 0.024 (0.021) and 0.012 (0.007) Å respectively towards the other ring; C(17) and C(20) have

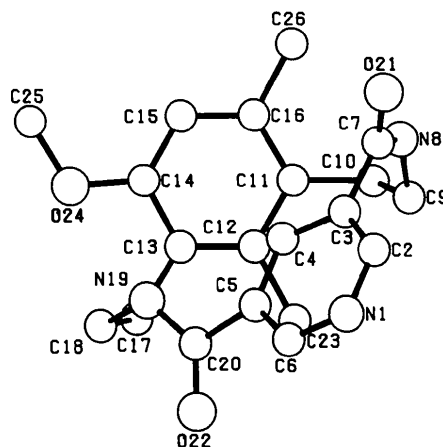


Fig. 1. Shape of the molecules and atomic numbering.

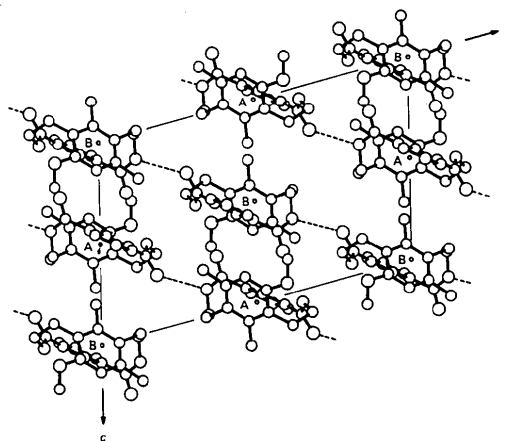


Fig. 2. Projection of the structure along [010]. Hydrogen bonds are indicated by dashed lines.

* Lists of structure factors, anisotropic temperature factors and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44057 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

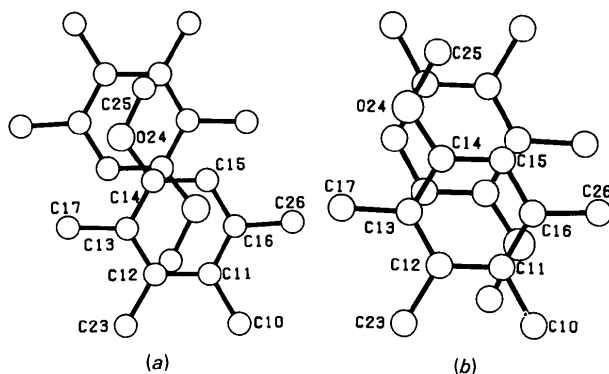


Fig. 3. Ring-ring interactions across a centre of symmetry. (a) Molecules *A*; (b) molecules *B*.

much larger deviations of 0.119 (0.124) and 0.185 (0.188) Å respectively, also towards the other ring. The pyridine ring points with C(4) towards the benzene ring; the nearest approaches of H(4) to the benzene ring are H(4)···C(11) 2.69 (2.77) Å and H(4)···C(12) 2.65 (2.69) Å. There are hydrogen bonds of lengths 2.949 (5) and 2.897 (4) Å between N(8*A*) and O(22*A*) ($-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$) and between N(8*B*)

and O(22*B*) ($\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$) respectively. These hydrogen bonds connect the molecules to form chains of molecules *A* and of molecules *B* in the [101] direction as illustrated in Fig. 2. The packing of the molecular chains is such that alternating layers of molecules *A* and of molecules *B* parallel to (010) can be distinguished. The interaction between the chains in a layer is between the 1-methoxy-3,5-dimethylbenzene groups across centres of symmetry. The overlap of these groups is indicated in Fig. 3; the ring-to-ring distances are 3.38 and 3.48 Å for molecules *A* and *B* respectively.

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Structure of Tetrafluoro-*p*-benzoquinone (*p*-Fluoranil) at 120 K

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Abstract. C₆F₄O₂, *M_r* = 180.0, monoclinic, *P*2₁/*c*, *a* = 6.524 (2), *b* = 5.354 (3), *c* = 8.825 (3) Å, β = 106.93 (3)°, *V* = 294.88 Å³, *Z* = 2, *D_m* = 1.90, *D_x*(298 K) = 1.90 g cm⁻³, MoKα, λ = 0.71069 Å, μ = 3.36 cm⁻¹, *F*(000) = 176, *T* = 120 K, final *R* = 0.043 (*wR* = 0.065) for 1046 reflections. Fluoranil exhibits distinct, albeit small, deviations from planarity. The departure from *D*_{2h} symmetry is discussed in terms of intramolecular interactions. The results are compared with those from room-temperature X-ray and electron diffraction studies.

Introduction. The molecular structures of a number of substituted *p*-benzoquinones, C₆O₂X₄ (*X* = H, CH₃, F

and Cl) have been determined by electron (Hagen & Hedberg, 1973, 1978; Schei, Hagen, Trætberg & Seip, 1980) and X-ray diffraction (Trotter, 1960; Chu, Jeffrey & Sakurai, 1962; Rabinovich, Schmidt & Ubell, 1967; van Weperen & Visser, 1972; Meresse, Cours-eille & Chanh, 1974; van Bolhuis & Kiers, 1978). The results of wide ranges of molecular structure determinations generally agree within experimental errors, although, of course, the concept of chemical bond lengths is implicitly defined in different ways by the two methods. Whereas this is also true for most of the *p*-benzoquinone systems studied hitherto, there are significant differences between the parameters of the *p*-fluoranil structures as determined by Schei *et al.*