

Fig. 2. Paire de molécules de l'isomère *E* de l'isonitrosocamphre, associées par liaisons hydrogène autour d'un centre de symétrie.

La molécule schématisée sur le Fig. 2 (ORTEP; Johnson, 1965) montre clairement qu'il s'agit bien de l'isomère *E* de la Fig. 1. Cette variété  $\beta$  de l'isomère *E* présente un arrangement cristallin où les molécules sont

associées par paires à l'aide de deux liaisons hydrogène équivalentes situées autour du centre de symétrie  $-\frac{1}{2}, \frac{1}{2}, 0$ :  $O(1)-H(1) = 0,91(5)$ ,  $H(1)\cdots N^i = 1,94(6)$ ,  $O(1)\cdots N^i = 2,785(4)$  Å,  $O(1)-H(1)\cdots N^i = 153(4)^\circ$  avec  $(i) = \bar{x}-1, 1-y, \bar{z}$ .

L'existence des deux formes cristallines  $\alpha$  et  $\beta$  est due vraisemblablement aux deux possibilités de formation de liaisons hydrogène intermoléculaires à l'état solide: soit  $N-O-H\cdots N$  (forme  $\beta$ ) soit probablement  $N-O-H\cdots O=C$  (forme  $\alpha$ ). Cela semble compatible avec les spectres d'absorption IR à l'état solide en milieu KBr. En effet pour la forme  $\alpha$  les bandes de vibration observées sont:  $\bar{\nu}_{OH} 3440$ ,  $\bar{\nu}_{CO} 1738$ ,  $\bar{\nu}_{CN} 1643$   $cm^{-1}$  tandis que pour la forme  $\beta$  les valeurs sont:  $\bar{\nu}_{OH} 3230$ ,  $\bar{\nu}_{CO} 1753$ ,  $\bar{\nu}_{CN} 1665$   $cm^{-1}$ . Dans les deux cas les valeurs  $\bar{\nu}_{OH}$  sont très différentes de celle correspondant à la vibration d'un OH libre ( $\bar{\nu} = 3650$   $cm^{-1}$ ) d'où l'existence de liaisons hydrogène. Pour la forme  $\alpha$ , on peut imaginer que les molécules sont liées en chaîne, parallèlement à un des axes  $2_1$  du groupe  $P2_12_12_1$ .

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## Structure of 5,14-Diacetyl-9b,9c,18b,18c-tetrahydrotetrabenzo[*b,b',f,f'*]cyclobuta-[1,2-*d:3,4-d'*]bisazepine

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**Abstract.**  $C_{32}H_{26}N_2O_2 \cdot 2\frac{2}{3}H_2O$ ,  $M_r = 518.6$ , trigonal,  $R\bar{3}$ ,  $a = 16.477(4)$  Å,  $\alpha = 116.8(2)^\circ$ ,  $V = 2019.2$  Å<sup>3</sup>,  $Z = 3$ ,  $D_m = 1.31$ ,  $D_x = 1.280$  Mg m<sup>-3</sup>,  $\lambda(Cu K\alpha) =$

$1.54178$  Å,  $\mu = 0.655$  mm<sup>-1</sup>,  $F(000) = 824$ ,  $T = 296$  K,  $R = 0.050$  for 1866 observed reflections. The molecule lies on a center of symmetry, and has a

*cis-anti-cis* configuration about the cyclobutane ring. The iminodibenzyl group has a folded conformation; the dihedral angle between the two planes of the benzene rings is  $115.7(2)^\circ$ . The water molecules arranged along the  $\bar{3}$  axis form hydrogen bonds which involve the disordered hydrogen atoms.

**Introduction.** The photodimerization of *N*-acetyl-dibenz[*b,f*]azepine yields the title compound. The structure of the photodimer in an anhydrous crystal has been reported by Harding (1983). The present X-ray work was performed in order to reveal the structure of the hydrated form. Iminodibenzyl and its related compounds are important pharmacological agents because of their antidepressant activity (Haffiger & Burckhardt, 1964). Large numbers of related compounds have been synthesized so far, and their stereochemistries have been studied (Kricka & Ledwith, 1974).

**Experimental.** Crystal grown from dichloromethane, transparent prism,  $0.3 \times 0.3 \times 0.4$  mm.  $D_m$  by flotation. Rigaku AFC-5RU diffractometer; graphite-monochromated Cu  $K\alpha$  radiation; lattice parameters from 20 reflections with  $18.8 < \theta < 25.8^\circ$ ; three standard reflections measured every 56 reflections, no significant change in intensities; 2174 reflections ( $-18 \leq h \leq 18$ ,  $0 \leq k \leq 18$ ,  $0 \leq l \leq 18$ ) in range  $0 < 2\theta < 120^\circ$ ; 1866 independent reflections with  $F_o > 3\sigma(F_o)$  used in further calculations, no absorption correction. Structure solved by *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), refined by full-matrix least squares;  $\sum w(|F_o| - |F_c|)^2$  minimized,  $w = [\sigma^2(F_o) + (0.023F_o)^2]^{-1}$ . H atoms except for water molecules from difference map, isotropic;  $R = 0.050$ ,  $wR = 0.067$ ,  $S = 1.3$ ,  $(\Delta/\sigma)_{\max} = 0.35$ , max. residual electron density  $0.8 \text{ e } \text{\AA}^{-3}$ . Scattering factors from *International Tables for X-ray Crystallography* (1974). All computations on a FACOM M382 in the Data Processing Center of Kyoto University, using *KPPXRAY* programs (Taga, Higashi & Iizuka, 1985).

**Discussion.** The final atomic parameters are given in Table 1.\* A perspective view of the molecule and the numbering scheme used are shown in Fig. 1. The asymmetric unit is half of the molecule. The cyclobutane ring is exactly planar owing to the crystallographic inversion center. The molecule has a *cis-anti-cis* configuration about the cyclobutane ring; the C(15)–C(10)–C(11)–C(12) torsion angle is

$-1.7(8)^\circ$ . Bond distances and bond angles are listed in Table 2. The C–C bond distances of  $1.576(8)$  and  $1.572(8)$  Å for the cyclobutane ring are significantly larger than the usual C–C single-bond distance, and they agree well with those observed in other planar cyclobutane rings, e.g.  $1.57$  and  $1.58$  Å for  $C_4Cl_8$  and  $1.573$  and  $1.566$  Å for tetraphenylcyclobutane (Margulis, 1965). They are, however, slightly longer than those in nonplanar rings, e.g.  $1.557$  and  $1.539$  Å for *trans-anti-trans*-tricyclo[6.4.0.0]dodecane (Salmon, Foltig, Streib & Kochi, 1974) and  $1.559$  and  $1.569$  Å for *cis-anti-cis*-tricyclo[8.6.0.0]hexadecane (Spek, Duisenberg, Timmermans & Mackor, 1985). The azepine ring has approximate mirror symmetry about a plane perpendicular to the C(10)–C(11) bond;

Table 1. Fractional coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters with e.s.d.'s in parentheses

$$B_{eq} = \frac{4}{3} \sum_i \beta_i a_i \cdot a_i$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
C(1)	-2113 (4)	1808 (4)	-1030 (4)	3.55 (13)
C(2)	-2012 (5)	1212 (4)	-672 (5)	4.26 (14)
C(3)	-550 (5)	2181 (5)	751 (5)	4.28 (11)
C(4)	827 (5)	3757 (4)	1830 (5)	3.48 (14)
N(5)	2157 (3)	5998 (3)	2606 (3)	2.52 (4)
C(6)	3269 (4)	8056 (4)	4953 (4)	2.98 (5)
C(7)	3372 (5)	9031 (4)	5709 (4)	3.59 (10)
C(8)	2456 (5)	8943 (4)	4890 (5)	3.60 (10)
C(9)	1424 (4)	7871 (4)	3312 (4)	3.20 (6)
C(10)	140 (4)	5709 (4)	796 (4)	2.73 (5)
C(11)	-890 (4)	3962 (4)	-447 (4)	2.76 (5)
C(12)	-743 (4)	3388 (4)	27 (4)	2.74 (5)
C(13)	720 (4)	4339 (4)	1454 (4)	2.67 (5)
C(14)	2269 (4)	7021 (4)	3389 (4)	2.44 (5)
C(15)	1294 (4)	6875 (4)	2519 (4)	2.49 (5)
C(16)	3385 (4)	6550 (4)	3044 (4)	3.05 (16)
O(17)	3251 (3)	5635 (3)	2398 (3)	4.38 (5)
C(18)	4888 (5)	8306 (5)	4315 (5)	4.29 (10)
O(W1)	1699 (7)	1699 (7)	1699 (7)	10.34 (20)
O(W2)	3922 (7)	4431 (7)	2897 (7)	12.36 (21)

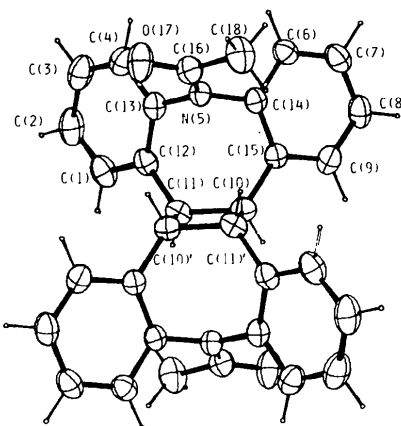


Fig. 1. Perspective view of the molecule with the atomic numbering scheme.

\* Lists of atomic parameters for H atoms, anisotropic thermal parameters for non-H atoms, and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42813 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond distances (Å) and bond angles (°)

C(1)—C(2)	1.386 (12)	C(8)—C(9)	1.384 (8)
C(1)—C(12)	1.397 (7)	C(9)—C(15)	1.392 (10)
C(2)—C(3)	1.375 (8)	C(10)—C(11)	1.576 (8)
C(3)—C(4)	1.384 (8)	C(10)—C(11')	1.572 (8)
C(4)—C(13)	1.388 (12)	C(10)—C(15)	1.504 (7)
N(5)—C(13)	1.445 (6)	C(11)—C(12)	1.505 (11)
N(5)—C(14)	1.442 (9)	C(12)—C(13)	1.391 (7)
N(5)—C(16)	1.367 (9)	C(14)—C(15)	1.397 (10)
C(6)—C(7)	1.384 (11)	C(16)—O(17)	1.222 (9)
C(6)—C(14)	1.386 (8)	C(16)—C(18)	1.503 (7)
C(7)—C(8)	1.381 (11)		
C(2)—C(1)—C(12)	121.1 (5)	C(1)—C(2)—C(3)	120.3 (5)
C(2)—C(3)—C(4)	119.9 (9)	C(3)—C(4)—C(13)	119.5 (6)
C(13)—N(5)—C(14)	115.2 (5)	C(13)—N(5)—C(16)	120.4 (6)
C(14)—N(5)—C(16)	123.8 (3)	C(7)—C(6)—C(14)	119.7 (7)
C(6)—C(7)—C(8)	119.8 (6)	C(7)—C(8)—C(9)	120.2 (7)
C(8)—C(9)—C(15)	121.4 (7)	C(11)—C(10)—C(15)	121.1 (6)
C(11)—C(10)—C(11')	90.0 (8)	C(10)—C(11)—C(12)	122.2 (4)
C(10)—C(11)—C(10')	90.0 (8)	C(1)—C(12)—C(11)	119.5 (4)
C(1)—C(12)—C(13)	117.4 (7)	C(11)—C(12)—C(13)	123.0 (4)
C(4)—C(13)—N(5)	119.1 (4)	C(4)—C(13)—C(12)	121.8 (4)
N(5)—C(13)—C(12)	119.0 (7)	N(5)—C(14)—C(6)	119.2 (6)
N(5)—C(14)—C(15)	119.1 (5)	C(6)—C(14)—C(15)	121.6 (7)
C(9)—C(15)—C(10)	119.8 (6)	C(9)—C(15)—C(14)	117.3 (5)
C(10)—C(15)—C(14)	122.9 (6)	N(5)—C(16)—O(17)	120.8 (4)
N(5)—C(16)—C(18)	118.1 (6)	O(17)—C(16)—C(18)	121.0 (7)

the C(10)—C(11)—C(12)—C(13) and C(11)—C(10)—C(15)—C(14) torsion angles are  $-40.6$  (9) and  $40.3$  (8)°, respectively, and N(5), C(10) and C(11) deviate from the least-squares plane of the C(1) benzene ring by 0.041, 0.719 and 0.073 Å, respectively, and from that of the C(6) ring by 0.006, 0.044 and 0.925 Å, respectively. The seven-membered-ring conformation differs from those of similar rings of iminodibenzyl (Reboul, Cristau, Estienne & Astier, 1980) and imipramine (Paulus, 1978; Post, Kennard & Horn, 1975). Rather it resembles those of rings with a double bond at C(10)—C(11), e.g. in iminostilbene (Reboul, Cristau, Soyfer & Estienne, 1980) and carbamazepine (Reboul, Cristau, Soyfer & Astier, 1981). The dihedral angle of  $115.7$  (5)° between the two planes of the benzene rings attached to the same azepine ring is obviously small in comparison with the corresponding angles of  $144.4$  (1)° for iminostilbene and  $126.6$  (1)° for carbamazepine. Thus the azepine ring seems to be deformed by the dimerization of the two azepine rings in the *cis* form about C(10)—C(11). However, N(5), C(13), C(14), C(16), O(17) and C(18) are coplanar within 0.05 Å, and N(5) and C(16) might keep their *sp*<sup>2</sup> character.

The crystal structure projected along the [111] axis is shown in Fig. 2. The molecules packed with van der Waals contacts make a tunnel along the  $\bar{3}$  axis. Water molecules are located in the tunnel, forming hydrogen bonds. A schematic diagram of the hydrogen bonding about the water molecules with interatomic distances and angles is given in Fig. 3. The rhombohedron consisting of eight O atoms lies on an inversion center, and the two rhombohedra are related by the other inversion center on the  $\bar{3}$  axis. Each water molecule is

surrounded by four O atoms. The O...O distances are, however, longer than the usual O...O hydrogen-bond distances, so the hydrogen bonds may be weak. The weakness of these bonds perhaps explains the fact that the crystalline water is easily removed from the crystal in a vacuum desiccator. By crystallographic symmetry, the H atoms attached to O(W1) necessarily occupy four positions if one lies on the  $\bar{3}$  axis, and the H atoms

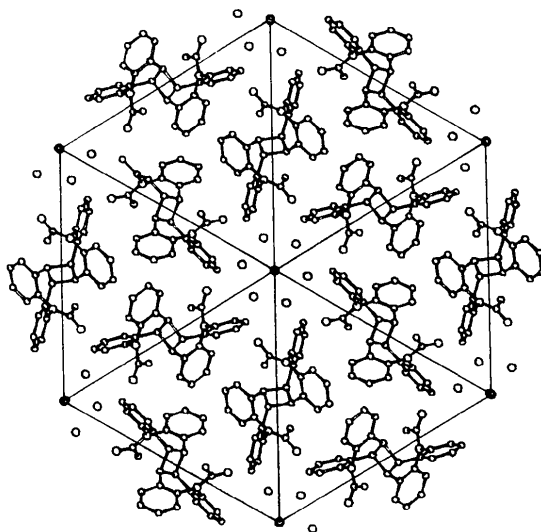


Fig. 2. Projection of the structure along the diagonal axis of the unit cell.

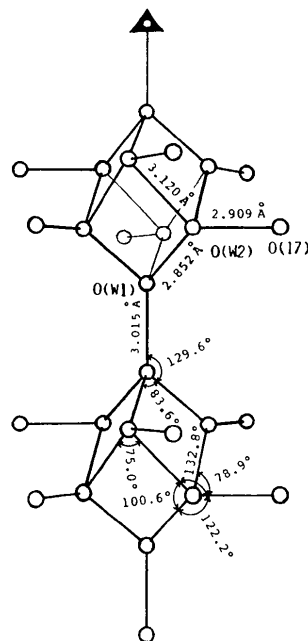


Fig. 3. Hydrogen-bonding diagram with O...O distances and O...O...O angles. E.s.d.'s for distances and angles are less than 0.005 Å and 0.8°, respectively.

involved in the hydrogen-bond system must be in a disordered state as observed in the structure of ice. Since the difference Fourier map did not give any definite peaks for the disordered H atoms, in the present analysis we assumed that the H atoms of each water molecule occupied four tetrahedral positions around the O atom with an equal probability, although several disordered models of the hydrogen bonds could be considered.

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## Structure du Complexe Dihydro-5,6 Pyrimidino[5,4-c]carbazole–[Bis(dihydro-5,6 Pyrimidino[5,4-c]carbazole)–Tétracyano-7,7,8,8 *p*-Quinodiméthane]–Eau (2/1/2)

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**Abstract.**  $2C_{14}H_{11}N_3 \cdot [2C_{14}H_{11}N_3 \cdot C_{12}H_4N_4] \cdot 2H_2O$ ,  $M_r = 1125.3$ ,  $P2_1/c$ ,  $a = 11.04$  (1),  $b = 15.146$  (9),  $c = 19.52$  (5) Å,  $\beta = 120.8$  (1)°,  $V = 2804$  (9) Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.31$ ,  $D_x = 1.33$  Mg m<sup>-3</sup>,  $Mo K\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 0.091$  mm<sup>-1</sup>,  $F(000) = 1176$ , room temperature, final  $R = 0.043$ ,  $wR = 0.051$  for 2523 independent reflections with  $I > 3\sigma(I)$ . The structure is composed of alternating stacks of two DPC molecules and one TCNQ molecule. The stacking direction is nearly parallel to the crystallographic  $a$  axis. The sandwich-like TCNQ molecules (between two DPC molecules), positioned on centres of symmetry are planar while the cyclohexadiene ring in the DPC molecule remains in a skew-chair conformation. The overlapping is rather large, essentially between the

pyrrole (of the DPC molecule) and the quinonoid (of the TCNQ molecule) rings. Moreover, another DPC molecule acts as a solvate and one water molecule is also inserted. Bond lengths in TCNQ show that the constituent molecules are essentially neutral.

**Introduction.** Les dérivés du dihydro-5,6 pyrimidino[5,4-c]carbazole (en abrégé DPC) à visée oncostatique et inspirés du modèle de l'ellipticine se sont montrés, au cours d'essais préliminaires, actifs sur la leucémie P388 de la souris. C'est la raison pour laquelle nous avons entrepris une étude radiocristallographique des différentes variétés polymorphiques, monocliniques I et II du DPC (Nguyen-Huy Dung, Viossat, Lancelot & Robba, 1984*a,b*).