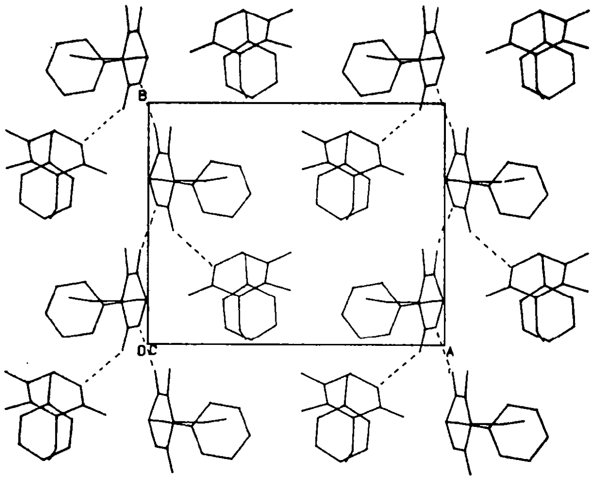

Fig. 2. The crystal structure of *cyclo*[-L-Phe-L-*N*(Me)-Abu-] viewed down **c**; dashed lines show the N—H···O hydrogen bonds [O(1*A*)···N(1A^{i}) 2·856 (6) Å, O(1*A*)—H(18)···N(1A^{i}) 158 (3)°, (i): $-x$, $0·5+y$, $-z$; N(1*B*)···O(2A^{ii}) 2·907 (5) Å, O(1*A*)—H(36)···N(1A^{i}) 170 (3)°, (ii): x, $1+y$, $-1+z$].

bonds. In effect, molecule *B* is only a hydrogen-bond donor while molecule *A* is a donor in one H bond and an acceptor in two bonds. The packing scheme is quite different from that observed in the other mono-*N*-methylated cyclic dipeptide, *cyclo*[-L-*N*(Me)-Phe-L-Phe-] (Gdaniec & Liberek, 1987) where two crystallographically independent molecules are joined by a pair of N—H···O hydrogen bonds to form dimers as distinct units in the crystal lattice.

The author thanks Professor B. Liberek of the University of Gdańsk for providing a sample of the compound. This work was partly supported by project RP.II.13.2.13.

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Structure of 1,4-Diaminoanthraquinone Dihydrate

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(*Received* 16 *December* 1987; *accepted* 1 *February* 1988)

Abstract. $C_{14}H_{10}N_2O_2.2H_2O$, $M_r = 274·28$, orthorhombic, *Pnma*, $a = 15·686$ (2), $b = 16·200$ (2), $c = 4·8507$ (3) Å, $V = 1232·6$ (2) Å^3, $Z = 4$, $D_m = 1·47$, $D_x = 1·478$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 0·87$ mm^{-1}, m.p. 541 K, $F(000) = 576$, $T = 293$ K, final $R = 0·039$ for 1024 unique reflections. The anthraquinone molecule has C_s symmetry in the crystal. The molecules are stacked along **c** with an interplanar spacing of 3·367 (2) Å. The dihedral angle between the molecules related by an *a* glide is 88·0 (1)°. The molecules related by a $\bar{1}$ and a 2_1 along **c** are linked together by three kinds of hydrogen bonds through the water molecules.

Introduction. The molecule of 1,4-diaminoanthraquinone has rather high molecular symmetry, C_{2v}. The present work has been undertaken as part of a study to obtain experimental data on the most probable space group for symmetrical molecules. In addition, tricyclic anthraquinones have recently drawn attention because of their anticancer activity (Neidle, 1984). Thus, it is also of value to determine the molecular structure and mode of molecular overlapping in the crystal for one of the fundamental compounds of the anthraquinones.

Experimental. Crystals grown by slow evaporation from pyridine, dark purple prisms elongated along **c**. D_m by

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flotation in aqueous KI. Systematic absences $0kl$ for $k+l$ odd, $hk0$ for h odd, indicating space group *Pnma* or $Pn2_1a$; reasonable structure from *Pnma*. Crystal 0·20 × 0·05 × 0·30 mm. Rigaku AFC-5 four-circle diffractometer. Lattice parameters determined with 20 reflections in the range $21 < 2\theta < 57°$ by least-squares method; intensities measured up to $(\sin\theta)/\lambda = 0{\cdot}5753$ Å^{-1}, ω–2θ scan method [scan speed 4° min^{-1} in ω, scan range (2θ): $1{\cdot}2° + 0{\cdot}15°\tan\theta$], Ni-filtered Cu $K\alpha$, 40 kV, 200 mA (rotating anode), background measured for 4 s on either side of the peak. Three standard reflections measured for every 57 reflections, fluctuation within 0·6% in F. Lorentz and polarization corrections; no absorption correction. All 1024 unique reflections (ranging over $h = 0$ to 18, $k = 0$ to 18, $l = 0$ to 5) used for refinement; 961 reflections larger than $1{\cdot}0\sigma(F_o)$. Structure solved by Patterson method, and refined (anisotropically for non-H atoms) by block-diagonal least squares; $\sum w(|F_o| - |F_c|)^2$ minimized, with $w = 1{\cdot}0/[\sigma(F_o)^2 - 0{\cdot}0392|F_o| + 0{\cdot}0021|F_o|^2]$ for $|F_o| > 0$, and $w = 2{\cdot}9878$ for $|F_o| = 0$; H-atom positions determined from difference Fourier map, and refined isotropically by least squares. Extinction correction for five strongest reflections [$I_{\text{corr}} = I_o(1 + 0{\cdot}87 \times 10^{-5}I_c)$]. $R = 0{\cdot}039$ for 1024 unique reflections, $wR = 0{\cdot}049$, $S = 1{\cdot}80$, $(\Delta/\sigma)_{\max}$ in final refinement cycle 0·08 for non-H atoms, 0·9 for H atoms; max. and min. $\Delta\rho$ in final difference Fourier map 0·11 and $-0{\cdot}16$ e Å^{-3}, atomic scattering factors from *International Tables for X-ray Crystallography* (1974), computations carried out at the Crystallographic Research Center, Institute for Protein Research, Osaka University, and at the Okayama University Computer Center; programs *RSSFR*-5 (Sakurai, 1967), *HBLS*-V and *DAPH* (Ashida, 1973), *MOLCON* (Fujii, 1979) and *ORTEP* (Johnson, 1965).

Discussion. Final atomic parameters are listed in Table 1.* The thermal ellipsoids of the molecules are shown in Fig. 1, with atomic numbering. Bond lengths and interbond angles are listed in Table 2.

The molecule has C_s symmetry in the crystal. The anthraquinone ring consisting of six-membered rings *A*, *B* and *C* (Fig. 1) is planar within 0·031 (2) Å. The dihedral angles between the planes of rings *A* and *B*, *B* and *C*, and *A* and *C* are 1·5 (1), 1·4 (1) and 0·0 (1)°, respectively. Ring *A* is planar within 0·001 (2) Å and N deviates by only 0·009 (2) Å from the plane. In ring *B*, the maximum deviation is 0·025 (2) Å at C(5). O(1) deviates by 0·101 (2) Å from the plane of ring *B*.

Table 1. *Final atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$$B_{\text{eq}} = \tfrac{4}{3}\textstyle\sum_i \beta_{ii}/a_i^{*2}.$$

	x	y	z	B_{eq}(Å^2)
O(1)	0·45335 (6)	0·08312 (5)	0·0139 (2)	3·88 (5)
N	0·57398 (8)	0·07905 (7)	0·3863 (3)	4·18 (6)
C(1)	0·56993 (8)	0·16203 (8)	0·3700 (3)	3·00 (5)
C(2)	0·62292 (8)	0·20872 (9)	0·5511 (3)	3·54 (6)
C(3)	0·29800 (8)	0·20728 (8)	−0·5422 (3)	3·52 (6)
C(4)	0·35030 (8)	0·16448 (8)	−0·3629 (3)	3·14 (5)
C(5)	0·45895 (7)	0·16035 (7)	0·0099 (3)	2·77 (5)
C(6)	0·40342 (8)	0·20684 (7)	−0·1814 (2)	2·59 (5)
C(7)	0·51638 (7)	0·20539 (7)	0·1860 (2)	2·63 (5)
O(*W*)	0·30148 (6)	0·00200 (6)	0·1718 (2)	4·80 (5)

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

The atoms related by a mirror plane in the molecule are shown with a prime.

O(1)–C(5)	1·254 (2)	C(3)–C(3′)	1·384 (3)
N–C(1)	1·348 (2)	C(4)–C(6)	1·393 (2)
C(1)–C(2)	1·426 (2)	C(5)–C(6)	1·479 (2)
C(1)–C(7)	1·413 (2)	C(5)–C(7)	1·440 (2)
C(2)–C(2′)	1·337 (3)	C(6)–C(6′)	1·398 (2)
C(3)–C(4)	1·382 (2)	C(7)–C(7′)	1·445 (2)
N–C(1)–C(2)	117·7 (1)	C(6)–C(5)–C(7)	118·9 (1)
N–C(1)–C(7)	124·1 (1)	C(4)–C(6)–C(5)	119·9 (1)
C(2)–C(1)–C(7)	118·2 (1)	C(1)–C(7)–C(5)	119·7 (1)
C(1)–C(2)–C(2′)	122·0 (1)	C(4)–C(6)–C(6′)	119·5 (1)
C(4)–C(3)–C(3′)	120·1 (1)	C(5)–C(6)–C(6′)	120·6 (1)
C(3)–C(4)–C(6)	120·4 (1)	C(1)–C(7)–C(7′)	119·8 (1)
O(1)–C(5)–C(6)	118·5 (1)	C(5)–C(7)–C(7′)	120·4 (1)
O(1)–C(5)–C(7)	122·7 (1)		

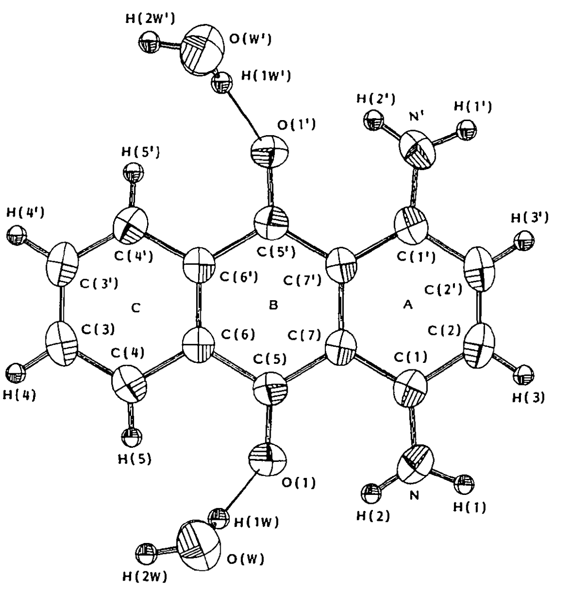

Fig. 1. View of the molecule with numbering of atoms. Ellipsoids of 50% probability are used for the non-H atoms; the H atoms are represented as spheres equivalent to $B = 1{\cdot}0$ Å^2. Atoms related by the mirror plane are denoted with a prime. The thin bonds show the hydrogen bond between the carbonyl group and the water molecule.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, and bond lengths and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44740 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Ring *C* is planar within 0·001 (2) Å. O(1) and N are linked by an intramolecular hydrogen bond [O(1)···N 2·617 (2), O(1)···H(2) 1·93 (2) Å, O(1)···H(2)—N 129 (1)°]. The N—C(1)—C(7) and O(1)—C(5)—C(7) angles are widened.

The C(1)—N length is shorter than the 1·38–1·42 Å found in anilines (Kashino, Tomita & Haisa, 1988), and the sum of the angles about N is 359 (1)°. This indicates that the N—C bond has a double-bond character. The C(5)—O(1) length is longer than the 1·20–1·23 Å found in some typical anthraquinones (Bailey & Brown, 1967*a*; Prakash, 1967; Schmalle, Jarchow, Hausen, Schulz, Krohn & Loock, 1986). Such a shortening of the C—N bond and a lengthening of the C=O bond are commonly found in 1-aminoanthraquinones (Bailey & Brown, 1967*b,c*; Brown & Mitchell, 1982), indicating a withdrawing of an electron from the amino group to the carbonyl O atom. Shortening of C(2)—C(2′) and lengthening of C(7)—C(7′) are noteworthy, as found in 1,4-bis(isopropylamino)anthraquinone (Brown & Mitchell, 1982).

The crystal structure projected along **c** is shown in Fig. 2. The plane of the anthraquinone molecule lies nearly parallel to (20$\bar{1}$), and makes an angle of 46·0 (1)° with the *c* axis. The interplanar distance between the stacking molecules is 3·367 (2) Å and a displacement between the molecules along the long molecular axis is 3·489 (2) Å. The molecules related by $\bar{1}$ are held together by two kinds of hydrogen bonds through the water molecule to form a sheet parallel to (100) [O(1)···O(*W*) 2·826 (2), O(1)···H(1*W*) 1·96 (2) Å, O(1)···H(1*W*)—O(*W*) 176 (2)°; O(*W*)···N^{ii} 3·184 (2), O(*W*)···H(1^{ii}) 2·26 (2) Å, O(*W*)···H(1^{ii})—N^{ii} 177 (2)°]. The sheets are stacked along **a** by van der Waals interactions between the molecules related by an *a* glide [the dihedral angle between the molecular planes being 88·0 (1)°] and by hydrogen bonds between the water molecules related by a 2_1 along **c** [O(*W*)···O(W^{iii}) 2·915 (2), O(*W*)···H($2W^{iii}$) 2·03 (2) Å, O(*W*)···H($2W^{iii}$)—O(W^{iii}) 167 (2)°]. A similar structure is found in 1,4-dihydroxynaphthalene [*Pnma*, $Z = 4$ (Gaultier & Hauw, 1967)]. Common features of both structures are the dimensions of *c*, the stacking mode of the molecules related by the *c* translation and the *a* glide, and the formation of a hydrogen bond around the 2_1 along **c**.

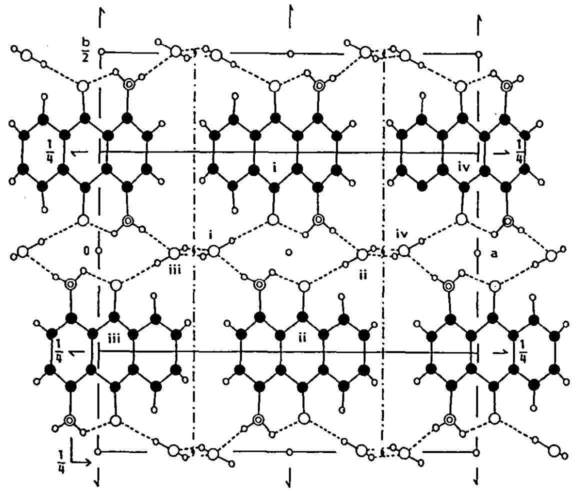

Fig. 2. The crystal structure projected along **c**. Hydrogen bonds are shown by broken lines. Symmetry codes: (i) x, y, z; (ii) $1-x, -y, 1-z$; (iii) $\frac{1}{2}-x, -y, \frac{1}{2}+z$; (iv) $\frac{1}{2}+x, y, \frac{1}{2}-z$.

The space group *Pnma* is frequently observed for crystals of compounds with molecular symmetry C_{2v} [1,4-dihydroxynaphthalene, 10-dicyanomethyleneanthrone (Silverman & Yannoni, 1967)] or C_s [1,8-dichloro-9-methylanthracene (Deliaca, Penfold & Robinson, 1969); 2,3,4,4-tetrachloro-1-oxo-naphthalene dihydride (Veenvliet & Migchelsen, 1971)].

The authors thank the Crystallographic Research Center, Institute for Protein Research, Osaka University, for the use of the facility.

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