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1*H*,4*H*-1-Methylpyridazino[1,2-*b*]benzo[*g*]phthalazine-6,13-dione*

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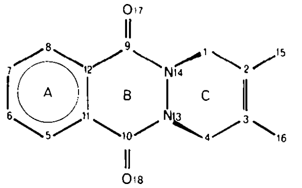
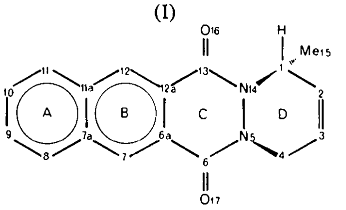
Abstract. $C_{17}H_{14}N_2O_2$, orthorhombic, $P2_12_12_1$, a = 17·647 (6), b = 9·760 (1), c = 7·890 (1) Å, Z = 4, D_x = 1·36 g cm^{-3}. Direct methods were used to determine the structure. Refinement by least squares gave R = 0·06. The molecule can be described as a strip twisted about 25° on average and bent about 5° from end to end. The methyl group is in a pseudo axial position.

Introduction. We recently described the crystal structure of the three-ring compound 2,3-dimethyl-4a,9a-diaza-1,4,4a,9,9a,10-hexahydroanthracene-9,10-dione (I) (Foces-Foces, Cano & García-Blanco, 1977). It seemed of interest to investigate the title compound (II) in order to ascertain the conformations of the pyridazine and diazaquinone rings, and, by comparison with (I), to see if there is any change in the pyridazine ring. No significance should be attached to the different chiralities of (I) and (II): they are drawn to match the listed coordinates, but the enantiomorph in either case would have been an equally acceptable solution.



(I)



(II)

A crystal 0·3 × 0·2 × 0·2 mm was used, and the lattice parameters and intensities were measured on a Philips PW 1100 four-circle diffractometer, with graphite-monochromated Mo $K\alpha$ radiation ($\omega/2\theta$ scan mode). 2905 reflections were recorded for $\theta \leq 33°$. Those reflections (1650) which had $I > 2\sigma(I)$ were considered as observed. The intensities were reduced to structure factors in the usual way. No absorption correction was considered necessary (μ = 0·98 cm^{-1}).

The structure was solved by the use of the *MULTAN* 74 system (Main, Woolfson, Lessinger, Germain & Declercq, 1974). An E map, computed from a set of 100 phases, revealed the positions of six of the 21 non-hydrogen atoms. The rest were obtained by means of the tangent formula and Fourier syntheses. All H atoms were located in a difference Fourier map.

A mixed least-squares refinement with positional and thermal parameters converged to R = 0·06. The reflections were weighted as follows: $w = 1/[f(F_o)]^2$, where $f(F_o) = 0{\cdot}99 - 0{\cdot}19|F_o| + 0{\cdot}14|F_o|^2$ when $0 < |F_o| \leq 1{\cdot}8$; $f(F_o) = 1{\cdot}61 - 0{\cdot}44|F_o| + 0{\cdot}04|F_o|^2$ when $1{\cdot}8 < |F_o| \leq 8{\cdot}0$; $f(F_o) = -0{\cdot}53 + 0{\cdot}12|F_o|$ when $8{\cdot}0 < |F_o| \leq 12{\cdot}0$; and $f(F_o) = -0{\cdot}14 + 0{\cdot}03|F_o|$ when $12{\cdot}0 < |F_o| \leq 150{\cdot}0$. The final weighted R_w was 0·07.

A final difference synthesis showed no peaks greater than 0·3 e Å^{-3}. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The positional parameters are listed in Table 1. The bond lengths and angles, with their estimated standard deviations, are given in Table 2. The conformational angular parameters are in Tables 3 and 4. Two perspective views of the molecule are shown in Fig. 1.†

Discussion. The pyridazine ring is considerably puckered and exhibits a half-chair conformation when viewed *via* the C(2)–C(3) bond; it is not a 'pure' half chair, but is slightly distorted. The atoms of the diazaquinone ring, including the attached O atoms, are almost coplanar (see Table 4), so its degree of puckering is low. Its conformation can be described as an envelope, but markedly distorted. The conformation

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* Crystal and Molecular Structure of Diazapolycyclic Compounds. IV.

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† Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33578 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

of these two rings may be described using the nomenclature introduced by Cano, Foces-Foces & García-Blanco (1977), although the estimators for the model E_1, E_2 are not fulfilled, and thus give rise to slight discrepancies in the values depending on the choice of φ_0. If we take the mean value, the conformational parameters are: pyridazine ring: $\tau_m = 26{\cdot}4°$, $q = 28{\cdot}6°$, $\Sigma = -1{\cdot}7°$, $\delta = 45{\cdot}2°$, $\alpha_1 = 21{\cdot}8$, $\alpha_2 = -23{\cdot}5°$; diazaquinone ring: $\tau_m = 3{\cdot}9°$, $q = 4{\cdot}7°$, $\Sigma = 108{\cdot}8°$, $\delta = 70{\cdot}0°$, $\alpha_1 = 89{\cdot}4$, $\alpha_2 = 19{\cdot}4°$. τ_m and q are high for pyridazine but low for diazaquinone, so the first is more puckered than the second. A 'perfect' half-chair at C(2)–C(3) would have $\Sigma = 0°$, $\delta = 0°$ whereas the pyridazine ring has $\Sigma = -1{\cdot}8°$, $\delta = 47{\cdot}2°$; thus the half-chair conformation is distorted. For the diazaquinone ring the perfect envelope 2,3 would have $\Sigma = \delta = 60°$ and at 1,2 $\Sigma = 80°$, $\delta = 60°$, so the observed envelope is quite distorted.

Although there is a similar conformation in (I) (Foces-Foces, Cano & García-Blanco, 1977), the absolute values for the amplitudes of torsion τ_m and q are higher in (II).

From the torsion angles (Table 3) we have calculated the distortion parameters (Winkler & Dunitz, 1971) about the C(13)–N(14) and C(6)–N(5) bonds; these are, respectively: $\chi_N = -27{\cdot}8$, $30{\cdot}6°$, $\chi_C = -5{\cdot}7$, $-0{\cdot}6°$, $\tau = 168{\cdot}0$, $170{\cdot}8°$. The mean bond angles for the groups at the N atoms are 118·1° and 117·7° respectively.

Some least-squares planes are given in Table 4 to illustrate the overall conformation of the molecule. Both aromatic rings can be considered coplanar. The molecule considered as a 'strip' can be described with reference to orthonormal axes $\{T,N,B\}$ (Fig. 2) (Foces-Foces, Cano & García-Blanco, 1977) by means of the

Table 1. *Final positional parameters* ($\times 10^4$, *for* H $\times 10^3$) *with their standard deviations, and bond distances* (Å) *for the hydrogen atoms*

	x	y	z	Bond length
C(1)	1594 (2)	2910 (3)	−2989 (3)	
C(2)	1944 (2)	1538 (4)	−2867 (4)	
C(3)	2248 (2)	1056 (4)	−1471 (4)	
C(4)	2257 (2)	1827 (3)	151 (3)	
N(5)	1758 (1)	3039 (2)	82 (2)	
C(6)	1618 (2)	3674 (3)	1599 (3)	
C(6*a*)	1409 (2)	5137 (3)	1520 (3)	
C(7)	1187 (2)	5800 (3)	2975 (3)	
C(7*a*)	991 (2)	7194 (3)	2931 (4)	
C(8)	738 (2)	7898 (4)	4422 (4)	
C(9)	558 (2)	9262 (4)	4333 (6)	
C(10)	618 (2)	9978 (3)	2818 (6)	
C(11)	839 (2)	9343 (3)	1347 (5)	
C(11*a*)	1037 (2)	7922 (3)	1379 (4)	
C(12)	1285 (2)	7235 (3)	−98 (4)	
C(12*a*)	1459 (2)	5861 (3)	−20 (3)	
C(13)	1639 (2)	5130 (3)	−1599 (3)	
N(14)	1776 (1)	3751 (2)	−1483 (2)	
C(15)	744 (2)	2839 (4)	−3258 (5)	
O(16)	1613 (2)	5679 (2)	−3001 (2)	
O(17)	1674 (2)	3033 (2)	2916 (2)	
H(1)	182 (2)	342 (4)	−382 (5)	0·91 (4)
H(2)	197 (2)	103 (4)	−392 (5)	0·97 (4)
H(3)	247 (3)	13 (4)	−147 (5)	0·99 (4)
H(4*a*)	279 (2)	210 (4)	45 (4)	1·01 (3)
H(4*b*)	204 (2)	127 (4)	106 (5)	0·98 (4)
H(7)	117 (2)	537 (3)	401 (4)	0·92 (3)
H(8)	73 (2)	746 (4)	550 (5)	0·95 (4)
H(9)	37 (3)	973 (5)	527 (5)	0·93 (4)
H(10)	47 (3)	1100 (5)	280 (6)	1·03 (5)
H(11)	93 (3)	983 (4)	30 (6)	0·96 (5)
H(12)	126 (3)	768 (4)	−109 (7)	0·89 (5)
H(15*a*)	52 (2)	238 (4)	−235 (6)	0·93 (4)
H(15*b*)	61 (3)	225 (5)	−425 (6)	1·00 (5)
H(15*c*)	54 (2)	379 (5)	−332 (5)	0·99 (4)

Table 2. *Bond lengths* (Å) *and valence angles* (°) *with standard deviations*

C(1)–C(2)	1·478 (5)	C(1)–C(15)	1·516 (5)	C(13)–O(16)	1·229 (3)	C(12)–C(12*a*)	1·377 (4)
C(2)–C(3)	1·312 (5)	N(5)–C(6)	1·370 (3)	C(6)–O(17)	1·217 (3)	C(7*a*)–C(8)	1·434 (5)
C(3)–C(4)	1·485 (4)	C(6)–C(6*a*)	1·476 (4)	C(6*a*)–C(7)	1·375 (4)	C(8)–C(9)	1·370 (6)
C(4)–N(5)	1·476 (4)	C(6*a*)–C(12*a*)	1·409 (4)	C(7)–C(7*a*)	1·404 (4)	C(9)–C(10)	1·389 (6)
N(5)–N(14)	1·418 (3)	C(12*a*)–C(13)	1·471 (4)	C(7*a*)–C(11*a*)	1·418 (4)	C(10)–C(11)	1·372 (6)
N(14)–C(1)	1·479 (3)	C(13)–N(14)	1·370 (4)	C(11*a*)–C(12)	1·414 (4)	C(11)–C(11*a*)	1·431 (5)

C(2)–C(1)–C(15)	112·4 (3)	C(6)–C(6*a*)–C(7)	119·4 (2)	C(7*a*)–C(11*a*)–C(12)	119·5 (3)
N(14)–C(1)–C(15)	110·6 (2)	C(7)–C(6*a*)–C(12*a*)	120·1 (2)	C(11)–C(11*a*)–C(12)	121·4 (3)
C(2)–C(1)–N(14)	111·1 (2)	C(6)–C(6*a*)–C(12*a*)	120·4 (2)	C(11*a*)–C(12)–C(12*a*)	119·7 (3)
C(1)–C(2)–C(3)	123·4 (3)	C(6*a*)–C(7)–C(7*a*)	120·4 (2)	C(6*a*)–C(12*a*)–C(12)	120·8 (2)
C(2)–C(3)–C(4)	123·1 (3)	C(7)–C(7*a*)–C(8)	121·4 (3)	C(6*a*)–C(12*a*)–C(13)	120·1 (2)
C(3)–C(4)–N(5)	111·6 (2)	C(8)–C(7*a*)–C(11*a*)	119·1 (3)	C(12)–C(12*a*)–C(13)	118·9 (2)
C(4)–N(5)–C(6)	116·0 (2)	C(11*a*)–C(7*a*)–C(7)	119·5 (3)	C(12*a*)–C(13)–O(16)	122·8 (3)
C(4)–N(5)–N(14)	114·3 (2)	C(7*a*)–C(8)–C(9)	119·7 (3)	C(12*a*)–C(13)–N(14)	117·2 (2)
C(6)–N(5)–N(14)	122·9 (2)	C(8)–C(9)–C(10)	121·1 (4)	N(14)–C(13)–O(16)	119·7 (2)
N(5)–C(6)–C(6*a*)	116·4 (2)	C(9)–C(10)–C(11)	121·5 (3)	N(5)–N(14)–C(13)	122·4 (2)
N(5)–C(6)–O(17)	119·9 (2)	C(10)–C(11)–C(11*a*)	119·5 (3)	N(5)–N(14)–C(1)	115·0 (2)
C(6*a*)–C(6)–O(17)	123·6 (2)	C(7*a*)–C(11*a*)–C(11)	119·1 (3)	C(1)–N(14)–C(13)	117·0 (2)

Table 3. *Torsion angles* (°) *with their standard deviations*

C(1)–C(2)–C(3)–C(4)	1·4 (5)	C(12*a*)–C(13)–N(14)–N(5)	−0·9 (4)	C(4)–N(5)–C(6)–C(6*a*)	155·2 (2)
C(2)–C(3)–C(4)–N(5)	11·5 (4)	C(13)–N(14)–N(5)–C(6)	−1·2 (4)	N(14)–N(5)–C(6)–O(17)	−173·7 (3)
C(3)–C(4)–N(5)–N(14)	−39·4 (3)	N(14)–N(5)–C(6)–C(6*a*)	5·8 (4)	N(14)–N(5)–C(6)–C(6*a*)	5·8 (4)
C(4)–N(5)–N(14)–C(1)	56·1 (3)	C(1)–N(14)–C(13)–O(16)	−23·0 (4)	H(1)–C(1)–C(2)–H(2)	−52 (4)
N(5)–N(14)–C(1)–C(2)	−40·4 (3)	C(1)–N(14)–C(13)–C(12*a*)	151·3 (2)	C(15)–C(1)–C(2)–H(2)	72 (3)
N(14)–C(1)–C(2)–C(3)	12·1 (4)	N(5)–N(14)–C(13)–O(16)	−175·3 (3)	H(2)–C(2)–C(3)–H(3)	−5 (4)
N(5)–C(6)–C(6*a*)–C(12*a*)	−8·5 (4)	N(5)–N(14)–C(13)–C(12*a*)	−0·9 (4)	H(3)–C(3)–C(4)–H(4*a*)	69 (4)
C(6)–C(6*a*)–C(12*a*)–C(13)	6·7 (4)	C(4)–N(5)–C(6)–O(17)	−24·2 (4)	H(3)–C(3)–C(4)–H(4*b*)	−52 (4)
C(6*a*)–C(12*a*)–C(13)–N(14)	−1·9 (4)				

Table 4. *Some conformational parameters describing the four-ring 'strip'*

Least-squares planes through the atoms stated (or marked with an asterisk) with their analytical expressions in direct space. The atomic deviations are in Å.

Plane through rings *A* and *B* (π_1 in Fig. 1*a*)

$$16\cdot7357x + 2\cdot3363y + 1\cdot6410z = 3\cdot8156$$

C(6)*	0·013	C(11*a*)*	−0·002	N(5)	−0·150
C(6*a*)*	−0·007	C(12)*	0·009	C(13)	−0·136
C(7)	0·014	C(12*a*)*	−0·008	N(14)	−0·211
C(7*a*)	0·005	C(1)	−0·958	C(15)	−2·441
C(8)*	−0·009	C(2)	−0·673	O(16)	−0·281
C(9)*	−0·006	C(3)	−0·048	O(17)	0·173
C(10)*	0·011	C(4)	0·413	H(1)	−0·605
C(11)*	−0·008				

Plane through 2,14 and centroid of (2,3,5,14) (π_2 in fig. 1*b*)

$$17\cdot1984x + 1\cdot8773y - 0\cdot9045z = 3\cdot8921$$

O(17)	−0·708	C(13)	0·035	C(4)	0·318
C(6)	−0·565	O(16)	0·220	C(1)	−0·334
N(5)	−0·306	C(3)	0·305	C(15)	−1·784
				H(1)	0·219

Plane through 1,13,14 (π_3)

$$16\cdot3559x + 1\cdot3827y - 2\cdot7428z = 3\cdot8296$$

C(15)	−1·326	O(16)	0·417	H(1)	0·662

Plane through 1,2,14 (π_4)

$$14\cdot4484x + 3\cdot3662y - 3\cdot6212z = 4\cdot3653$$

C(15)	−1·154	H(1)	0·793

Plane through 1,5,11 (π_5)

$$-2\cdot0517x + 8\cdot0491y + 4\cdot3670z = 0\cdot7097$$

C(2)	−1·123	N(14)	1·298

Plane through 13,14,16 (π_6)

$$17\cdot3449x + 1\cdot7417y + 0\cdot3569z = 3\cdot6801$$

Plane through 1,14,15 (π_7)

$$0\cdot7788x + 7\cdot9665y - 4\cdot5448z = 3\cdot8008$$

The angle between the line joining centroids of rings *A* and *B* and the line joining centroids of rings *C* and *D* is 4·5°.

Torsion angles: 9–10–2–3 = 29·5 (3), 7*a*–11*a*–2–3 = 28·7 (3), 6*a*–12*a*–2–3 = 29·5 (3)°.

Angles $\pi_1 \wedge \pi_2 = 19$, $\pi_5 \wedge \pi_4 = 86$, $\pi_6 \wedge \pi_7 = 81$°.

Plane	θ	φ	τ	κ
Ring *A*	0°	–	90°	0°
Ring *B*	0	–	90	0
Ring *C*	5	120°	92	4
Ring *D*	25	171	114	4

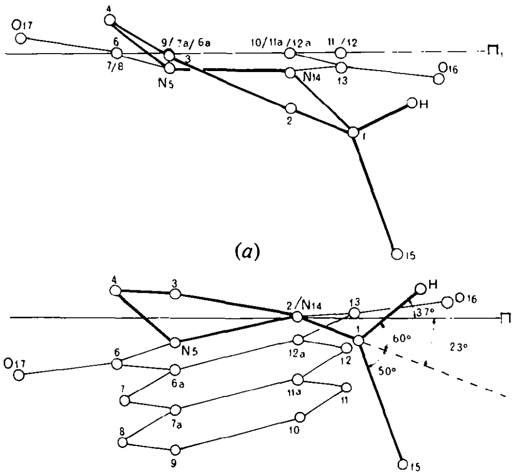

Fig. 1. The conformation of the rings showing the relative positions of C(15) and O(16), viewed along (*a*) the plane of the two benzene rings *A* and *B*, and (*b*) the plane through atoms 1, 2 and 14.

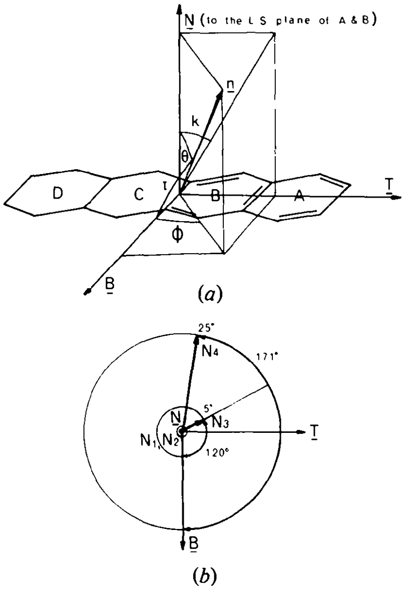

Fig. 2. (*a*) Orthonormal reference frame for the 'strip' description. (*b*) The φ angles (°).

angular parameters (τ,θ) or (φ,κ). But, as was pointed out by the referee, it is more significant to base the reference frame on the unit normal, N, to the aromatic moiety. It seems that the θ and φ parameters reveal changes more clearly. The four rings are then characterized by their normal N_i (Table 4) to give an idea of the overall twist (about 25° from end to end). The overall bend is described by an angle of about 5° formed between the line joining the centroids of both aromatic rings and the line joining the centroids of the other two rings.

The bonds C(1)—C(15) and C(1)—H(1) lie at 50 and 60° with respect to the plane through N(14), C(2) and C(1). However, the orientation of C(15) must be regarded as only pseudo axial since the dihedral angle between the planes [C(1),C(2),N(14)] and {N(14), C(2) and the centroid of [C(2),C(3),N(5),N(14)]} is a mere 23° instead of the ideal 54·74° (see Fig. 1).

We are grateful to Professor M. Lora-Tamayo and co-workers for suggesting the problem and supplying the material. We are also in debt to the referee for clarifying some ideas. We thank the Centro de Proceso de Datos del Ministerio de Educación y Ciencia (Madrid) for the use of the Univac 1108 computer. Most of the computations were performed with the XRAY system of crystallographic programs (Stewart, Kundell & Baldwin, 1970).

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SHORT COMMUNICATIONS

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Centaurepensin. A redetermination of its absolute configuration by X-ray crystallography.

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The present study shows that the absolute configuration of centaurepensin is opposite to the one previously reported [Mason, Hewson, Kennard & Pettersen (1972). *Chem. Commun.* pp. 460–461].

The crystal structure and absolute configuration of centaurepensin (chlorohyssopifolin A) have been reported (Mason, Hewson, Kennard & Pettersen, 1972; Hewson, Pettersen & Kennard, 1972). Recently, however, chemical studies (Gonzalez, Bermejo, Bretón, Massanet, Dominguez & Amaro, 1976) indicate that the absolute configuration is the opposite of that reported. The present investigation has been undertaken in order to clarify this situation.

Crystals of $C_{19}H_{24}Cl_2O_7$ are monoclinic, space group $P2_1$, with a = 10·467 (2), b = 9·248 (1), c = 11·504 (2) Å, β = 113·12 (1)°, D_c = 1·41 g cm^{-3}, Z = 2, μ(Cu $K\alpha$) = 31·96 cm^{-1}. A spherical crystal of radius $\simeq$ 0·25 mm was used to collect the intensities of all (1812) independent Friedel pairs in the range $2 < \theta < 65°$. A four-circle automatic diffractometer and monochromated Cu $K\alpha$ radiation were used. Data were corrected for absorption effects. 1793 observed Friedel pairs were used for anisotropic full-matrix least-squares refinement (Stewart, Kundell & Baldwin, 1970) of the previously reported atomic parameters (Hewson, Pettersen & Kennard, 1972). A weighting scheme was applied to prevent bias in $w(F_o - |F_c|)^2$. The present non-hydrogen atomic coordinates have been tested against the published ones in terms of a δp half-normal probability plot (Abrahams & Keve, 1971) which shows that all the δp terms lie on a line