2,3-Dihydroxy-2,3-dimethyl-4a,9a-diaza-1,2,3,4,4a,9,9a,10-octahydroanthracene-9,10-dione*

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Abstract. $C_{14}H_{16}N_2O_4$, monoclinic, $C2/c$, $a = 16.375$ (2), $b = 7.016$ (1), $c = 23.960$ (3) Å, $\beta = 96.81$ (1)°, $Z = 8$, $D_x = 1.34$ g cm^{-3}. The structure was solved by direct methods and refined to $R = 4.6\%$ for 1515 observed reflexions. The six-membered C ring has a chair conformation with the hydroxyl groups *trans*-axial to each other.

Introduction. The crystal and molecular structure of the title compound [(IV) in Fig. 1] has been determined as part of a broad project on tetracycline analogues and related compounds, including intermediate products in their synthesis (Foces-Foces, Cano & García-Blanco, 1977a).

Systematic absences indicated space groups Cc or $C2/c$. Accurate cell dimensions were obtained by least-squares refinement of the setting angles for 67

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reflexions with $\theta \le 25°$. A trigonal-prismatic crystal, slightly truncated at the lateral edges, approximately 0.13 mm in height and with base sides of 0.47 mm, was used for data collection. 2420 independent reflexions up to $\theta = 25°$ were measured by an ω–2θ scan on a
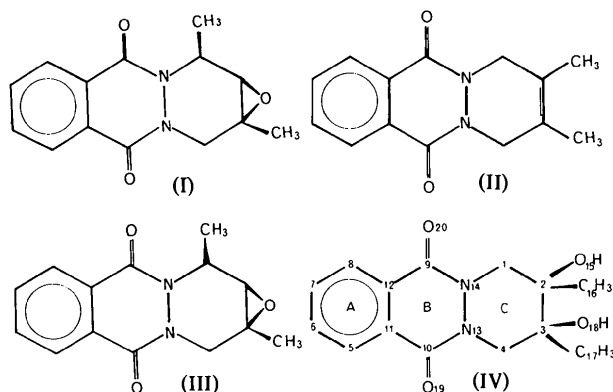

Fig. 1. Schematic drawings of the related molecules [(IV) is the title compound, showing the numbering of the atoms].

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		x	y	z	Bond length
C(1)	3748 (2)	−794 (4)	5196 (1)	H(1a)	339 (2)	−184 (5)	513 (1)	0.94 (4)
C(2)	3655 (2)	135 (4)	5755 (1)	H(1b)	434 (2)	−118 (5)	512 (2)	1.01 (4)
C(3)	4121 (2)	2045 (4)	5790 (1)	H(4a)	414 (2)	440 (5)	526 (1)	0.98 (4)
C(4)	3812 (2)	3244 (4)	5277 (1)	H(4b)	324 (2)	360 (5)	527 (1)	0.96 (4)
C(5)	3895 (2)	3382 (6)	3242 (2)	H(5)	420 (3)	457 (7)	329 (2)	0.97 (5)
C(6)	3631 (3)	2582 (8)	2729 (2)	H(6)	381 (3)	328 (6)	240 (2)	1.00 (5)
C(7)	3223 (3)	867 (8)	2690 (2)	H(7)	297 (3)	43 (8)	232 (2)	0.98 (5)
C(8)	3077 (3)	−81 (7)	3171 (2)	H(8)	286 (3)	−128 (7)	317 (2)	0.91 (5)
C(9)	3219 (2)	−370 (5)	4206 (1)	H(15)	258 (3)	−41 (7)	576 (2)	0.81 (5)
C(10)	4014 (2)	3274 (4)	4285 (1)	H(16a)	454 (3)	−144 (6)	624 (2)	0.94 (5)
C(11)	3757 (2)	2424 (5)	3733 (1)	H(16b)	365 (3)	−243 (8)	616 (2)	1.00 (6)
C(12)	3343 (2)	689 (5)	3696 (1)	H(16c)	392 (3)	−72 (7)	659 (2)	0.97 (5)
N(13)	3880 (1)	3248 (3)	4744 (1)	H(17a)	428 (2)	250 (5)	665 (2)	0.99 (4)
N(14)	3498 (1)	433 (3)	4706 (1)	H(17b)	344 (3)	334 (5)	637 (2)	0.96 (4)
O(15)	2810 (1)	618 (3)	5785 (1)	H(17c)	434 (3)	440 (7)	634 (2)	1.01 (5)
C(16)	3972 (2)	−1229 (5)	6222 (2)	H(18)	522 (3)	255 (7)	576 (2)	0.81 (5)
C(17)	4008 (3)	3176 (5)	6317 (2)					
O(18)	4966 (1)	1567 (3)	5779 (1)					
O(19)	4318 (2)	4872 (3)	4338 (1)					
O(20)	2903 (2)	−1958 (4)	4190 (1)					

Philips PW 1100 four-circle diffractometer, with graphite-monochromated Mo $K\alpha$ radiation. 1515 reflexions with $I > 2\sigma(I)$ were considered as observed. The intensities were corrected for Lorentz and polarization factors but not for absorption ($\mu = 1\cdot07$ cm^{-1}).

The structure was solved by direct methods (*MULTAN* 74; Main, Woolfson, Lessinger, Germain & Declercq, 1974), space group $C2/c$ being assumed. 19 out of 20 non-hydrogen atoms were located from an E map (125 E's) calculated with the set of phases having the highest combined figure of merit. The

remaining atom was located in a Fourier synthesis. After least-squares refinement of positional and thermal parameters, a difference map revealed all the H atoms. Mixed refinement (anisotropic for the heavy atoms and isotropic for the H atoms) yielded $R = 4\cdot6\%$ and $R_w = 7\cdot4\%$. Refinements in the alternative space group Cc were not successful in terms of R, U_{ij} and distances.

Weights were assigned as a function of $|F_o|$ to obtain $\langle w\Delta^2\rangle$ approximately constant over ranges of F_o and $\sin\theta/\lambda$. A final difference synthesis showed no residual electron density greater than $0\cdot19$ e Å^{-3}.

Atomic scattering factors for all atoms were those from *International Tables for X-ray Crystallography* (1974).

All atomic coordinates are listed in Table 1* together with the C—H bond lengths. Bond distances, valence angles and torsion angles are presented in Table 2.

Table 2. *Bond distances* (Å), *bond angles* (°) *and some torsion angles* (°) *describing the geometry of the molecule*

C(1)—C(2)	1·513 (4)	C(6)—C(7)	1·374 (8)
C(1)—N(14)	1·474 (4)	C(7)—C(8)	1·376 (7)
C(2)—C(3)	1·539 (4)	C(8)—C(12)	1·391 (6)
C(2)—O(15)	1·435 (4)	C(9)—C(12)	1·463 (5)
C(2)—C(16)	1·516 (5)	C(9)—O(20)	1·227 (4)
C(3)—C(4)	1·525 (4)	C(9)—N(14)	1·354 (4)
C(3)—C(17)	1·520 (5)	C(10)—C(11)	1·465 (5)
C(3)—O(18)	1·427 (3)	C(10)—O(19)	1·228 (4)
C(4)—N(13)	1·472 (4)	C(10)—N(13)	1·354 (4)
C(5)—C(6)	1·375 (6)	C(11)—C(12)	1·390 (5)
C(5)—C(11)	1·396 (5)	N(13)—N(14)	1·417 (3)

C(2)—C(1)—N(14)	113·9 (2)	C(12)—C(9)—N(14)	117·5 (3)
C(1)—C(2)—C(3)	108·8 (3)	C(12)—C(9)—O(20)	122·3 (3)
C(1)—C(2)—O(15)	110·2 (2)	N(14)—C(9)—O(20)	120·1 (3)
C(1)—C(2)—C(16)	108·6 (3)	C(11)—C(10)—N(13)	117·4 (3)
C(3)—C(2)—O(15)	105·5 (2)	C(11)—C(10)—O(19)	122·4 (3)
C(3)—C(2)—C(16)	112·7 (3)	N(13)—C(10)—O(19)	120·2 (3)
O(15)—C(2)—C(16)	111·0 (3)	C(10)—C(11)—C(12)	119·9 (3)
C(2)—C(3)—C(4)	108·7 (2)	C(5)—C(11)—C(12)	119·6 (3)
C(2)—C(3)—C(17)	113·1 (3)	C(5)—C(11)—C(10)	120·4 (3)
C(2)—C(3)—O(18)	105·6 (2)	C(9)—C(12)—C(11)	120·4 (3)
C(4)—C(3)—C(17)	108·7 (3)	C(8)—C(12)—C(11)	119·7 (4)
C(4)—C(3)—O(18)	110·2 (3)	C(8)—C(12)—C(9)	119·9 (3)
C(17)—C(3)—O(18)	110·6 (3)	C(4)—N(13)—C(10)	119·3 (2)
C(3)—C(4)—N(13)	112·7 (2)	C(4)—N(13)—N(14)	113·8 (2)
C(6)—C(5)—C(11)	119·5 (4)	C(10)—N(13)—N(14)	122·6 (3)
C(5)—C(6)—C(7)	121·2 (5)	C(1)—N(14)—N(13)	113·3 (2)
C(6)—C(7)—C(8)	119·8 (4)	C(1)—N(14)—C(9)	119·6 (2)
C(7)—C(8)—C(12)	120·3 (4)	C(9)—N(14)—N(13)	122·0 (3)

C(1)—N(14)—C(9)—C(12)	−151·8 (3)
C(1)—N(14)—C(9)—O(20)	25·6 (4)
N(13)—N(14)—C(9)—C(12)	1·5 (4)
N(13)—N(14)—C(9)—O(20)	178·9 (3)
C(4)—N(13)—C(10)—C(11)	−156·1 (3)
C(4)—N(13)—C(10)—O(19)	22·0 (4)
N(14)—N(13)—C(10)—C(11)	−0·9 (4)
N(14)—N(13)—C(10)—O(19)	177·2 (3)
O(15)—C(2)—C(3)—O(18)	178·1 (2)
C(16)—C(2)—C(3)—C(17)	−64·2 (3)
H(1a)—C(1)—C(2)—O(15)	−54 (2)
H(1b)—C(1)—C(2)—O(15)	−179 (2)
H(1a)—C(1)—C(2)—C(16)	68 (2)
H(1b)—C(1)—C(2)—C(16)	−57 (2)
H(4a)—C(4)—C(3)—C(17)	63 (2)
H(4b)—C(4)—C(3)—C(17)	−59 (2)
H(4a)—C(4)—C(3)—O(18)	−58 (2)
H(4b)—C(4)—C(3)—O(18)	−180 (2)

Discussion. The numbering system of the molecule is shown in Fig. 1. The mean angles around N(13) and N(14) are 118·6 and 118·3°. As expected, the conformational parameters χ_N (−24·8; −26·7°), χ_C (1·9; 2·6°) and τ (10·6; 13·6°) given by Winkler & Dunitz (1971) show deformations which are greater at the N than at the C atoms.

A perspective view of the molecule, as seen parallel to the benzene ring plane, is shown in Fig. 2. The least-squares plane through rings A and B in (IV) shows that they are planar within 0·03 Å. O(20) and O(19) deviate from this plane by 0·07 and −0·12 Å respectively.

Intermolecular hydrogen bonds have been found between the carbonyl O atoms and the OH groups: O(20)^i···O(15) = 2·82 Å, O(20)^i···H(15)—O(15) = 171°; O(19)^{ii}···O(18) = 2·79 Å, O(19)^{ii}···H(18)—O(18) = 172° [(i) $-x + \frac{1}{2}$, $-y - \frac{1}{2}$, $-z + 1$; (ii) $-x + 1$, $-y + 1$, $-z + 1$].
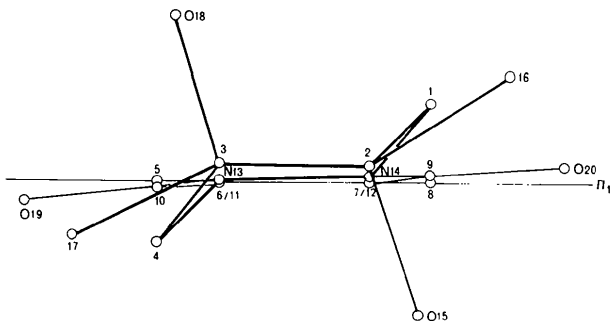

Fig. 2. Perspective view of the molecule as seen parallel to the plane through the benzene ring.

Table 3. *Comparison of intra-annular torsion angles (°) in the C rings of the related compounds (Fig. 1)*

	(I)[a]	(II)[b]	(III)[c]	(IV)[d]
C(1)–C(2)–C(3)–C(4)	0·8 (3)	−0·1 (2)	0·1 (2)	54·5 (3)
C(2)–C(3)–C(4)–N(13)	19·6 (2)	−6·3 (2)	24·2 (2)	−55·3 (3)
C(3)–C(4)–N(13)–N(14)	−4·1 (2)	24·6 (1)	−52·7 (2)	53·8 (3)
C(4)–N(13)–N(14)–C(1)	−32·3 (2)	−36·6 (1)	57·6 (2)	−50·8 (3)
N(13)–N(14)–C(1)–C(2)	50·7 (2)	28·9 (2)	−30·3 (2)	52·3 (3)
N(14)–C(1)–C(2)–C(3)	−34·6 (3)	−10·8 (2)	1·9 (2)	−54·2 (3)

References: (a) Foces-Foces, Cano & Garcia-Blanco (1977a). (b) Foces-Foces, Cano & Garcia-Blanco (1977b). (c) Foces-Foces, Cano & Garcia-Blanco (1978). (d) This work.

The hydroxyl groups are *trans*–axial to each other. O(15) and O(18) deviate by 2·1 and 1·5° respectively from the theoretical axial position. The deviations of the equatorial methyl C atoms, C(17) and C(16), are 2·3 and 3·4° respectively.

The C ring has a chair conformation, while in other related compounds [(I), (II) and (III) in Fig. 1] (Foces-Foces, Cano & Garcia-Blanco, 1977a,b, 1978) it has approximately diplanar, half-chair and envelope conformations respectively, as shown in Table 3.

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# The Structure of 2-(2,6-Dimethylphenylimino)-3,3-dimethyl-4,4-diphenylthietane

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Abstract. $C_{25}H_{25}NS$, orthorhombic, $P2_12_12_1$, $Z = 4$, $a = 12·598$ (3), $b = 17·763$ (4), $c = 9·376$ (3) Å, $D_c = 1·16$ g cm^{-3}, μ(Cu $K\alpha$) = 13·2 cm^{-1}. The structure was solved by direct methods and refined by full-matrix least squares to an R value of 0·061. The thietane ring is puckered with dihedral angles of 20 and 21° and contains a $C(sp^3)$–$C(sp^3)$ single bond distance of 1·591 Å.

Introduction. As a part of a study on the molecular structure of the 1:1 adducts between thiobenzophenone (I) and substituted ketenimines (II)

$Ph_2C=S$ $R_2^1C=C=N–R^2$ (a) $R^1 = Ph; R^2 = p\text{-}MeC_6H_4$
   (I)   (II)   (b) $R^1 = Me; R^2 = 2,6\text{-}Me_2C_6H_3$
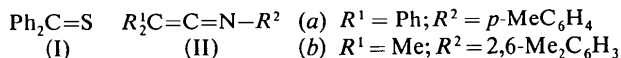
we have recently determined (Dondoni, Battaglia, Giorgianni, Gilli & Sacerdoti, 1977; Sacerdoti, Bertolasi, Gilli, Dondoni & Battaglia, 1977) the crystal structure of the adduct between (I) and (IIa). Rather unexpectedly this turned out to be a six-membered heterocycle, *i.e.* a 4H-3,1-benzothiazine. In the present paper the crystal structure of the product of the reaction between (I) and (IIb) is reported, proving that such reaction leads to a 2-iminothietane derivative (III) by a 2 + 2 cyclo-addition.

(III)