Table 3. *Distances (Å) of atoms from different planes in the molecule*

Plane 1: plane fitted to the C atoms of the phenyl ring

$$0\cdot46914x + 0\cdot48589y + 2\cdot29650z = 1\cdot00000$$

Plane 2: plane through the C(7), N and O atoms of the amide group

$$0\cdot06545x + 0\cdot53452y + 2\cdot39539z = 1\cdot00000$$

	Plane 1	Plane 2		Plane 1	Plane 2
C(1)	0·003 (3)	–	N	–	0·000 (0)
C(2)	0·004 (3)	–	O	–	0·000 (0)
C(3)	–0·007 (2)	–	H(1)	0·03 (2)	–
C(4)	0·002 (2)	–0·012 (2)	H(2)	0·03 (2)	–
C(5)	0·005 (2)	–	H(3)	0·01 (2)	–
C(6)	–0·007 (3)	–	H(4)	0·00 (2)	–
C(7)	0·069 (2)	0·000 (0)	H(5)	0·01 (2)	–
C(8)	–	–0·033 (2)	H(6)	–	0·08 (2)

terephthalamide (Harkema, Gaymans, van Hummel & Zylberlicht, 1979). From Table 3 it can be concluded that C(7) and C(8) deviate significantly from the planes of the phenyl ring and the amide group respectively.

The molecules of TMDB are connected by N–H···O hydrogen bonds of length 2·999 (4) Å. Hydrogen bonds are formed between molecules related by translation along *a*. Each molecule is hydrogen bonded to two neighbors, giving rise to a one-dimensional hydrogen-bonding scheme.

References

BLAKE, C. C. F. & SMALL, R. W. H. (1972). *Acta Cryst.* B28, 2201–2206.

GAYMANS, R. J. & HARKEMA, S. (1977). *J. Polym. Sci. Polym. Phys. Ed.* 15, 587–590.

HARKEMA, S. & GAYMANS, R. J. (1977). *Acta Cryst.* B33, 3609–3611.

HARKEMA, S., GAYMANS, R. J., VAN HUMMEL, G. J. & ZYLBERLICHT, D. (1979). *Acta Cryst.* B35, 506–508.

JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

WILLIS, B. T. M. & PRYOR, A. W. (1975). *Thermal Vibrations in Crystallography*, pp. 101–102. Cambridge Univ. Press.

The Correct Structural Formula for Anthralin*

BY F. R. AHMED

*Division of Biological Sciences, National Research Council of Canada, Ottawa, Canada K1A 0R6*

Abstract. $C_{14}H_{10}O_3$, $M_r = 226\cdot23$, monoclinic, $A2/a$, $a = 20\cdot857$ (3), $b = 9\cdot264$ (3), $c = 11\cdot225$ (3) Å, $\beta = 104\cdot79$ (2)°, $Z = 8$, $d_o = 1\cdot433$, $d_c = 1\cdot433$ Mg m^{-3}, $R = 0\cdot055$ and $R_w = 0\cdot056$ for 1118 observed reflexions. Anthralin (or dithranol) is confirmed as 1,8-dihydroxy-9-anthrone instead of 1,8,9-anthracenetriol which is the formula presently assigned in pharmaceutical literature. The molecule is almost planar with approximate mirror symmetry, and includes intramolecular O–H···O···H–O bonds associated with an elongated C=O length of 1·261 (4) Å at the central O atom.

Introduction. Anthralin is a parasiticide used as ointment or paint in the treatment of psoriasis, ringworm infections and other chronic dermatosis. It is listed as a reference standard in the current *United States Pharmacopeia* (1975), and under dithranol in the *British Pharmacopeia* (1973) with the structural

formula 1,8,9-anthracenetriol or 1,8,9-trihydroxy-anthracene, (I). Spectroscopic examination of anthralin by Avdovich & Neville (1980) led to the keto structure 1,8-dihydroxy-9-anthrone, (II), and the present X-ray analysis has confirmed this assignment.

(I)   (II)
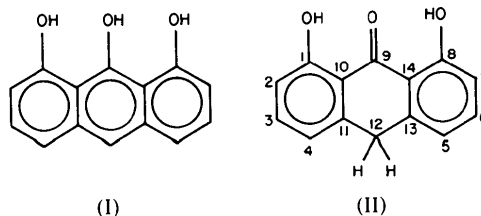
X-ray measurements were carried out on a Nonius CAD-4 diffractometer with a thin-plate crystal 0·33 × 0·23 × 0·07 mm, and Ni-filtered Cu *K*α radiation at a take-off angle of 3·0°. The cell dimensions were derived by least squares from the angular settings of 15 centered reflexions ($\theta = 37$–48°). The intensities were recorded by ω–2θ scans for all reflexions within one hemisphere up to $\theta = 65°$ for scan ranges of $\Delta\theta = (0\cdot8$

+ 0·16 tan θ)° at θ speeds ≤2° min⁻¹. The scans were extended by 0·25 $\Delta\theta$ for background measurements at each end of the scan. Three reflexions which were monitored every 50 min for scaling showed maximum random variations of ±3% from their mean values. The net intensities were corrected for scale, and for Lorentz and polarization effects but not for absorption, μ = 0·787 mm⁻¹. After averaging equivalent reflexions, 1119 were classified as observed and 692 as unobserved, $I < 1\cdot5\sigma(I)$. The density was measured by flotation in aqueous KI solution.

The phases of 247 reflexions with $|E| > 1\cdot2$ were estimated by the symbolic-addition procedure (Karle & Karle, 1963), but the resulting E map produced two images of the molecule with a separation equivalent to a strong intermolecular vector. Although the occurrence of double images in E maps has been observed for several structures, the separation by an intermolecular vector has not been reported heretofore. The correct molecular position was taken as the average of the two images. Partial refinement followed by a difference map at $R = 0\cdot11$ produced all the H positions.

Refinement by block-diagonal least squares on $\sum w(|F_o| - |F_c|)^2$ ($w = \{1 + [(|F_o| - 25)/20]^2\}^{-1}$), excluding 200 and the unobserved reflexions, converged at $R = 0\cdot055$ and $R_w = 0\cdot056$ for the observed reflexions; mean and maximum shifts were 0·1 and 0·5

Table 1. *Fractional coordinates* ($\times10^4$; $\times10^3$ *for* H) *and* B_{eq} (Å²)

$$B_{eq} = \tfrac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
C(1)	1545 (2)	4729 (4)	7524 (3)	4·8
C(2)	2138 (2)	4151 (4)	7409 (4)	5·7
C(3)	2131 (2)	2959 (4)	6676 (4)	6·3
C(4)	1540 (2)	2332 (4)	6059 (4)	5·5
C(5)	−928 (2)	2282 (4)	4976 (3)	5·2
C(6)	−1517 (2)	2896 (5)	5061 (3)	5·7
C(7)	−1517 (2)	4101 (4)	5764 (3)	5·4
C(8)	−925 (2)	4718 (4)	6389 (3)	4·2
C(9)	312 (2)	4750 (3)	6960 (3)	4·1
C(10)	934 (2)	4113 (4)	6883 (3)	4·1
C(11)	939 (2)	2884 (4)	6146 (3)	4·3
C(12)	304 (2)	2183 (4)	5482 (3)	5·3
C(13)	−327 (2)	2864 (3)	5590 (3)	4·1
C(14)	−316 (2)	4113 (3)	6318 (3)	3·8
O(1)	1579 (1)	5899 (3)	8261 (2)	6·4
O(8)	−952 (1)	5913 (3)	7072 (2)	5·5
O(9)	312 (1)	5875 (3)	7593 (2)	5·5
H(2)	257 (2)	457 (4)	791 (3)	5·9 (1·1)
H(3)	255 (2)	260 (5)	660 (3)	5·2 (1·0)
H(4)	155 (2)	154 (4)	558 (3)	3·3 (0·8)
H(5)	−95 (2)	145 (4)	443 (3)	3·6 (0·8)
H(6)	−195 (2)	253 (4)	459 (4)	4·8 (0·9)
H(7)	−193 (2)	454 (4)	585 (3)	3·0 (0·8)
H(12, 1)	30 (2)	115 (4)	570 (3)	5·8 (1·1)
H(12, 2)	30 (2)	213 (4)	462 (3)	4·4 (0·9)
H(O1)	108 (2)	628 (5)	809 (4)	8·9 (1·4)
H(O8)	−46 (2)	616 (4)	748 (3)	5·1 (1·0)

of the e.s.d.'s $\{[\sum w\Delta^2/(m - n)]^{1/2} = 0\cdot94\}$. Only three of the 692 unobserved reflexions were calculated higher than 1·5 times their threshold amplitudes, and the residual electron density in the final difference map was within −0·22 and 0·13 e Å⁻³. The refined parameters are listed in Table 1.* Scattering factors were those of Hanson, Herman, Lea & Skillman (1964) for C and O, and of Stewart, Davidson & Simpson (1965) for H. All computations were performed with the NRC program system (Ahmed, Hall, Pippy & Huber, 1973).

Discussion. The molecule is approximately planar except for the two H atoms on C(12); $\chi^2 = 8\cdot8$, 32·7, and 0·8 for rings A, B, and C, respectively, but is considerably higher (304·9) for the mean plane of the 14 C atoms. The interplanar angles are $A–B = 1\cdot54$, $B–C = 1\cdot77$ and $A–C = 0\cdot45°$. O(1), O(8) and O(9) are displaced by −0·015 (3), 0·021 (3) and 0·000 (3) Å from the planes of their respective rings, and by −0·057 (3), 0·022 (3) and 0·032 (3) Å from the mean plane of the 14 C atoms.* The molecules in the unit cell are stacked head to tail in a zigzag fashion as shown in the projection along the normal to the mean planes (Fig. 1), with interplanar spacings of 3·611 (5) and 3·647 (5) Å.

The molecule has an approximate mirror plane through O(9), C(9) and C(12) normal to the molecular plane. Equivalent bond lengths and angles across the mirror plane are in good agreement, Table 2, where the maximum deviations are 0·008 (8) Å and 0·8 (4)°. The mean values for the two chemically equivalent halves of the molecule are presented in Fig. 2.

* Lists of structure factors and anisotropic thermal parameters, and details of some mean planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35580 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
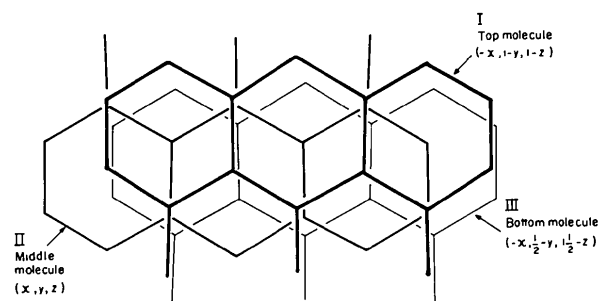

Fig. 1. Molecular stacking viewed along the normal to the molecular plane. Adjacent molecules are rotated by 180° and shifted sideways by ±1·2 Å. Interplanar spacings are 3·61 and 3·65 Å.

Table 2. *Bond lengths* (Å) *and angles* (°)

Equivalent values across the mirror plane are listed for each distance and angle.

|	Left side	Right side		Left side	Right side		Left side	Right side
C(1)–C(2)	1·384 (6)	1·379 (6)	C(2)–C(1)–C(10)	120·5 (4)	120·6 (3)	C(10)–C(11)–C(12)	120·4 (3)	120·6 (3)
C(1)–C(10)	1·414 (6)	1·409 (6)	C(2)–C(1)–O(1)	117·3 (3)	117·7 (3)	C(1)–C(10)–C(11)	119·0 (3)	118·5 (3)
C(1)–O(1)	1·354 (4)	1·356 (4)	C(10)–C(1)–O(1)	122·3 (3)	121·7 (3)	C(1)–C(10)–C(9)	120·7 (3)	121·5 (3)
C(2)–C(3)	1·375 (6)	1·367 (6)	C(1)–C(2)–C(3)	119·6 (4)	120·0 (4)	C(9)–C(10)–C(11)	120·4 (3)	120·0 (3)
C(3)–C(4)	1·379 (6)	1·379 (6)	C(2)–C(3)–C(4)	120·7 (4)	120·5 (4)	C(10)–C(9)–O(9)	119·9 (3)	119·1 (3)
C(4)–C(11)	1·380 (6)	1·377 (6)	C(3)–C(4)–C(11)	121·3 (4)	121·1 (4)	C(10)–C(9)–C(14)	120·9 (3)	–
C(11)–C(12)	1·492 (6)	1·492 (6)	C(4)–C(11)–C(10)	118·9 (4)	119·2 (3)	C(11)–C(12)–C(13)	117·7 (3)	–
C(11)–C(10)	1·409 (5)	1·413 (4)	C(4)–C(11)–C(12)	120·6 (3)	120·2 (3)			
C(10)–C(9)	1·448 (6)	1·450 (5)						
C(9)–O(9)	1·261 (4)	–						
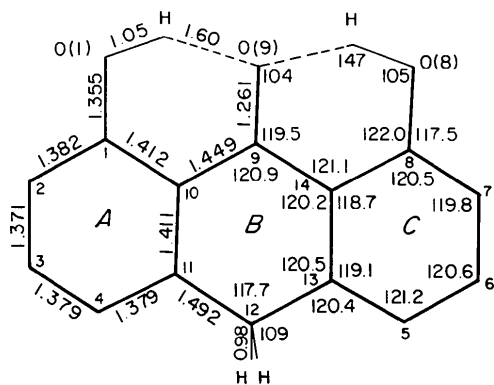
Fig. 2. Mean bond lengths (Å) and angles (°). E.s.d.'s are 0·003–0·004 Å and 0·2–0·3°.

The H atoms of the two hydroxyl groups are directed towards O(9) to form two intramolecular hydrogen bonds O(1)–H···O(9)···H–O(8) (Fig. 2), where the O···O separations are 2·556 (3) and 2·551 (3) Å. No intermolecular interactions shorter than van der Waals contacts are observed, the shortest being O(1)···H(3') = 2·38 (4) Å. The double-bond character of C(9)=O(9) seems to have been weakened by the involvement of O(9) in two intramolecular hydrogen bonds. Its length is 1·261 (4) Å, compared to 1·254 (3) Å for C=O···HO in nalidixic acid (Huber,

Gowda & Acharya, 1980) and 1·23 (1) Å for ketones (*Molecular Structures and Dimensions*, 1972).

References

Ahmed, F. R., Hall, S. R., Pippy, M. E. & Huber, C. P. (1973). NRC Crystallographic Programs for the IBM/ 360 System. Accession Nos. 133–147 in *J. Appl. Cryst.* 6, 309–346.

Avdovich, H. & Neville, G. A. (1980). *Can. J. Spectrosc.* In the press.

British Pharmacopeia (1973). p. 176. London: HMSO.

Hanson, H. P., Herman, F., Lea, J. D. & Skillman, S. (1964). *Acta Cryst.* 17, 1040–1044.

Huber, C. P., Gowda, D. S. S. & Acharya, K. R. (1980). *Acta Cryst.* B36, 497–499.

Karle, I. L. & Karle, J. (1963). *Acta Cryst.* 16, 969–975.

Molecular Structures and Dimensions (1972). Vol. A1, Part S2. Utrecht: Oosthoek.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* 42, 3175–3187.

United States Pharmacopeia (1975). Vol. XIX. Easton: Mack PF Printing Co.