

angles describing the hydrogen bonding in the phenyl carbamate complex are presented in Table 5. There are no intermolecular contacts, other than the hydrogen bonding, which are shorter than 3.6 Å.

We wish to thank the Robert A. Welch Foundation for financial support (P-074). This is FASTBIOS contribution number 88.

References

- DUNITZ, J. D., DOBLER, M., SEILER, P. & PHIZACKERLEY, R. P. (1974). *Acta Cryst.* **B30**, 2733–2738.
 GOLDBERG, I. (1975). *Acta Cryst.* **B31**, 754–762.
 HARKEMA, S., VAN HUMMEL, G. J., DAASVATN, K. & REINHOUDT, D. N. (1981). *J. Chem. Soc. Chem. Commun.* pp. 368–369.

- JOHNSON, C. K. (1971). *ORTEP II*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.
 KNOCHEL, A., KOPF, J., OEHLER, J. & RUDOLPH, G. (1978). *J. Chem. Soc. Chem. Commun.* pp. 595–596.
 LARSON, A. C. (1970). In *Crystallographic Computing*, edited by F. R. AHMED, S. R. HALL & C. P. HUBER, pp. 291–294. Copenhagen: Munksgaard.
 MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J. P. (1978). *MULTAN 78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
 STEWART, J. M., MACHIN, P. A., DICKINSON, C., AMMON, H. L., HECK, H. & FLACK, H. (1976). The XRAY 76 System. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.
 WEBER, E. & VÖGTLE, F. (1980). *Angew. Chem. Int. Ed. Engl.* pp. 1030–1032.

Acta Cryst. (1982). **B38**, 1248–1251

1,1',8,8'-Tetrahydroxy-10,10'-bi-9(10H)-anthrone

BY M. WHITEFIELD

Dermal Laboratories Ltd, Hitchin, Hertfordshire, England

AND K. HENRICK AND P. G. OWSTON

Department of Chemistry, The Polytechnic of North London, Holloway Road, London N7 8DB, England

(Received 16 July 1981; accepted 4 November 1981)

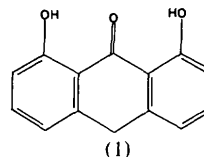
Abstract

$C_{28}H_{18}O_6$, $M_r = 450.4$, $F(000) = 840$, is monoclinic, $C2/c$, with $a = 17.751$ (3), $b = 7.581$ (2), $c = 16.316$ (3) Å, $\beta = 106.64$ (3)°, $V = 2103.7$ Å³, $Z = 4$, $D_{\text{calc}} = 1.420$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 0.06$ mm⁻¹. The structure was solved by direct methods. The final R and R_w values were 0.066 and 0.061 respectively for 846 unique observed reflections, $I > 3\sigma(I)$. There is a crystallographic twofold symmetry axis perpendicular to the C(10)–C(10') bond which links the two halves of the molecule, and each half is markedly less planar than the monomeric precursor, 1,8-dihydroxy-9(10H)-anthrone. The C(10)–C(10') bond is long (1.62 Å) and probably weaker than a normal bond.

Introduction

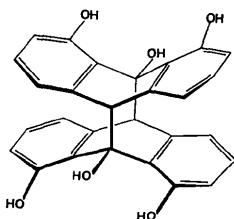
Since it was first synthesized in 1915 (Bayer & Co., 1915) and used clinically (Unna, 1916), dithranol

(1) has remained the most widely prescribed preparation used exclusively for the treatment of psoriasis (Weigand & Everett, 1967). Its mode of action involves its ability to oxidize readily within the epidermal tissues which, by enzymatic inhibition, results in a slowing down of cellular proliferation (Fisher & Maibach, 1975), with subsequent clinical clearance.



Spectroscopic (Avdovitch & Neville, 1980) and crystallographic (Ahmed, 1980) examination of dithranol has recently shown that it exists as the keto tautomer, 1,8-dihydroxy-9(10H)anthrone (1). When (1) was dissolved in acetone, Segal, Katz & van Duuren (1971) were able to obtain a dimeric species to

which they assigned the structure (3). A dimeric species was shown to be present in commercial grades of (1) (Elsabbagh, Whitworth & Schramm, 1979), together with dihydroxyanthraquinone. Since the mechanism of chemical oxidation may be related to the pharmacological activity of dithranol we have determined the precise structure of the dimeric oxidation product by X-ray crystallography.



(3)

Experimental

A crystal with dimensions 0.16 × 0.15 × 0.12 mm was selected. The crystal data showed the systematic absences hkl ($h + k = 2n + 1$) and $h0l$ ($l = 2n + 1$, $h = 2n + 1$), establishing the space group as Cc or $C2/c$. The centrosymmetric space group was found to be correct from the successful refinement of the structure. Intensity data were collected on a Philips PW 1100 diffractometer with Mo $K\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$) and a θ - 2θ scan mode for reflections with $6 \leq 2\theta \leq$

Table 1. Atomic coordinates and isotropic thermal parameters ($\text{\AA}^2 \times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
C(1)	0.3828 (3)	0.4901 (8)	-0.0064 (4)	47 (1)
C(2)	0.3430 (3)	0.6487 (8)	-0.0256 (4)	52 (1)
C(3)	0.3626 (4)	0.7870 (9)	0.0289 (4)	55 (1)
C(4)	0.4229 (3)	0.7727 (8)	0.1058 (4)	49 (1)
C(4a)	0.4631 (3)	0.6152 (7)	0.1271 (3)	39 (1)
C(10)	0.5226 (3)	0.5990 (7)	0.2133 (3)	39 (1)
C(10a)	0.5757 (3)	0.4404 (7)	0.2226 (3)	36 (1)
C(5)	0.6468 (3)	0.4343 (8)	0.2866 (4)	50 (1)
C(6)	0.6934 (4)	0.2850 (9)	0.3021 (4)	57 (1)
C(7)	0.6708 (4)	0.1394 (9)	0.2516 (4)	58 (1)
C(8)	0.6020 (3)	0.1419 (8)	0.1840 (3)	49 (1)
C(8a)	0.5533 (3)	0.2937 (7)	0.1682 (3)	38 (1)
C(9)	0.4857 (3)	0.3045 (8)	0.0925 (3)	44 (1)
C(9a)	0.4442 (3)	0.4710 (7)	0.0716 (3)	38 (1)
O(1)	0.3612 (2)	0.3571 (6)	-0.0636 (3)	49 (3)
O(8)	0.5850 (3)	-0.0038 (6)	0.1334 (3)	54 (2)
O(9)	0.4662 (2)	0.1725 (5)	0.0448 (3)	52 (2)
H(2)	0.303 (3)	0.634 (6)	-0.084 (3)	91 (19)
H(3)	0.339 (3)	0.904 (7)	0.022 (3)	88 (19)
H(4)	0.435 (2)	0.872 (5)	0.143 (2)	38 (13)
H(10)	0.557 (2)	0.706 (6)	0.223 (2)	49 (14)
H(5)	0.661 (2)	0.539 (5)	0.316 (2)	29 (12)
H(6)	0.747 (4)	0.293 (8)	0.351 (4)	145 (29)
H(7)	0.692 (3)	0.022 (8)	0.258 (3)	92 (20)
H(O1)	0.400 (3)	0.267 (8)	-0.039 (4)	96 (26)
H(O8)	0.537 (3)	0.017 (8)	0.093 (3)	76 (21)

60°. During the course of data collection three standard reflections, measured every 2 h to monitor crystal quality and alignment, were constant within $\pm 5\%$.

The variance of intensity was calculated as $\{[\sigma(I)]^2 + (0.04I)^2\}^{1/2}$, where $[\sigma(I)]$ is the variance due to counting statistics, and the term in I^2 allows for other sources of error. I and $\sigma(I)$ were corrected for Lorentz and polarization factors. Absorption corrections were not applied. Equivalent reflections were averaged to give 1902 unique reflections.

The structure was solved by direct methods with *SHELX76* (Sheldrick, 1976). Using $E > 1.1$ the third E map from the multiresolution Σ_2 sign expansion (figure of merit = 2.175) revealed the positions of all 17 non-hydrogen atoms. The H atoms were found in a subsequent difference Fourier synthesis. All the atoms, including H, were refined isotropically without constraint, using full-matrix least-squares methods. Refine-

Table 2. Interatomic distances and angles

(i) Bond lengths (\AA)

C(1)–C(2)	1.384 (7)	C(1)–C(9a)	1.427 (7)
C(2)–C(3)	1.354 (8)	C(3)–C(4)	1.402 (8)
C(4)–C(4a)	1.383 (7)	C(4a)–C(10)	1.502 (6)
C(4a)–C(9a)	1.398 (7)	C(10)–C(10a)	1.508 (7)
C(10)–C(10 ^b)	1.622 (9)	C(10a)–C(5)	1.389 (7)
C(10a)–C(8a)	1.407 (7)	C(5)–C(6)	1.382 (8)
C(6)–C(7)	1.366 (8)	C(7)–C(8)	1.392 (7)
C(8)–C(8a)	1.418 (7)	C(8a)–C(9)	1.457 (7)
C(9)–C(9a)	1.452 (7)	C–H 0.93–1.06 (6), (0.98)	
C(1)–O(1)	1.352 (6)	C(8)–O(8)	1.360 (6)
C(9)–O(9)	1.255 (6)	O(1)–H(O1)	0.97 (6)
O(8)–H(O8)	0.92 (5)	O(9)–H(O1)	1.68 (6)
O(9)–H(O8)	1.74 (6)	O(1)–O(9)	2.582 (6)
O(8)–O(9)	2.565 (6)		

(ii) Bond angles ($^\circ$)

O(1)–C(1)–C(2)	117.8 (5)	C(7)–C(8)–C(8a)	120.4 (6)
O(1)–C(1)–C(9a)	122.2 (5)	C(7)–C(8)–O(8)	117.5 (6)
C(2)–C(1)–C(9a)	120.0 (6)	C(8a)–C(8)–O(8)	122.0 (5)
C(1)–O(1)–H(O1)	102 (3)	C(8)–O(8)–H(O8)	107 (4)
C(1)–C(2)–C(3)	120.4 (6)	C(10a)–C(8a)–C(8)	118.6 (5)
C(2)–C(3)–C(4)	121.0 (7)	C(10a)–C(8a)–C(9)	120.4 (5)
C(3)–C(4)–C(4a)	119.9 (6)	C(8)–C(8a)–C(9)	120.7 (5)
C(4)–C(4a)–C(10)	118.7 (5)	C(8a)–C(9)–C(9a)	119.2 (5)
C(4)–C(4a)–C(9a)	120.1 (5)	C(8a)–C(9)–O(9)	119.7 (5)
C(10)–C(4a)–C(9a)	121.1 (5)	C(9a)–C(9)–O(9)	121.0 (5)
C(4a)–C(10)–C(10a)	114.3 (5)	H(O1)–O(9)–C(9)	100 (2)
C(10)–C(10a)–C(5)	120.6 (5)	H(O1)–O(9)–H(O8)	154 (3)
C(10)–C(10a)–C(8a)	120.7 (5)	H(O8)–O(9)–C(9)	103 (2)
C(5)–C(10a)–C(8a)	118.7 (5)	C(1)–C(9a)–C(4a)	118.6 (5)
C(10a)–C(5)–C(6)	122.2 (6)	C(1)–C(9a)–C(9)	120.3 (5)
C(5)–C(6)–C(7)	119.6 (7)	C(9)–C(9a)–C(4a)	121.1 (5)
C(6)–C(7)–C(8)	120.4 (7)	O(1)–H(O1)–O(9)	152 (5)
O(8)–H(O8)–O(9)	147 (5)	C(4a)–C(10)–C(10 ^b)	109.1 (5)
C(10a)–C(10)–C(10 ^b)	110.6 (5)		

(iii) Non-bonding intermolecular and intramolecular contacts (\AA)

C(5)–C(4a ^b)	3.04 (1)	C(5)–C(9a ^b)	3.19 (1)
C(10a)–C(4a ^b)	3.04 (1)	C(10)–C(4a ^b)	2.55 (1)
C(10)–C(4 ^b)	3.12 (1)	O(8)–H(O1 ^b)	2.58 (5)
O(1)–H(6 ^{III})	2.39 (5)	O(8)–H(7)	2.36 (5)
O(9)–H(O8 ^b)	2.66 (5)		

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$; (ii) $1 - x, -y, -z$; (iii) $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$.

ment converged to conventional and weighted R values of 0.066 and 0.061 respectively for 846 reflections with $I > 3\sigma(I)$ and a weighting factor, $w = 1/\sigma^2(F_o)$. Neutral-atom scattering factors were used (Cromer & Mann, 1968). The final refined parameters are listed in Table 1.* A final difference map showed no significant features, with the maximum residual density 0.31 e \AA^{-3} .

Results and discussion

The dimeric compound has the chemical composition $C_{28}H_{18}O_6$ and is the oxidation product 1,1',8,8'-tetrahydroxy-10,10'-bi-9(10H)-anthrone (2) (see Fig.

* Lists of structure factors, torsion angles and least-squares-planes data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36531 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

1). The molecule exists as a discrete unit in the solid state and has a crystallographic twofold symmetry axis perpendicular to $C(10)-C(10')$. The principal bond lengths and angles are listed in Table 2. The dimer exists as the ketonic form with a $C(9)-O(9)$ bond length of 1.255 (6) \AA , much less than the phenolic $C-O$ distances of 1.352 (6) and 1.360 (6) \AA at $C(1)$ and

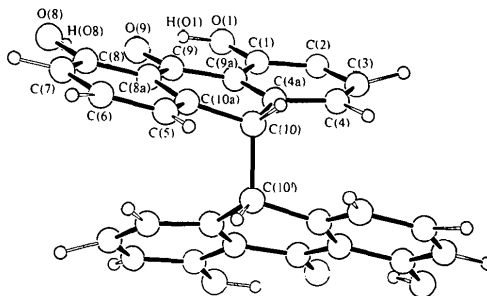
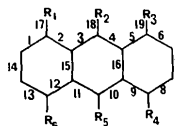


Fig. 1. A perspective view of (2) (ORTEP, Johnson, 1965).

Table 3. Bond lengths (\AA) in the anthracene portions of some related molecules

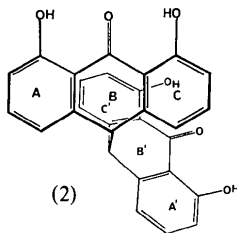


Compound	R_1	R_2	R_3	R_4	R_5	R_6	Reference
(1)	OH	=O	OH	H	H_2	H	(a)
(2)	OH	=O	OH	H	Dimer	H	This work
(4)	H	=O	H	H	Dimer	H	(b)
(5)	H	=O	H	H	=O	H	(c)
(6)	OH	=O	NO_2	OH	=O	NO_2	(d)
(7)	OH	=O	OH	H	=O	H	(e, f, g)
(8)	Cl	=O	Cl	H	=O	H	(h)

Bond	Compound							Mean
	(1)	(2)	(4)	(5)	(6)	(7)	(8)	
1	1.384 (6)	1.384 (7)	1.38	1.383	1.395 (6)	1.43	1.33	1.384
2	1.414 (6)	1.427 (7)	1.39	1.391	1.385 (6)	1.49	1.48	1.425
3	1.448 (6)	1.452 (7)	1.48	1.490	1.456 (6)	1.49	1.42	1.462
4	1.450 (5)	1.457 (7)	1.48	1.495	1.470 (6)	1.50	1.49	1.477
5	1.409 (6)	1.418 (7)	1.40	1.391	1.368 (6)	1.44	1.46	1.412
6	1.379 (6)	1.392 (7)	1.37	1.391	1.383 (6)	1.41	1.38	1.386
7	1.367 (6)	1.366 (8)	1.39	1.392	1.351 (6)	1.34	1.37	1.368
8	1.379 (6)	1.382 (8)	1.40	1.383	1.395 (6)	1.38	1.37	1.384
9	1.377 (6)	1.389 (7)	1.39	1.391	1.385 (6)	1.41	1.35	1.384
10	1.492 (6)	1.508 (7)	1.51	1.490	1.456 (6)	1.49	1.43	1.482
11	1.492 (6)	1.502 (6)	1.51	1.495	1.470 (6)	1.50	1.42	1.484
12	1.380 (6)	1.383 (7)	1.40	1.391	1.368 (6)	1.38	1.47	1.396
13	1.379 (6)	1.402 (8)	1.40	1.391	1.383 (6)	1.44	1.41	1.401
14	1.375 (6)	1.354 (8)	1.38	1.392	1.351 (6)	1.34	1.32	1.359
15	1.409 (5)	1.398 (7)	1.40	1.404	1.418 (6)	1.37	1.41	1.401
16	1.413 (4)	1.407 (7)	1.40	1.404	1.418 (6)	1.41	1.41	1.409
17	1.354 (4)	1.360 (6)	—	—	1.336 (5)	1.27	—	1.33
18	1.261 (4)	1.255 (6)	—	—	1.219 (5)	1.25	—	1.25
19	1.356 (4)	1.352 (6)	—	—	—	1.35	—	1.35

References: (a) Ahmed (1980). (b) Ehrenberg (1967). (c) Bailey & Brown (1967). (d) Prakash (1965). (e) Lonsdale, Milledge & El Sayed (1966). (f) Lonsdale, Walley & El Sayed (1966). (g) Prakash (1967). (h) Mikhno, Ezhkova & Kolokolov (1972).

C(8). The C(10)–C(10') bond [1.622 (9) Å] is long, indicating that cleavage of the dimer (2) at C(10) should occur easily. Similar long dimer C–C bond distances have been found in di-*p*-anthracene (Ehrenberg, 1966) (1.61 Å) and in 10,10'-bi-9(10*H*)-anthrone (Ehrenberg, 1967) (1.60 Å).



The C–C bond lengths within the C₁₄ skeleton in the dimer (2) are almost identical with corresponding values in the monomer (1) (Ahmed, 1980), and also with the mean values for a range of similar compounds (Table 3). It appears that relatively extensive substitution in the aromatic nucleus has no significant effect on the bond lengths in the anthrone ring system. The only significant difference in bond lengths and bond angles between the monomer and dimer is in the angle at C(10) which is more nearly tetrahedral in (2) [C(4a)–C(10)–C(10a) = 117.7 (3)° in (1) and 114.3 (5)° in (2)].

The O atoms at C(1), C(8) and C(9) make up a very strong hydrogen-bonded unit with short hydrogen bonds, O(9)···H(O1) = 1.68 (6) and O(9)···H(O8) = 1.74 (6) Å [with O(1)···O(9) 2.582 and O(8)···O(9) 2.565 Å]. These hydrogen bonds are approximately symmetrical about O(9) and force a small in-plane splaying such that the extreme outside angles O(1)–C(1)–C(2) and O(8)–C(8)–C(7) are decreased from the normal value of 120 to *ca* 117.5°, accompanied by an increase of the angles O(1)–C(1)–C(9a) and O(8)–C(8)–C(8a) to *ca* 122.1°.

Each half of the dimer is planar to within 0.3 Å and the least-squares planes of the two halves make an angle of 36.3° to each other. The molecule adopts a skew conformation with the torsion angle H(10)–C(10)–C(10')–H(10') = 64°. The distortions appear to result from the formation of the C(10)–C(10') bond: C(10) is displaced by 0.39 Å from the rest of the carbon skeleton, and each half of the dimer is folded (angle 168°) about the C(9)···C(10) line. The skew conformation appears to be responsible for minor distortions in ring C, which is subject to intra-dimer forces and deviates from

planarity by ±0.02 Å, whereas ring A is free from such forces and is planar to within 0.004 Å.

Although *peri* interactions in 1,8-disubstituted naphthalenes are well known (Gore & Henrick, 1980), little information is available on the details of molecular distortions in 1,8,9-trisubstituted anthracenes (Dellaca, Penfold & Robinson, 1969). It appears that any *peri* steric strain in compound (2) is largely relieved by out-of-plane bending rather than by bond-length or bond-angle deformations whereas the monomer (1) is remarkably planar and free from distortion.

There are no inter-dimer contact distances of any significance which would explain why the molecule adopts a *cisoid* conformation rather than a less-overlapped *transoid* conformation about C(10)–C(10').

References

- AHMED, F. R. (1980). *Acta Cryst.* **B36**, 3184–3186.
 AVDOVITCH, H. W. & NEVILLE, G. A. (1980). *Can. J. Spectrosc.* **25**, 110–115.
 BAILEY, M. & BROWN, C. J. (1967). *Acta Cryst.* **22**, 392–396.
 Bayer & Co. (1915). German patent 296091.
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
 DELLACA, R. J., PENFOLD, B. R. & ROBINSON, W. T. (1969). *Acta Cryst.* **B25**, 1589–1594.
 EHRENBURG, M. (1966). *Acta Cryst.* **20**, 177–182.
 EHRENBURG, M. (1967). *Acta Cryst.* **22**, 482–487.
 ELSABBAGH, H. M., WHITWORTH, C. W. & SCHRAMM, L. C. (1979). *J. Pharm. Sci.* **68**, 388–390.
 FISHER, L. B. & MAIBACH, H. I. (1975). *J. Invest. Dermatol.* **64**, 338–341.
 GORE, P. H. & HENRICK, K. (1980). *Acta Cryst.* **B36**, 2462–2465.
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
 LONSDALE, K., MILLEDGE, H. J. & EL SAYED, K. (1966). *Acta Cryst.* **20**, 1–13.
 LONSDALE, K., WALLEY, D. & EL SAYED, K. (1966). *Acta Cryst.* **20**, 13–17.
 MIKHNO, O. A., EZHKOVA, Z. I. & KOLOKOLOV, B. N. (1972). *Sov. Phys. Crystallogr.* **17**, 580–583.
 PRAKASH, A. (1965). *Z. Kristallogr.* **122**, 272–278.
 PRAKASH, A. (1967). *Acta Cryst.* **22**, 439.
 SEGAL, A., KATZ, C. & VAN DUUREN, B. L. (1971). *J. Med. Chem.* **14**, 1152–1156.
 SHEDRICK, G. M. (1976). *SHELX 76*. Program for crystal structure determination. Univ. of Cambridge, England.
 UNNA, P. G. (1916). *Dermatol. Wochenschr.* **62**, 116–183.
 WEIGAND, D. A. & EVERETT, M. A. (1967). *Arch. Dermatol.* **96**, 554–559.