Fig. 1 shows the projections of the two structures along the b axis. In both cases the molecular packing is dominated by an extensive network of hydrogen bonds. Rows of molecules along the a axis form hydrogen bonds involving the two *trans* H atoms and the O atom of the adjacent molecule of the same height. The lengths $N(1) \cdots O^i$ and $N(2) \cdots O^i$ [(i) $1 + x, y, z$] for the o-isomer are 2·944 (2) and 2·913 (2) Å [$N(1)-H \cdots O^i$ = 140·0 (2), $N(2)-H(1) \cdots O^i$ = 142·7 (2)°]. The corresponding distances for the p-isomer are 2·913 (1) and 2·895 (1) Å respectively [$N(1)-H \cdots O^i$ = 156·7 (2), $N(2)-H(1) \cdots O^i$ = 145·7 (2)°]. Another type of hydrogen bond is formed along the screw axes and involves the *cis* H. The lengths of the $N(2) \cdots O^{ii}$ [(ii) $\bar{x}, y - \frac{1}{2}, \frac{1}{2} - z$] distances are 3·094 (2) Å for the o- [$N(2)-H(2) \cdots O^{ii}$ = 176·2 (3)°] and 3·018 (2) Å for the p- compound [$N(2)-H(2) \cdots O^{ii}$ = 174·5 (7)°]. These arrangements are reminiscent of the structure of urea (Vaughan & Donohue, 1952), in which one O is linked to four H atoms of adjacent molecules.

The presence of pairs of hydrogen bonds between moieties of the same height influences the relative orientation, and hence the conformation, of the aromatic rings. In fact a smaller value of the internal rotation angle around the $N(1)-C(1)$ bond would induce very close intermolecular distances between adjacent tolyl rings, that could only be accommodated by weakening the hydrogen bonds. Thus, it can be anticipated that the isolated molecules may have a smaller equilibrium value for this torsion angle (larger values on the other hand would completely offset the contribution to resonance energy). Preliminary calculations with PCILO methods (Malrieu, 1977) show in fact most probable values around 30° for both isomers. As mentioned in the *Introduction*, the ac-

cessibility of fairly low values for this angle (*i.e.* a flat overall molecular shape) is crucial for a good interaction with the sweet-taste-receptor site. Complete internal-energy calculations based on the present molecular parameters will shortly be published elsewhere, together with a detailed discussion on the possible interactions of our model with the sweet-taste-receptor site.

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Structure of Anthralin Dimer*

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Abstract. $C_{28}H_{18}O_6$, M_r = 450·45, monoclinic, $C2/c$, a = 17·708 (2), b = 7·566 (1), c = 16·263 (1) Å, β = 106·60 (1)°, V = 2088·08 Å³, D_x = 1·433, D_m = 1·43 (1) Mg m⁻³, Z = 4, $F(000)$ = 936, $\mu(Cu K\alpha)$ = 0·790 mm⁻¹, $\lambda(Cu K\alpha_1)$ = 1·54056 Å. The crystal structure has been determined and refined with 778 observed reflexions, $I > 1·5\sigma(I)$, to R = 0·041 and R_w = 0·052. The structural formula has been established

as 1,1',8,8'-tetrahydroxy-10,10'-bi-9(10H)-anthrone. The molecule consists of two halves related by a crystallographic twofold axis normal to the central C—C bond linking the two anthracene moieties. This bond is stretched to a length of 1·612 (7) Å, and its nearest endocyclic angle is 114·5 (3)° compared to 117·7 (3)° in anthralin. The three O atoms of each half are interlinked by intramolecular O—H···O···H—O hydrogen bonds. The results of this study are comparable to those recently published [Whitefield, M.; Henrick, K. & Owston, P. G. (1982), *Acta Cryst.* B38, 1248–1251] except for some minor errors in the earlier report.

Introduction. Recent studies of anthralin, $C_{14}H_{10}O_3$, by spectroscopic techniques (Avdovich & Neville, 1980) and by a crystallographic analysis (Ahmed, 1980) established its structural formula as 1,8-dihydroxy-9-anthrone. Anthralin is known to undergo spontaneous dimerization and oxidation in Me_2CO (Segal, Katz & Van Duuren, 1971), and a recent examination by Caron & Shroot (1981) of some anthralin ointments showed that 20–30% of the samples' contents were of anthralin dimer. While Caron & Shroot (1981) assumed the molecular formula (I) for the dimer, an early analysis of its NMR spectrum was interpreted by Segal *et al.* (1971) in favour of formula (II). However, we are not aware of any definitive publication where the correct structural formula of the dimer was established. The present X-ray analysis shows the exact geometry of the dimer and provides the first proof that it has the molecular formula (I).
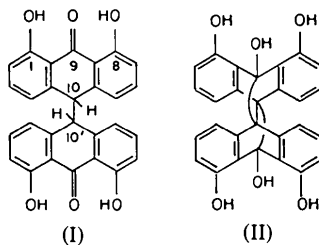
Anthralin dimer forms pale-yellow prismatic crystals, most of which are twinned; hence the X-ray measurements were made on a single crystal in the form of a thin wafer of dimensions 0·33 × 0·10 × 0·02 mm, mounted with its large face (100) normal to the φ axis of an Enraf–Nonius CAD-4F diffractometer. Using Ni-filtered Cu radiation, the cell parameters were derived by a least-squares fit of the angular settings for 15 reflexions, $\theta = 30$–40°, and the intensity data were measured by ω–2θ scans for a quadrant limited by $\theta = 60°$. The scan ranges were for $\omega = 1·5(1·20 + 0·20 \tan \theta)°$ and at ω scan speeds between 0·6 and 2·5° min⁻¹. Three standard reflexions, measured every

50 min of radiation time, showed small fluctuations within ±2·1% of their mean values. The net intensities were scaled and corrected for Lorentz and polarization effects. Of 1476 unequivalent reflexions measured, only 781 with $I > 1·50\sigma(I)$ were considered observed. The general weakness of the diffraction pattern was attributed to the small crystal size which could not be avoided.

The calculated E statistics for this structure were in favour of the centrosymmetric space group $C2/c$. The structure was solved by the symbolic addition procedure (Karle & Karle, 1963) utilizing the 214 reflexions with $|E| > 1·20$. After refinement of the C and O parameters to $R = 0·088$, the H atoms were located from a difference map and refined with isotropic thermal parameters. Near the end of the refinement, the 18 strongest intensities were corrected for extinction from a linear plot of $(F_c/F_o)^2$ vs net counts, resulting in corrections of 1·008–1·126 for the $|F_o|$ values. However, the three strongest reflexions still had high discrepancies and were given zero weights in the block-diagonal least-squares refinement, as were all the unobserved reflexions. The quantity minimized was $\sum w(F_o - F_c)^2$ with $w^{-1} = 1 + [(|F_o| - 20)/25]^2$ in the last three cycles, which resulted in an unbiased distribution of $w(\Delta F)^2$. For the final cycle, $R = 0·041$ for the observed reflexions, $R_w = 0·052$, maximum and mean parameter shifts were 0·4σ and 0·1σ, and

(I)   (II)

Table 1. *Fractional coordinates* ($\times 10^4$; $\times 10^3$ *for* H) *and equivalent isotropic thermal parameters* (Å²)

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

	x	y	z	B_{eq}/B_{iso}
C(1)	1017 (2)	1402 (5)	1838 (2)	3·8 (1)
C(2)	1701 (2)	1371 (6)	2504 (3)	4·6 (1)
C(3)	1923 (2)	2844 (6)	3007 (2)	4·9 (1)
C(4)	1467 (2)	4362 (6)	2875 (2)	3·8 (1)
C(5)	−772 (2)	7731 (5)	1052 (2)	4·0 (1)
C(6)	−1371 (2)	7875 (6)	287 (3)	4·6 (1)
C(7)	−1572 (2)	6476 (6)	−258 (2)	4·6 (1)
C(8)	−1169 (2)	4899 (5)	−66 (2)	3·7 (1)
C(9)	−145 (2)	3054 (5)	925 (2)	3·4 (1)
C(10)	228 (2)	5981 (5)	2136 (2)	3·1 (1)
C(11)	−368 (2)	6163 (5)	1269 (2)	3·1 (1)
C(12)	−564 (2)	4707 (5)	711 (2)	3·1 (1)
C(13)	538 (2)	2924 (5)	1687 (2)	3·1 (1)
C(14)	759 (2)	4412 (5)	2224 (2)	3·2 (1)
O(1)	848 (2)	−47 (4)	1330 (2)	5·2 (1)
O(2)	−342 (2)	1731 (4)	444 (2)	4·7 (1)
O(3)	−1384 (2)	3567 (4)	−641 (2)	5·1 (1)
H(2)	204 (2)	29 (5)	263 (2)	4·6 (8)
H(3)	242 (2)	281 (5)	346 (2)	4·6 (9)
H(4)	165 (2)	544 (6)	323 (3)	7·0 (11)
H(5)	−68 (2)	877 (5)	145 (2)	4·4 (8)
H(6)	−166 (2)	900 (5)	16 (2)	5·8 (9)
H(7)	−199 (2)	647 (4)	−81 (2)	3·9 (8)
H(10)	59 (2)	707 (4)	226 (2)	2·2 (6)
H(O1)	30 (3)	22 (6)	93 (3)	8·4 (13)
H(O3)	−99 (3)	245 (7)	−36 (3)	10·6 (15)

$[\sum w\varDelta^2/(m - n)]^{1/2}$ was 1·26. The residual electron density distribution in the final difference map was within −0·13 and 0·12 e Å^{-3}. The scattering-factor curves were those from *International Tables for X-ray Crystallography* (1974) and of Stewart, Davidson & Simpson (1965) for H. All computations were performed with the NRC crystallographic program system (Ahmed, Hall, Pippy & Huber, 1973). The refined atomic parameters of the asymmetric half-molecule are listed in Table 1.*

Discussion. A perspective view of the molecular structure of the dimer, viewed along the diad axis, is presented in Fig. 1. Its projection down the C(10)—C(10′) bond showing the relative orientations of the two molecular halves is given in Fig. 2. Equivalent atoms of the two halves are at (x,y,z) and $(-x, y, \frac{1}{2} - z)$, but a complete eclipse of the two halves in the projection in Fig. 2 can be achieved if one half is rotated round the C(10)—C(10′) bond by ~64° which is the torsion angle C(14)—C(10)—C(10′)—C(14′). The

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* Lists of structure factors, anisotropic thermal parameters for the non-H atoms and some mean planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36969 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
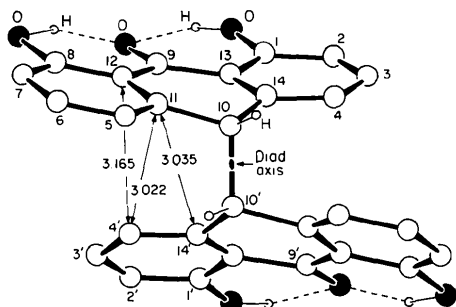

Fig. 1. A perspective view of anthralin dimer along the diad axis which relates the two equivalent halves. The interatomic distances are in Å; $\sigma = 0.005$ Å.

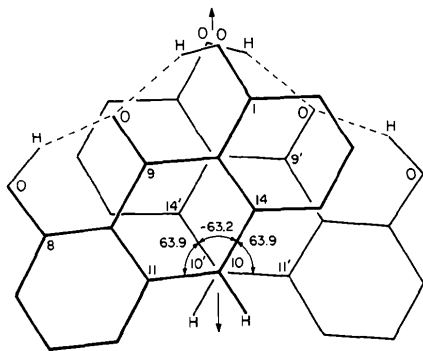Fig. 2. A projection of the dimer down the interlinking C(10)—C(10′) bond. The torsion angles (°) quoted have $\sigma = 0.4°$.

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

Values which are symmetrically across the C(9)···C(10) diagonal are listed on the same line.

C(1)—C(2)	1·375 (6)	C(8)—C(7)	1·380 (6)
C(1)—C(13)	1·410 (5)	C(8)—C(12)	1·411 (5)
C(1)—O(1)	1·354 (5)	C(8)—O(3)	1·353 (5)
C(2)—C(3)	1·372 (6)	C(7)—C(6)	1·361 (6)
C(3)—C(4)	1·385 (6)	C(6)—C(5)	1·390 (6)
C(4)—C(14)	1·391 (5)	C(5)—C(11)	1·378 (5)
C(14)—C(10)	1·496 (5)	C(11)—C(10)	1·507 (5)
C(14)—C(13)	1·410 (5)	C(11)—C(12)	1·406 (5)
C(9)—C(13)	1·467 (5)	C(9)—C(12)	1·445 (5)
C(9)—O(2)	1·257 (5)		
C(10)—C(10′)	1·612 (7)*		
O(1)—H(O1)	1·02 (5)	O(3)—H(O3)	1·11 (5)
C(2)—C(1)—C(13)	120·1 (3)	C(7)—C(8)—C(12)	120·2 (3)
C(2)—C(1)—O(1)	117·3 (3)	C(7)—C(8)—O(3)	117·5 (3)
O(1)—C(1)—C(13)	122·6 (3)	O(3)—C(8)—C(12)	122·3 (3)
C(1)—C(2)—C(3)	119·6 (4)	C(8)—C(7)—C(6)	120·2 (4)
C(2)—C(3)—C(4)	121·8 (4)	C(7)—C(6)—C(5)	120·8 (4)
C(3)—C(4)—C(14)	119·9 (3)	C(6)—C(5)—C(11)	120·3 (3)
C(4)—C(14)—C(10)	120·0 (3)	C(5)—C(11)—C(10)	119·5 (3)
C(4)—C(14)—C(13)	118·7 (3)	C(5)—C(11)—C(12)	119·6 (3)
C(10)—C(14)—C(13)	121·3 (3)	C(10)—C(11)—C(12)	120·7 (3)
C(1)—C(13)—C(9)	120·8 (3)	C(8)—C(12)—C(9)	120·7 (3)
C(1)—C(13)—C(14)	119·8 (3)	C(8)—C(12)—C(11)	118·8 (3)
C(9)—C(13)—C(14)	119·1 (3)	C(9)—C(12)—C(11)	120·5 (3)
O(2)—C(9)—C(13)	119·2 (3)	O(2)—C(9)—C(12)	120·5 (3)
C(12)—C(9)—C(13)	120·3 (3)		
C(14)—C(10)—C(11)	114·5 (3)		
C(14)—C(10)—C(10′)	111·3 (3)	C(11)—C(10)—C(10′)	108·9 (3)

* The e.s.d. includes a factor of $\sqrt{2}$ since the atoms are related.

mean planes of the two anthracene moieties diverge from C(10)—C(10′) at an interplanar dihedral angle of 39·6 (4)°. These main features, together with an elongated C(10)—C(10′) to 1·612 (7) Å and a more tetrahedral endocyclic angle at C(10) [114·5 (3) compared to 117·7 (3)° in anthralin] seem to produce the fit needed to minimize the repulsive forces between atoms of the two equivalent halves. With this arrangement, C(4) is still at relatively short van der Waals contacts of 3·022 (5) and 3·165 (5) Å from C(11′) and C(12′) as shown in Fig. 1. In the dimer of 9-anthraldehyde (Ehrenberg, 1968) the two C—C bonds linking the two anthracene moieties are 1·61 Å as in the present structure.

The crystallographically non-equivalent bond lengths and angles are listed in Table 2. As observed for anthralin, corresponding values across the C(9)···C(10) diagonal are equal within the accuracy of the determination and have been listed on the same line for ease of comparison. The only exception is in the C(11)—C(10)—C(10′) and C(14)—C(10)—C(10′) angles which differ by a significant value of 2·4 (4)°. The mean values for the bond lengths and angles which are symmetrically across the C(9)···C(10) diagonal are presented on the schematic drawing in Fig. 3, together with the corresponding mean values for anthralin. Corresponding mean bond lengths and angles in the two structures are approximately equal except for the endocyclic angle C(11)—C(10)—C(14) which is 117·7 (3)° in anthralin and 114·5 (3)° in the dimer. The latter angle is almost half-way between the
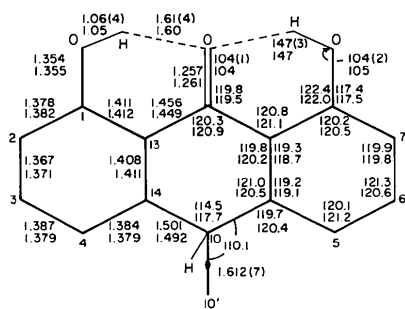
Fig. 3. Mean bond lengths (Å) and angles (°) for the dimer (top) and anthralin (bottom). The e.s.d.'s are 0·004–0·005 Å and 0·2–0·3° for the dimer, and 0·003–0·004 Å and 0·2–0·3° for anthralin, unless stated.

values expected for tetrahedral and trigonal geometries (114·7°).

While each of the three rings in anthralin is approximately planar, the dimer has slightly non-planar outer rings and a central ring which is in a distorted chair form.* The ring involving C(8) has the least overlap with the other half of the molecule (Fig. 2) and shows deviations within $\pm 0\cdot 010$ (4) Å, $\chi^2 = 17\cdot 7$, while that involving C(1) has deviations within $-0\cdot 016$ (4) and $0\cdot 008$ (4) Å, $\chi^2 = 47\cdot 8$. C(9), C(10), C(11), C(12), C(13) and C(14) of the central ring deviate from their mean plane by $-0\cdot 065$, $-0\cdot 127$, $0\cdot 065$, $0\cdot 030$, $-0\cdot 002$ and $0\cdot 099$ Å ($\sigma = 0\cdot 004$ Å), respectively, where those with negative signs are towards the other half of the molecule.

The three O atoms on each half of the molecule are interlinked by two hydrogen bonds, O—H$\cdots$O$\cdots$H—O, with geometry similar to anthralin. The dimers are separated by normal van der Waals contacts. The C—H bonds are in the range 0·97 (3)–1·03 (3) Å.

After this paper was accepted for publication, a report of an independent study of the same compound appeared in this journal (Whitefield, Henrick & Owston, 1982) (hereafter WHO). The molecular structure, bond lengths, valence angles and mean-plane calculations agree fairly closely in both studies. However, the following errors have been noted in WHO's report: (a) F(000) was incorrectly given as 840 instead of 936; (b) the cell dimensions were calculated incorrectly as $a = 17\cdot 751$ (3), $b = 7\cdot 581$ (2), $c = 16\cdot 316$ (3) Å, $\beta = 106\cdot 64$ (3)° compared to our values

* See deposition footnote.

of 17·708 (2), 7·566 (1), 16·263 (1) Å and 106·60 (1)°, respectively; (c) the atom numbers in the two outer rings of the anthracene moiety were interchanged in WHO's Fig. 1.

The large differences |0·043 (1), 0·015 (2), 0·053 (3) Å| in the lengths quoted for a, b, c required further investigation. Thus, we measured manually the 2θ values for some high-order reflexions on a Picker diffractometer with Mo radiation using a narrow vertical slit at a small take-off angle at $+2\theta$ and -2θ. The results were found to be in good agreement with those calculated using our cell dimensions and the wavelengths $\lambda(K\alpha_1) = 0\cdot 70926$, $\lambda(K\alpha_2) = 0\cdot 715343$, $\lambda_{w.m.} = 0\cdot 71069$ Å. The 2θ values calculated using WHO's cell dimensions indicated that WHO probably measured the $K\alpha_1$ peaks but used $\lambda_{w.m.}$ in calculating the cell dimensions. Applying the correction $\lambda\alpha_1/\lambda_{w.m.} = 0\cdot 998$ to WHO's values gives $a = 17\cdot 715$ (3), $b = 7\cdot 566$ (2), $c = 16\cdot 283$ (3) Å, which are reasonably close to our measurements.

The effect of refinement with the wrong cell dimensions has produced mean errors of 0·007 Å and 0·6° in the bond lengths and valence angles, and maximum errors of 0·017 (9) Å and 2·3 (7)°, respectively. These discrepancies are rather minor and not significant.

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