

Fig. 2. Views of the structure along [100] and [001].

The authors are indebted to the Office of Naval Research for partial support of this project, and to the Tulane Computer Center for running their programs. Grateful acknowledgement is made to Dr H. B. Jonassen for suggesting the problem and valuable discussions, to Dr J. C. Fanning for providing the crystals, to Dr W. H. Bernard for helpful suggestions, and to Dr G. J. Palenik for calculating the least-squares planes.

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## The Crystal Structure of 10,10'-Dianthronyl

BY MARIANNE EHRENBERG

*Department of Chemistry, University College, Gower Street, London W.C.1, England*

(Received 30 June 1966)

The crystal structure of 10,10'-dianthronyl has been determined from three-dimensional X-ray data. The atomic coordinates and anisotropic temperature factors have been refined by the method of least squares. The dimer has twofold symmetry perpendicular to the C(10)–C(10') bond and the planes of the two half-molecules make an angle of  $145^{\circ}18'$  with each other. The thermal vibrations indicate libration of the two half-molecules about C(10)–C(10').

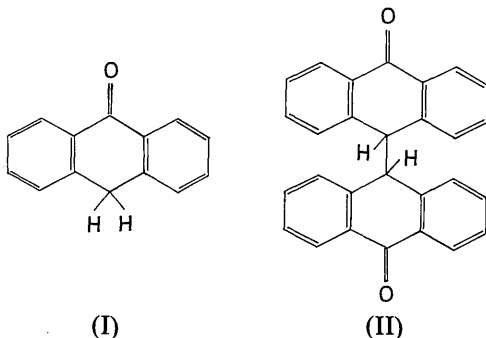
#### Introduction

In the course of studies of the diamagnetic anisotropy of organic crystals Lasheen (1963, 1964) crystallized

anthrone from acetic acid and from ethyl alcohol, and in both cases he obtained two types of crystal, which he assumed to be two modifications of anthrone. Srivastava (1957*a,b*, 1961) had determined a crystal

structure of anthrone (I) with cell dimensions which agreed with those of one of Lasheen's types. But what is the structure of Lasheen's second type?

Search of the literature suggested that this second type is 10,10'-dianthranyl (II), which is formed from anthrone by oxidation in an acid solution. Mass-spectrometer traces confirmed that it is a dimer.



**Experimental**

*Crystal data*

10,10'-Dianthranyl, (C<sub>14</sub>H<sub>9</sub>O)<sub>2</sub>

M.W. 386.452.

Monoclinic:

$a = 13.68 \pm 0.04$ ,  $b = 7.751 \pm 0.003$ ,  $c = 17.92 \pm 0.04$  Å.

$\beta = 91.1 \pm 0.3^\circ$ .

(The errors given are three times the standard errors of the averages of a number of measurements).

$D_c$  (Z=4) = 1.351 g.cm<sup>-3</sup>

$D_m$  = 1.353 g.cm<sup>-3</sup>

m.p. 254°C.

Total number of electrons per unit cell,  $F(000) = 816$ .

Systematic absences:  $hkl$ :  $h+k+l = 2n+1$

$h0l$ :  $h = 2n+1$  ( $l = 2n+1$ )

$0k0$ : ( $k = 2n+1$ )

Space group:  $I2/a$

Molecular symmetry: twofold axis.

*Description of crystals*

The crystals of dianthranyl, obtained from a warm solution of anthrone in acetic acid, appear together with crystals of anthrone and have the same yellow colour. They frequently form at the extremities of anthrone needles as small platelets, the large faces being {010}.

The density, equal to 1.353 g.cm<sup>-3</sup>, was determined by means of a modified density gradient column (Low & Richards, 1952) prepared from sodium iodide and water.

*X-ray data*

For the X-ray work a crystal with dimensions 0.35 × 0.55 × 0.17 mm<sup>3</sup> was used.

The unit-cell dimensions were determined from rotation photographs about the three principal axes and from an oscillation photograph using a high-order reflexion. The space-group absences were found from Weissenberg photographs.

Multiple-film packs of equi-inclination Weissenberg photographs were taken for  $k=0 \rightarrow 7$  and for  $h=0$  and  $l=0$ , using Cu  $K\alpha$  and Cu  $K\beta$  radiation. Integrated intensities were obtained with the use of a Joyce-Loebl Flying Spot Microdensitometer. A few very strong reflexions fell outside the range of this instrument and

Table 1. *Positional and thermal parameters*

The values of  $U$  are defined by the temperature factor exponent [ $-2\pi^2(h^2a^2U_{11} + \dots + 2klb^*c^*U_{23} + \dots)$ ].

	$\bar{x}$ (Å)	$\bar{y}$ (Å)	$\bar{z}$ (Å)	$U_{11}$	$U_{22}$	$U_{33}$	$2U_{12}$	$2U_{23}$	$2U_{13}$
C(1)	-1.235	-0.524	3.578	0.0422	0.0503	0.0346	0.0142	-0.0046	-0.0121
C(2)	-1.433	-1.755	4.134	0.0460	0.0674	0.0313	0.0220	0.0139	-0.0112
C(3)	-1.972	-2.782	3.350	0.0591	0.0450	0.0404	0.0220	0.0309	0.0017
C(4)	-2.326	-2.537	2.016	0.0459	0.0301	0.0388	0.0154	0.0081	-0.0070
C(5)	-2.159	0.426	-1.979	0.0359	0.0424	0.0324	-0.0028	0.0043	0.0104
C(6)	-1.801	1.649	-2.540	0.0471	0.0554	0.0414	-0.0107	0.0236	0.0240
C(7)	-1.347	2.679	-1.726	0.0523	0.0457	0.0607	-0.0133	0.0281	0.0250
C(8)	-1.212	2.473	-0.367	0.0438	0.0324	0.0605	-0.0119	0.0035	0.0031
C(9)	-1.350	1.067	1.662	0.0461	0.0322	0.0464	0.0009	-0.0151	-0.0252
C(10)	-2.620	-1.030	0.033	0.0322	0.0199	0.0300	0.0026	-0.0037	-0.0027
C(11)	-2.082	0.225	-0.596	0.0262	0.0300	0.0324	0.0058	-0.0012	0.0038
C(12)	-1.576	1.262	0.209	0.0294	0.0263	0.0429	-0.0011	-0.0015	-0.0013
C(13)	-1.571	-0.274	2.234	0.0344	0.0346	0.0321	0.0103	-0.0114	-0.0118
C(14)	-2.141	-1.287	1.447	0.0339	0.0245	0.0318	0.0208	0.0018	-0.0033
O	-0.944	1.993	2.385	0.1170	0.0423	0.0554	-0.0325	-0.0228	-0.0736
H(1)	-0.811	0.270	4.184			0.0635			
H(2)	-1.175	-1.930	5.173			0.0350			
H(3)	-2.115	-3.763	3.775			0.0282			
H(4)	-2.751	-3.334	1.416			0.0375			
H(5)	-2.499	-0.377	-2.623			0.0253			
H(6)	-1.878	1.792	-3.609			0.0658			
H(7)	-1.100	3.637	-2.153			0.0576			
H(8)	-0.818	3.264	0.262			0.0244			
H(9)	-2.327	-1.870	-0.574			0.0294			
				$U(\text{isotropic})$					

Table 2. Observed and calculated structure factors

All reflexions in the Cu sphere not listed have estimated and calculated values below the lowest recorded value.

H	K	L	F OBS	F CALC	H	K	L	F OBS	F CALC	H	K	L	F OBS	F CALC	H	K	L	F OBS	F CALC	H	K	L	F OBS	F CALC	H	K	L	F OBS	F CALC																									
0	0	0	37.57	37.57	1	1	1	3.96	3.96	2	2	2	4.44	4.44	3	3	3	5.87	5.87	4	4	4	7.34	7.34	5	5	5	8.81	8.81	6	6	6	10.28	10.28	7	7	7	11.75	11.75	8	8	8	13.22	13.22	9	9	9	14.69	14.69	10	10	10	16.16	16.16

\* indicates *F*(obs) values which could not be estimated owing to Laue streaks or coincidence with β spots  
 - indicates *F*(obs) values which are affected by extinction or under-estimation.

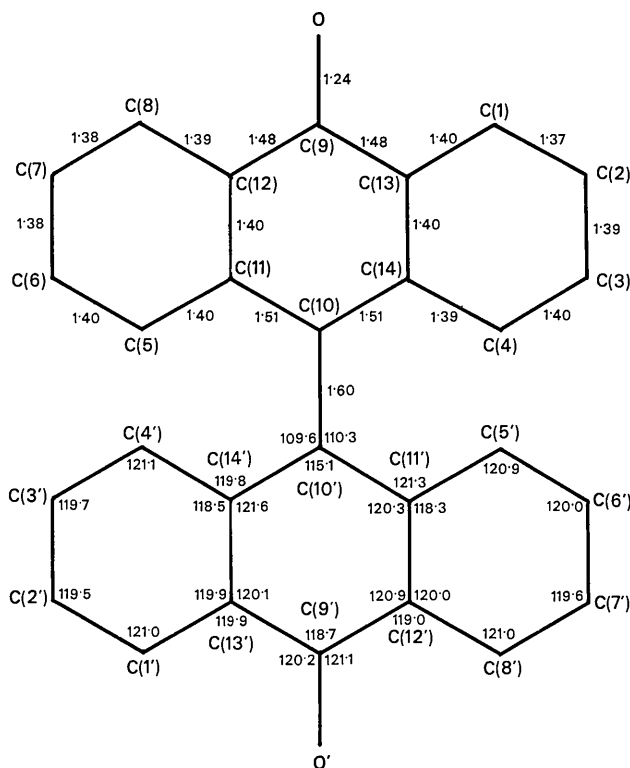


Fig. 1. Schematic drawing of dimer showing bond lengths (Å) and angles ( $^{\circ}$ ).

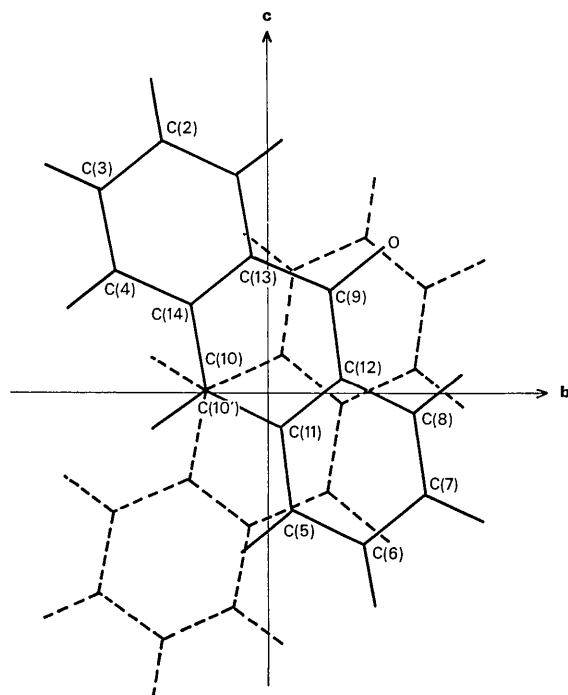


Fig. 2. Projection of the dimer along  $[a]$ .

these were estimated by eye using a graduated intensity scale. Very weak reflexions were neglected. All data were corrected by the appropriate Lorentz-polarization factors and the eye-estimated reflexions also by Phillips's correction, which makes allowance for the extension of spots on upper layer Weissenberg photographs.

### Structure analysis

On a mass spectrometer trace taken from a sample of the crystals under investigation a series of peaks appeared in the region of 386 a.m.u.; these peaks were not present when anthrone was used. This indicated therefore the presence of a dimer related to anthrone and not anthrone itself. Dimroth (1901) observed the formation of dianthrone when anthrone or anthranol was oxidized by air or any other oxidizing agent.

A Patterson projection on (010) located the half-molecules in planes perpendicular to  $[a]$  separated by the spacing of  $d_{400}$  while the (100) Patterson projection gave an indication of the tilt of the molecule with respect to the other two axes. Trial calculations, carried out on a limited number of reflexions, unambiguously fixed the orientation of the molecule and its origin.

A series of least-squares refinements of the atomic positions of the carbon and oxygen atoms using diagonal terms only (Milledge, 1960) resulted in a discrepancy index of 16%, when contributions of the hydrogen atoms were added (but not refined) and the temperature factors for carbon and oxygen were changed from isotropic to anisotropic values. In order to expedite the further refinement process subsequent cycles were carried out with a computer program which calculates block diagonals (Cruickshank *et al.*, 1960) and a weighting scheme in which  $w \propto 1/F$ .

A discrepancy index of  $R=5.8\%$  was reached when the ratio of average coordinate shift to e.s.d. was 0.5.

Table 1 gives the final positional and thermal parameters and Table 2 lists  $F_{\text{obs}}$  and  $F_{\text{calc}}$  values using these parameters.

### Description of the structure

Fig. 1 shows the bond lengths and angles of the molecule. The standard deviations of the bond lengths vary between 0.004 and 0.006 Å and those of the angles between 16 and 22' of arc. All bond lengths and angles have normal values within the limits of error, apart from the bond between C(10) and C(10'), which is longer than a normal single C-C bond. A similar value of 1.61 Å has been found for the bond between the 9 and 10 positions in dipara-anthracene (Ehrenberg, 1966).

Each molecule has a twofold axis of symmetry perpendicular to the C(10)-C(10') bond, coinciding with the twofold axis in the unit cell. C(10) is 0.321 Å from the best plane through the half-molecule, indicating a considerable pull towards the second half of the molecule. The normals to the planes of the two parts of the

dimer are inclined at  $145^{\circ}18'$  to each other. The half-molecules each have a bend of  $10^{\circ}12'$  and their relative orientation viewed along C(10)-C(10') shows the staggered configuration of the atoms in the neighbourhood of C(10) (Fig.2). The angle between the normals

to planes through C(9), C(10), C(10') and C(10), C(10'), C(9') is  $74^{\circ}12'$ .

The intermolecular distances (Fig.3) between the oxygen atom at the equivalent point  $x, y, z$  and C(3) and C(4) at  $x, 1+y, z$ , and C(2) at  $\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$  are

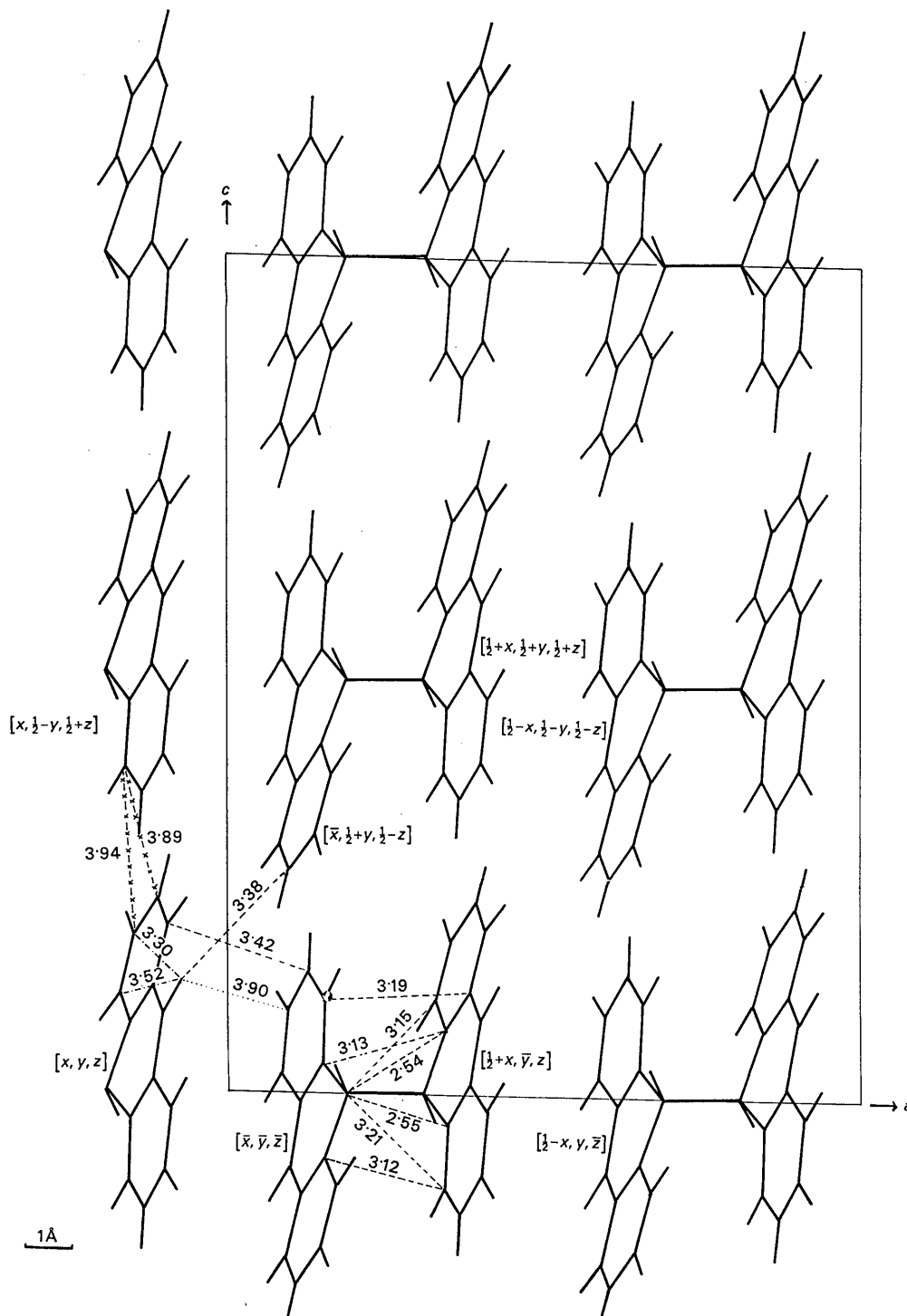


Fig.3. Projection of the structure along  $[b]$ . Contacts  $x, y, z$  to  $\bar{x}, 1-y, \bar{z}$ : dotted line;  $x, y, z$  to  $x, 1+y, z$ : chain dotted lines;  $x, 1+y, z$  to  $\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$ : dashes and crosses.

3.30, 3.52 and 3.38 Å respectively. All other intermolecular distances involving the oxygen atom are greater than 3.9 Å. These distances are too large to suggest any C-H...O bonds and it must be inferred that only van der Waals forces exist in the crystal.

Table 3. *Orientation and magnitudes of the thermal ellipsoids*

The direction cosines  $l, m, n$  give the orientation relative to the orthogonal axes  $a^*, b$  and  $c$ .

	<i>B</i>	<i>l</i>	<i>m</i>	<i>n</i>
C(1)	4.42	-0.5486	-0.7953	0.2579
	3.22	0.6439	-0.5987	-0.4764
	2.42	0.5333	-0.0953	0.8405
C(2)	5.72	-0.3609	-0.9270	-0.1023
	3.65	0.8364	-0.2733	-0.4751
	2.08	0.4125	-0.2570	0.8740
C(3)	5.33	-0.7423	-0.5814	-0.3332
	4.06	0.6348	-0.4509	-0.6274
	2.02	0.2145	-0.6773	0.7038
C(4)	3.92	-0.9200	-0.3070	0.2435
	3.18	-0.0949	-0.4284	-0.8986
	1.97	0.3802	-0.8498	0.3650
C(5)	3.39	0.0957	-0.9825	-0.1596
	3.07	0.8208	-0.0128	0.5710
	2.27	-0.5631	-0.1857	0.8053
C(6)	4.91	-0.0710	-0.8503	-0.5214
	4.30	0.8432	-0.3304	0.4240
	2.12	-0.5328	-0.4096	0.7405
C(7)	5.65	0.3635	0.3678	0.8559
	4.44	0.7872	-0.6126	-0.0710
	2.41	-0.4982	-0.6996	0.5122
C(8)	4.78	0.0011	0.0617	0.9981
	3.66	0.9197	-0.3919	0.0232
	2.35	-0.3926	-0.9179	0.0572
C(9)	4.83	-0.6705	-0.1999	0.7145
	2.92	-0.6529	0.6125	-0.4401
	2.14	-0.3525	-0.7615	-0.5439
C(10)	2.66	-0.8434	-0.1509	0.5157
	2.29	-0.5315	0.0933	-0.8419
	1.54	0.0789	-0.9841	-0.1588
C(11)	2.58	0.1841	-0.0202	0.9827
	2.50	0.4602	0.8852	-0.0681
	1.92	-0.8685	0.4648	0.1723
C(12)	3.40	-0.1058	-0.0410	0.9935
	2.32	0.9768	-0.1913	0.0961
	2.07	-0.1862	-0.9807	-0.0603
C(13)	3.59	-0.6083	-0.5788	0.5431
	2.32	-0.6244	0.7714	0.1228
	2.08	0.4900	0.2644	0.8307
C(14)	3.23	-0.8381	-0.5225	0.1568
	2.52	-0.0576	-0.2011	-0.9779
	1.39	0.5425	-0.8286	0.1384
O	10.83	-0.9080	0.1047	0.4056
	4.47	-0.2020	0.7389	-0.6429
	1.76	-0.3670	-0.6657	-0.6498

### Thermal vibrations

The magnitudes and orientations of the thermal ellipsoids for each atom, derived from the  $U_{ij}$  values quoted in Table 1, are given in Table 3, where  $l, m, n$ , are the direction cosines relative to orthogonal axes  $a^*, b, c$ .

The oxygen atom performs the largest thermal vibration normal to the plane of the half-molecule and it carries with it C(9) to which it is bonded.

The maximum thermal coefficients for all other atoms increase with increasing distances from the centre of inertia, *i.e.* those of C(10), C(11), C(12), C(13) and C(14) have maximum values below 3.5 Å<sup>2</sup>, C(1), C(4), C(5), C(8) about 4 Å<sup>2</sup> and C(2), C(3), C(6) and C(7) about 5 Å<sup>2</sup>. The directions of these maximum vibrations indicate a rotation of the half-molecules about the C(10)-(C10') bond, *i.e.* parallel to  $[a]$ .

Analyses of the thermal data in terms of rigid body vibrations (Cruickshank, 1956) about axes parallel and perpendicular to C(10)-C(10') and about the inertia axes show in both cases large differences between  $U_{obs}$  and  $U_{calc}$  so that the vibrations cannot be interpreted as those of a rigid body.

I wish to thank Professor Dame Kathleen Lonsdale, F.R.S., for suggesting the problem and for continued encouragement, and Dr C. J. Brown for helpful discussions.

The work was carried out as part of a research project supported by the Science Research Council. We also acknowledge with thanks the help received from Ferranti Ltd. and International Computers and Tabulators Ltd. for the gift and servicing of the Pegasus computer used.

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