

The Crystal Structure of *N,N'*-Diphenyl-1,8-diaminoanthraquinone

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The crystal structure of *N,N'*-diphenyl-1,8-diaminoanthraquinone has been worked out with three-dimensional X-ray intensity data. There are two molecules in an orthorhombic unit cell, the twofold symmetry axis of which coincides with the twofold axis of the molecule. 687 structure amplitudes were used for the refinement, resulting in $R=7.3\%$, and standard deviations of 0.007 \AA in the atomic coordinates. The phenyl rings are inclined by 61.8° to the anthraquinone nucleus, which itself is not quite planar. There is a likelihood of hydrogen-bond formation between the two nitrogen atoms and one of the oxygen atoms, of length 2.578 \AA .

Introduction

The crystal structure determination of this compound was undertaken as part of our investigations of the shape and properties of substituted anthraquinones, and because it formed an isomeric pair with *N,N'*-diphenyl-1,5-diaminoanthraquinone, the structure of which has also been determined (Bailey & Brown, 1967). Good dark-blue crystals were readily obtained by recrystallizing the reaction product of 1,8-dichloroanthraquinone and aniline.

Experimental

Unit-cell dimensions were determined from both rotation and Weissenberg photographs about each of the principal axes. The crystal symmetry is orthorhombic and the axis lengths are

$$a = 21.312, b = 9.205, c = 4.855 \text{ \AA}.$$

The space group, derived from the absent reflexions $\{h00\}$ with h odd, and $\{00l\}$ with l odd, is $P2_12_1$. As there are only two molecules in the unit cell, it follows that the twofold axis of the molecule coincides with the twofold axis of symmetry of the lattice. The density determined by flotation in sodium iodide solution was 1.360 g.cm^{-3} , compared with 1.361 required by the X-ray data.

Intensity data were obtained from Weissenberg photographs about \mathbf{b} (zero layer only) and \mathbf{c} (zero and four layers) by comparison with a time-exposure calibrated film strip. The usual correction factors were applied and the structure amplitudes placed approximately on the absolute scale by Wilson's statistical method. Further scaling was done on the computer. No allowance was made for absorption or extinction as the crystals used were very small needles.

Determination of the structure

The trial structure was very readily determined from considerations of the unit cell and space group; the limitation of having the twofold molecular axis lying along \mathbf{b} enabled a set of x and y coordinates to be written down which gave a number of $F(hk0)$ in approximate agreement with the values observed. This $[c]$ projection was refined by successive Fourier syntheses and structure factor calculations. Approximate z coordinates were then deduced by geometry. Three-dimensional refinement then followed on the computer, using programs written by Cruickshank & Pilling (1961). Anisotropic temperature factors were calculated and hydrogen atoms were included at their calculated positions assuming C-H and N-H to be 1.08 \AA , but these were not refined. After several cycles of structure factors and least-squares calculations, all the 687 terms were included, and the R value was 7.3% . The shifts indicated by the last cycles for both the positional and thermal parameters were less than one-half the standard deviations. The final set of coordinates is given in Table 1, and the comparison between observed and calculated structure amplitudes is shown in Table 2.

Description of the structure

Molecules of *N,N'*-diphenyl-1,8-diaminoanthraquinone exist as separate identities in the crystal lattice with only van der Waals forces holding them together. The bond lengths and angles are shown in Fig. 1, together with the numbering of the atoms used in this work. The mean C-C distance in the benzene ring is 1.383 \AA , compared with 1.382 \AA in the 1,5-isomer. In the outer ring of the anthraquinone nucleus the C-C length is 1.391 \AA , compared with 1.396 \AA in the isomer (Bailey & Brown, 1967). The C=O distance (1.218 \AA)

is shorter when the oxygen atom does not accept a hydrogen bond than when it does (1.250 Å). Examination of the system where hydrogen bonding (N–H–O) might occur shows disturbances in the normal bond lengths, similar to those found in the 1,5-isomer. Because this effect is found in two structures, there is a strong probability that C(1), N, H(1), O(1), C(7) and C(6) are involved in a resonating ring system. The

C(1)–N and C(7)–C(6) bonds are shorter at 1.358 and 1.467 Å than would be expected, while the C(7)–O(1) and C(6)–C(1) bonds at 1.250 and 1.432 Å are longer than usual. It would be an interesting study to investigate how the lone pair electrons from the oxygen and nitrogen atoms contribute to these effects.

The equation of the mean plane through the anthraquinone nucleus is

Table 1. *Atomic parameters*

The values of B_{ij} are defined by the coefficients in the formula $\exp[-\frac{1}{4}(h^2a^2B_{11} + 2hka^*b^*B_{12} + \dots)]$.

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{13}
C(1)	0.0860	0.4478	0.3628	4.03	6.21	3.71	0.19	0.42	0.49
C(2)	0.1226	0.3639	0.5419	4.19	6.64	4.78	0.77	1.65	-0.35
C(3)	0.1199	0.2137	0.5382	5.16	7.68	5.32	1.03	2.40	1.67
C(4)	0.0800	0.1441	0.3676	4.52	5.61	5.55	0.75	1.05	1.56
C(5)	0.0424	0.2206	0.1882	4.75	4.93	4.30	0.34	0.33	1.64
C(6)	0.0434	0.3729	0.1841	3.67	4.79	4.40	0.22	0.26	1.20
C(7)	0	0.4496	0	4.41	4.12	4.73	0	0	0.48
C(8)	0	0.1377	0	5.73	4.19	6.30	0	0	2.65
C(9)	0.1345	0.6788	0.5085	4.78	4.73	4.49	0.18	0.79	-1.24
C(10)	0.1145	0.7815	0.6931	5.59	3.87	5.64	0.19	0.66	-0.67
C(11)	0.1594	0.8636	0.8325	6.62	4.70	5.46	0.24	-0.41	-1.28
C(12)	0.2219	0.8446	0.7858	5.80	5.92	5.57	-0.01	-0.20	-1.29
C(13)	0.2422	0.7399	0.6048	4.68	8.01	5.91	-0.19	0.77	-1.54
C(14)	0.1984	0.6572	0.4594	4.86	6.89	4.86	0.41	-1.27	0.18
N	0.0892	0.5951	0.3584	5.65	4.92	6.89	0.44	0.42	-2.14
O(1)	0	0.5854	0	5.20	4.83	6.34	0	0	-3.25
O(2)	0	0.0054	0	8.24	4.84	7.98	0	0	0.31
H(1)	0.0554	0.6529	0.2340						
H(2)	0.1536	0.4174	0.6856						
H(3)	0.1499	0.1516	0.6732						
H(4)	0.0775	0.0270	0.3717						
H(10)	0.0650	0.7985	0.7296						
H(11)	0.1443	0.9439	0.9806						
H(12)	0.2557	0.9121	0.8915						
H(13)	0.2918	0.7217	0.5751						
H(14)	0.2137	0.5774	0.3109						

Mean e.s.d. for coordinates = 0.007 Å, for B_{ij} = 0.30 Å².

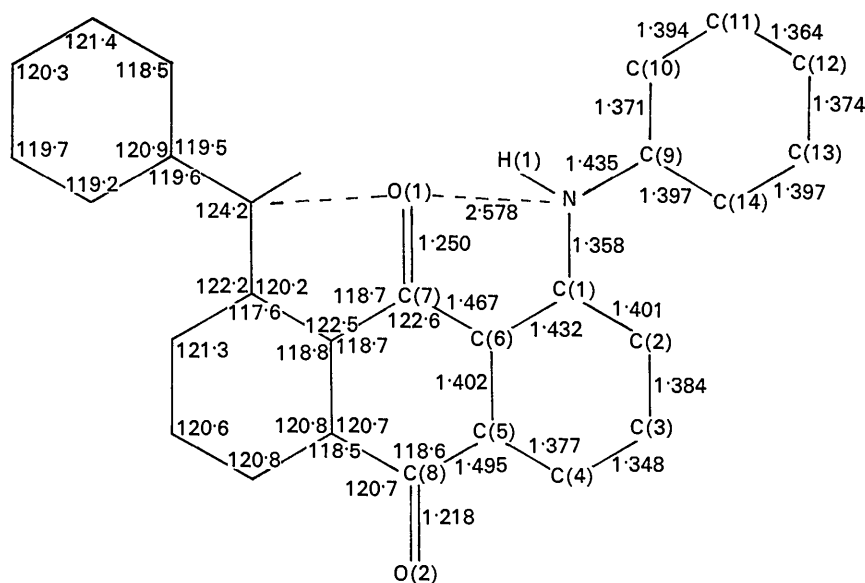


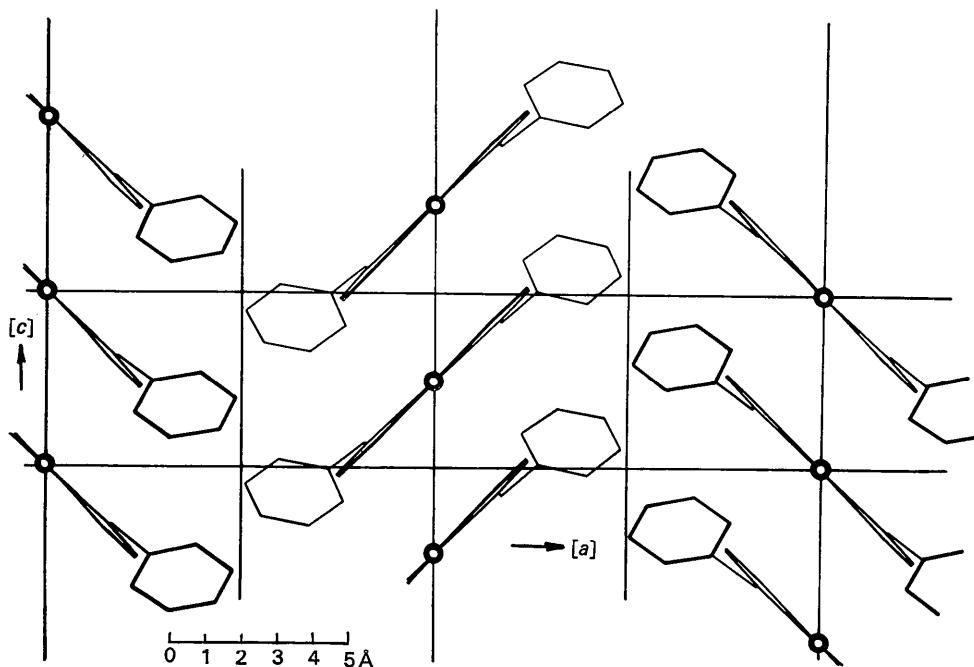
Fig. 1. Bond lengths and inter-bond angles.

Table 2. Observed and calculated structure amplitudes and phase angles

Table with 48 columns (H, K, L, F(OBS), F(CALC), alpha) and multiple rows of data points, organized into 12 groups of 4 columns each.

Table 2 (cont.)

H	K	L	F(OBS)	F(CALC)	α	H	K	L	F(OBS)	F(CALC)	α	H	K	L	F(OBS)	F(CALC)	α	H	K	L	F(OBS)	F(CALC)	α								
6	5	3	3.0	3.0	308	14	8	3	3.7	3.3	336	6	1	4	10.1	10.9	127	3	3	4	3.4	3.6	77	3	6	4	4.0	4.0	236		
7	5	3	5.7	5.3	13	15	8	3	3.3	3.1	49	7	1	4	7.4	7.7	164	3	3	4	3.4	3.3	175	3	6	4	3.8	3.3	258		
8	5	3	3.4	3.3	0							8	1	4	6.2	6.0	108	4	3	4	7.8	6.9	200	4	6	4	5.6	5.4	110		
9	5	3	3.7	3.3	358	0	0	3	3.9	3.5	90	10	1	4	3.7	3.6	333	5	3	4	3.5	3.6	133	5	6	4	5.6	6.0	264		
11	5	3	5.7	5.9	357	10	9	3	3.9	3.0	92	12	1	4	3.6	4.6	299	6	3	4	3.7	3.5	273	6	6	4	6.7	7.5	105		
13	5	3	3.7	3.3	354	11	9	3	3.4	3.9	35	14	1	4	4.0	3.5	130	7	3	4	3.5	7.1	34	7	6	4	3.9	3.2	250		
14	5	3	4.5	3.7	226	12	9	3	3.2	3.4	103	16	1	4	5.3	5.6	229	8	3	4	3.7	3.3	234	8	6	4	3.7	3.8	40		
15	5	3	3.0	3.5	9							17	1	4	3.6	4.4	82	9	3	4	3.8	3.9	209								
0	6	3	30.7	30.7	270	0	0	4	3.6	3.7	0	18	1	4	3.7	5.0	260	15	3	4	3.5	3.2	30	0	7	4	3.6	3.8	180		
1	6	3	6.4	8.4	137	1	0	4	3.9	5.0	180	19	1	4	2.1	2.3	97	16	3	4	3.4	3.0	268	3	7	4	3.6	3.8	125		
2	6	3	9.3	8.6	155	3	0	4	3.1	3.2	0	20	1	4	3.0	3.2	252	18	3	4	4.3	4.7	204	4	7	4	5.2	5.7	356		
3	6	3	10.3	11.2	27	4	0	4	3	3.7	0												1	4	4	3.5	3.3	353			
4	6	3	4.5	5.4	68	5	0	4	6.9	7.6	0	0	3	4	3.3	3.6	180	1	4	4	3.5	3.3	353	5	7	4	3.6	3.8	137		
5	6	3	3.4	3.5	167	6	0	4	11.7	13.7	0	1	3	4	3.9	3.0	87	3	4	4	4.6	4.4	3	6	7	4	4.3	4.7	329		
6	6	3	3.4	3.6	285	7	0	4	10.3	11.3	0	2	3	4	3.7	3.2	85	3	4	4	3.7	3.6	42	7	7	4	3.4	3.6	331		
7	6	3	4.9	3.6	258	8	0	4	9.3	10.3	0	3	3	4	5.1	4.8	196	4	4	4	4.6	4.0	144	8	8	4	3.4	3.4	222		
8	6	3	3.4	3.6	285	10	0	4	3.9	3.5	0	4	3	4	10.6	12.6	324	5	4	4	3.7	3.9	251								
9	6	3	4.9	5.3	170	11	0	4	3.9	2.9	0	5	3	4	5.6	4.7	126	6	4	4	5.6	5.3	262								
10	6	3	3.4	3.7	158	12	0	4	7.9	8.2	160	6	3	4	4.9	5.2	111	7	4	4	4.9	4.7	229								
						14	0	4	4.0	3.0	0	7	3	4	7.2	7.6	117	8	4	4	3.9	3.4	177								
						15	0	4	3.8	3.1	180	8	3	4	3.7	3.0	338	11	4	4	3.8	3.6	77								
						16	0	4	8.4	8.6	0	9	3	4	3.6	3.5	9	15	4	4	3.4	3.7	292								
						17	0	4	3.5	3.6	180	12	3	4	4.0	3.2	358	16	4	4	3.3	3.9	160								
						18	0	4	6.6	7.5	0	15	3	4	2.6	2.5	81														
						19	0	4	4.3	4.9	180	16	3	4	3.6	3.7	57	2	5	4	3.8	3.2	223								
												17	3	4	3.4	3.7	356	3	5	4	3.8	3.7	353								
												19	3	4	3.8	3.9	42	4	5	4	3.8	3.3	0								
												20	3	4	1.5	1.6	47	5	5	4	4.9	4.3	37								
																		7	5	4	4.9	4.4	325								
												0	3	4	5.7	6.1	0														
												1	3	4	4.0	3.8	343							0	6	4	4.9	5.3	0		

Fig. 2. Projection of structure along *b*.

$$0.7051 X - 0.0450 Y - 0.7077 Z = 0.1421$$

$$0.0233 X - 0.6814 Y + 0.7315 Z = 2.3851$$

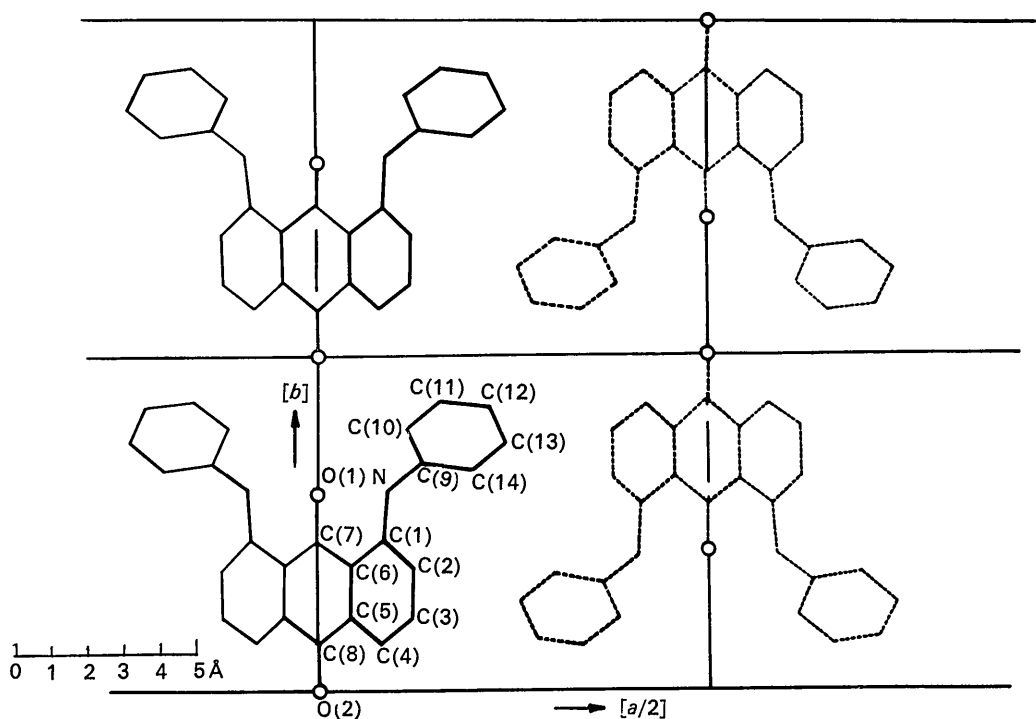
but the out-of-plane distances (average 0.03 Å) indicated that a better fit would be obtained if the outer and central rings were taken separately. When this was done, their normals made an angle of 2.6°, and the mean out-of-plane distance was only 0.01 Å. This slight divergence from planarity may well be due to experimental error, seeing that the number of terms used in the refinement was not very large.

The equation of the mean plane through the substituent phenyl ring is

from which the average displacement is 0.006 Å. This plane makes an angle of 61.8° with the mean plane through the anthraquinone ring system.

The closest intermolecular approaches are between molecules along *c*, where there are a number of C-C contacts from 3.47 Å upwards. The nearest C-O approach is C(10)-O(1') = 3.38 Å.

Projections of the structure along *b* and *c* are shown in Figs. 2 and 3. Attempts at further analysis of the thermal vibrations showed that the molecule could

Fig. 3. Projection of structure along c .

not be treated as a rigid body, and computer programs for dealing fully with more complex vibrations are not yet ready.

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The Crystal Structure of So-Called α - LaAl_4 ($\text{La}_3\text{Al}_{11}$)

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An analysis of the structure of what is known in the literature as α - LaAl_4 revealed that the correct formula is $\text{La}_3\text{Al}_{11}$. Analogous formulae seem to apply to ' α - CeAl_4 ', ' α - PrAl_4 ' and ' α - NdAl_4 '. $\text{La}_3\text{Al}_{11}$ crystallizes in the space group $Immm$; $a=4.431$, $b=13.142$, $c=10.132$ Å. There are two formula units in the unit cell. The structure was refined by least-squares methods to a weighted R index of 7.9%. Details of the structure are presented and its relation to ' β - LaAl_4 ' is discussed.

Introduction

Hitherto LaAl_4 has been known to occur in two different modifications, but the various investigators disagree about the transition temperature. According to

Gschneidner's (1961) review the phase transition takes place at $813 \pm 3^\circ\text{C}$, whereas Buschow (1965*a*) found experimental evidence for a phase change at 915°C .

There has been considerable confusion about the structure of LaAl_4 . The oldest publication (Rossi, 1933)