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The Crystal Structure of Dipara-Anthracene

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The structure of dipara-anthracene proposed by Hengstenberg & Palacios has been confirmed and refined with the use of three-dimensional X-ray data. The crystals are orthorhombic with cell dimensions: $a=8{\cdot}127$, $b=12{\cdot}08$, $c=18{\cdot}85$ Å. The space group is *Pbca*.

An attempt has been made to assess the accuracy of the parameters arising from refinements of two independent sets of three-dimensional data.

Introduction

In the course of an investigation of the three forms of bi(anthracene-9,10-dimethylene) our attention was drawn to dipara-anthracene for which a structure has been proposed by Hengstenberg & Palacios (1928–32). The close relation between the two substances prompted a review and extension of this work.

At the same time an attempt was made to find the accuracy and relative merits of parameters arising from two independent sets of three-dimensional data. The sets of data were limited in different ways: in one case data were collected from a crystal mounted about [*b*] and correlated using three layers about [*c*], and in the second case about [*c*] and correlated using two layers about [*a*]. Either choice is justifiable and probably corresponds to procedures followed in a large number of structure determinations which do not claim special accuracy. Finally both sets of data were combined and the three structures thus obtained were compared with each other and with that proposed by Hengstenberg & Palacios.

Experimental

Crystal data

Dipara-anthracene, $(C_{14}H_{10})_2$.
M.W. 356·44.
Orthorhombic
$a=8{\cdot}127 \pm 0{\cdot}015$ Å.
$b=12{\cdot}08 \pm 0{\cdot}01$.
$c=18{\cdot}85 \pm 0{\cdot}03$.
(The errors given are three times the standard errors of the averages of a number of measurements).
Density, calculated ($Z=4$) 1·28 g.cm^{-3}.
measured 1·26 g.cm^{-3} (S.T.P.).
Total number of electrons per unit cell, $F(000)=752$.
Systematic absences: $hk0$: $h=2n+1$.
$0kl$: $k=2n+1$.
$h0l$: $l=2n+1$.
Space group *Pbca*.
Molecular symmetry: centre.

Description of crystals

The crystals of dipara-anthracene were supplied by Dr J.H. Golden of the Ministry of Aviation E.R.D.E. They were recrystallized from nitrobenzene as thin colourless plates of thickness 0·05 to 0·09 mm, tabular parallel to {001} and with {010} and {110} faces present. Their density was determined by flotation in aqueous potassium iodide solution at S.T.P.

X-ray data

The unit-cell dimensions were determined from rotation photographs of crystals mounted about the three principal axes, and the space group absences were found from Weissenberg photographs.

Two independent sets of limited three-dimensional intensity data were collected, the first set consisting of equi-inclination Weissenberg photographs taken for $l=0 \rightarrow 2$ on one crystal and for $k=0 \rightarrow 5$ on another. For the second set of data one crystal only was used, first mounted about [*c*] for photographs $l=0 \rightarrow 6$ and then remounted about [*a*] for $h=0 \rightarrow 1$. Film packs were used for both sets of data and 230 and 280 reflexions with observable intensities were recorded in the two cases respectively. The blackening of the reflexions produced by the Cu $K\alpha$ and Cu $K\beta$ radiations was estimated by visual comparison with an intensity scale. The values were corrected by the appropriate Lorentz–polarization factors, Phillips's correction, which makes allowance for the extension of spots on upper layer Weissenberg photographs, and at the final stage by an experimentally determined extinction correction, as follows. The true intensity I_T is assumed to be related to the observed intensity I_{obs} by the relation:

$$I_T=\alpha I_{obs}+\beta I^2_{obs} \quad \text{or} \quad I_T/I_{obs}=\alpha+\beta I_{obs}$$

where α and β are constants to be determined for any particular crystal. For the correct structure $I_T/I_{obs}=[F_{calc}/F_{obs}]^2$ and hence α and β can be found from a plot of $[F_{calc}/F_{obs}]^2$ against I_{obs}. It was assumed in this case that the above holds for a structure that has refined to an R index of about 10%. For the first set of data only the intensities obtained for $k=0 \rightarrow 5$ (190 reflexions) were corrected for extinction and consequently used for further refinement, as the remaining reflexions had been obtained from a different crystal. The values for α and β are

first set $\alpha=0{\cdot}96$, $\beta=0{\cdot}00005$ ($R=10{\cdot}34\%$)
second set $\alpha=0{\cdot}992$, $\beta=0{\cdot}00006$ ($R=10{\cdot}86\%$)

Table 1. *Final parameters using combined data and anisotropic temperature factors*

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

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{31}	U_{12}
C(1)	0·2354	−0·0908	−0·1292	0·0480	0·0506	0·0581	0·0014	0·0038	0·0025
C(2)	0·1961	−0·1888	−0·1663	0·0589	0·0661	0·0403	0·0121	−0·0037	0·0052
C(3)	0·0821	−0·2640	−0·1418	0·0541	0·0534	0·0373	0·0033	0·0014	0·0089
C(4)	0·0066	−0·2464	−0·0769	0·0385	0·0384	0·0353	0·0091	−0·0003	−0·0019
C(5)	0·1023	−0·1096	0·1557	0·0497	0·0489	0·0472	0·0001	0·0023	−0·0047
C(6)	0·2235	−0·0636	0·1968	0·0502	0·0722	0·0448	−0·0044	−0·0036	0·0005
C(7)	0·3321	0·0124	0·1716	0·0569	0·0589	0·0448	−0·0050	0·0012	−0·0022
C(8)	0·3234	0·0467	0·0995	0·0405	0·0467	0·0531	0·0004	−0·0017	−0·0004
C(9)	0·1845	0·0315	−0·0221	0·0369	0·0407	0·0491	0·0123	0·0033	−0·0020
C(10)	−0·0395	−0·1207	0·0338	0·0468	0·0472	0·0628	0·0074	0·0036	0·0055
C(11)	0·0928	−0·0776	0·0831	0·0333	0·0424	0·0313	−0·0010	0·0043	0·0065
C(12)	0·2054	−0·0008	0·0567	0·0332	0·0390	0·0425	0·0039	0·0005	0·0023
C(13)	0·1575	−0·0735	−0·0658	0·0310	0·0417	0·0353	0·0081	−0·0002	−0·0002
C(14)	0·0436	−0·1490	−0·0357	0·0366	0·0392	0·0313	0·0057	0·0028	0·0034
H(15)	0·3227	−0·0280	−0·1504						
H(16)	0·2506	−0·1877	−0·2181						
H(17)	0·0550	−0·3366	−0·1691						
H(18)	−0·0844	−0·2971	−0·0501						
H(19)	0·0110	−0·1728	0·1781						
H(20)	0·2247	−0·0642	0·2571						
H(21)	0·4157	0·0609	0·2064						
H(22)	0·3961	0·1235	0·0810						
H(23)	0·2885	0·0774	−0·0448						
H(24)	−0·0917	−0·1934	0·0576						

B (isotropic) for hydrogen atoms $=3{\cdot}5$

The standard deviations calculated for the fractional coordinates of the carbon atoms lie between

0·0013 and	0·0017	for x/a
0·0010	0·0012	y/b
0·0007	0·0008	z/c

Table 2. *Observed and calculated structure factors*

The values listed are ¼ the absolute values.

H	K	L	F(OBS)	F(CALC)
2	0	0	-15.93	-16.28
4	0	0	4.48	4.42
6	0	0	3.16	2.82
8	0	0	-5.25	-5.31
0	2	0	35.16	33.33
0	4	0	5.91	5.91
0	6	0	-12.11	-11.81
0	8	0	3.33	3.19
0	12	0	4.26	4.41
0	0	2	31.46	32.37
0	0	4	-26.87	-25.08
0	0	6	9.06	8.02
0	0	8	-22.79	-22.30
0	0	10	-13.55	-13.62
2	1	0	[illegible]	30.24
2	2	0	[illegible]	-40.67
2	3	0	[illegible]	18.81
2	4	0	-11.12	-11.88
2	5	0	10.76	11.13
2	6	0	-4.77	-5.05
2	7	0	-3.38	-3.03
2	8	0	8.75	10.04
2	9	0	-3.50	-3.52
2	10	0	-5.02	-5.57
2	11	0	-3.69	-4.30
4	2	0	-5.29	-5.64
4	3	0	-6.93	-6.78
4	8	0	3.37	2.67
4	9	0	4.15	4.59
6	1	0	3.19	3.17
6	2	0	4.03	4.05
6	4	0	7.59	8.11
6	6	0	4.15	4.54
8	2	0	-3.38	-3.82
8	6	0	-4.38	-4.53
8	7	0	3.63	3.14
10	4	0	2.47	3.40
0	2	1	1.49	1.39
0	4	1	4.18	4.35
0	6	1	-6.70	-5.28
0	8	1	-4.32	-4.29
1	1	1	25.98	28.56
1	2	1	13.36	14.08
1	3	1	-12.01	-12.16
1	5	1	-9.25	-10.46
1	6	1	-6.27	-5.78
1	7	1	2.89	2.36
1	8	1	-8.41	-8.34
1	10	1	-6.20	-7.27
2	1	1	4.40	4.57
2	2	1	10.41	11.50
2	3	1	4.55	4.30
2	4	1	-3.38	-3.74
2	5	1	7.05	7.32
3	1	1	-5.49	-5.81
3	2	1	2.58	2.57
3	3	1	-8.04	-8.04
3	4	1	4.01	4.16
3	7	1	4.55	4.29
3	11	1	-3.90	-3.82
4	1	1	-7.72	-7.62
4	2	1	-3.03	-3.10
4	4	1	3.04	2.63
4	6	1	3.27	3.25
4	7	1	4.02	3.05
4	8	1	3.06	3.31
5	1	1	3.67	3.90
5	5	1	5.84	6.30
5	7	1	3.23	2.89
5	8	1	3.70	4.09
6	2	1	-4.63	-4.58
6	3	1	-3.48	-3.75
6	6	1	-3.11	-3.19
7	1	1	-3.65	-4.47
7	4	1	-5.84	-6.08
8	1	1	4.89	5.05
0	2	2	10.67	10.20
0	4	2	-2.07	-1.35
0	8	2	5.85	5.53
1	0	2	-2.98	-2.33
1	1	2	-10.40	-11.00
1	2	2	-24.59	-26.34
1	3	2	26.87	28.43
1	4	2	-7.39	-7.75
1	5	2	-3.21	-3.31
1	6	2	-5.04	-5.06
1	7	2	2.98	2.81
1	8	2	-2.81	-3.03
1	11	2	4.00	4.72
2	0	2	16.24	16.46
2	1	2	-3.78	-4.30
2	2	2	-13.35	-13.27
2	3	2	2.86	2.72
2	4	2	-10.67	-10.12
2	6	2	-3.75	-3.29
2	9	2	-2.82	-2.87
2	11	2	-4.40	-4.77
3	0	2	-3.49	-3.22
3	1	2	-3.39	-3.29
3	2	2	-5.61	-5.99
3	4	2	12.14	12.48
3	5	2	-8.15	-8.32
3	6	2	4.37	4.51
3	8	2	3.54	3.89
3	9	2	-6.46	-7.43
3	10	2	-3.76	-4.90
4	0	2	2.28	2.03
4	1	2	2.30	1.92
4	2	2	-4.15	-4.18
4	6	2	2.89	2.87
4	7	2	5.33	5.42
4	8	2	6.72	7.61
5	0	2	6.74	7.11
5	1	2	-5.57	-5.77
5	5	2	2.80	2.58
5	7	2	4.16	4.53
5	8	2	3.76	3.66
5	9	2	4.56	3.93
6	0	2	4.96	5.84
7	4	2	-3.75	-4.64
8	0	2	-3.45	-3.38
8	2	2	-3.32	-3.71
9	0	2	3.90	3.54
9	2	2	3.12	3.18
10	4	2	2.75	3.22
0	2	3	-9.05	-8.67
0	4	3	-9.40	-9.25
0	6	3	-3.40	-3.23
1	1	3	13.51	15.39
1	2	3	-19.98	-19.98
1	3	3	2.01	2.11
1	4	3	-4.60	-5.15
1	5	3	5.08	4.88
1	7	3	4.56	4.66
1	11	3	-3.89	-3.44
2	1	3	7.02	7.72
2	2	3	13.33	13.48
2	4	3	13.92	14.44
2	5	3	-2.74	-2.13
2	8	3	-4.57	-4.77
2	9	3	-3.75	-4.08
3	1	3	-5.91	-6.22
3	2	3	6.08	7.04
3	3	3	-19.94	-20.99
3	5	3	-7.71	-7.83
3	6	3	7.28	7.38
4	1	3	-6.95	-7.15
4	2	3	-4.61	-3.92
4	3	3	-4.47	-4.65
4	5	3	5.61	5.32
4	7	3	8.64	10.15
4	9	3	3.91	4.16
5	1	3	6.24	6.12
5	2	3	-3.29	-3.06
5	3	3	6.62	6.12
5	4	3	-6.07	-6.20
5	7	3	5.02	5.19
6	2	3	-3.99	-4.14
6	3	3	-3.72	-3.38
6	5	3	-3.88	-3.82
8	1	3	5.39	5.50
9	1	3	-4.96	-4.76
0	2	4	5.89	5.33
0	4	4	-4.43	-4.51
0	6	4	13.02	13.06
0	12	4	-3.90	-3.29
1	0	4	6.74	6.74
1	1	4	-5.99	-6.23
1	2	4	12.05	12.70
1	3	4	4.28	3.73
1	4	4	-6.18	-6.38
1	6	4	-6.23	-6.10
1	9	4	-3.34	-3.05
1	11	4	3.53	3.00
2	0	4	5.05	5.72
2	1	4	-13.77	-16.53
2	2	4	2.97	3.54
2	3	4	-8.02	-7.79
2	4	4	-11.43	-11.63
2	5	4	-9.12	-8.61
2	6	4	3.19	2.30
3	0	4	5.67	6.22
3	1	4	-6.74	-6.94
3	2	4	-2.26	-1.99
3	3	4	11.93	12.35
3	4	4	-3.63	-3.86
3	6	4	7.19	7.53
3	7	4	-3.65	-2.90
3	8	4	5.14	5.38
3	9	4	-4.27	-3.99
4	0	4	6.26	6.51
4	3	4	3.90	4.01
4	7	4	7.74	8.05
5	1	4	-3.42	-2.75
5	2	4	-4.57	-4.02
5	4	4	-4.32	-4.44
5	5	4	-5.58	-5.45
5	11	4	4.66	4.81
6	0	4	3.66	3.24
7	0	4	4.07	4.56
7	1	4	-3.80	-3.90
9	0	4	5.19	5.31
0	2	5	2.86	2.40
0	4	5	5.71	5.39
0	6	5	5.20	4.95
0	12	5	5.02	5.80
1	1	5	2.63	2.33
1	3	5	-6.03	-6.10
1	4	5	-5.49	-5.24
1	6	5	4.07	3.08
1	7	5	3.73	3.74
2	1	5	5.45	5.82
2	2	5	-9.31	-9.46
2	3	5	-10.17	-9.38
2	4	5	3.54	3.64
2	5	5	-8.20	-8.13
2	6	5	-3.64	-3.62
3	2	5	-4.82	-4.52
3	3	5	-3.68	-3.04
3	4	5	-5.05	-4.88
3	5	5	-3.65	-2.74
4	1	5	8.52	8.43
4	2	5	6.53	6.33
4	3	5	-7.16	-7.30
4	4	5	4.88	4.60
4	5	5	4.92	4.86
4	7	5	5.09	5.90
4	9	5	4.95	5.22
5	1	5	6.54	6.74
6	11	5	-3.08	-3.39
0	2	6	-3.60	-3.69
0	4	6	-3.96	-3.44
0	6	6	12.52	11.62
1	0	6	-4.17	-4.06
1	2	6	-2.70	-2.40
1	4	6	-4.70	-4.69
1	5	6	3.67	3.74
2	0	6	-6.86	-7.16
2	1	6	4.11	4.27
2	2	6	4.18	4.31
2	3	6	-11.33	-11.75
2	4	6	-6.81	-6.51
2	5	6	-7.69	-7.92
3	0	6	12.97	13.69
3	2	6	8.17	8.52
3	4	6	-9.89	-10.12
4	2	6	4.95	5.02
4	4	6	-6.02	-6.03
5	2	6	-5.89	-5.19
5	3	6	6.58	5.84
7	0	6	6.36	7.71
0	2	7	7.59	8.30
0	4	7	13.52	13.60
1	1	7	-3.75	-4.05
1	3	7	-3.32	-2.53
1	4	7	-6.83	-6.39
1	6	7	-6.21	-5.77
1	7	7	4.71	4.76
2	1	7	6.39	6.02
2	4	7	-8.56	-8.26
3	1	7	4.46	3.89
3	3	7	5.52	5.39
4	1	7	5.41	4.13
4	4	7	4.90	4.84
6	3	7	-6.18	-6.31
0				
0	2	8	-7.46	-7.23
0	4	8	-5.60	-5.62
1	0	8	17.21	16.89
1	1	8	-2.81	-2.62
1	7	8	-4.84	-4.89
1	8	8	-5.11	-5.43
2	2	8	6.25	6.32
2	3	8	-10.07	-8.96
2	4	8	5.56	4.97
3	0	8	3.87	4.46
3	1	8	5.43	4.81
4	2	8	5.30	5.00
4	4	8	-5.83	-4.90
5	0	8	5.29	5.98
6	0	8	-4.37	-5.41
7	0	8	4.43	5.10
0	10	9	6.49	7.64
1	1	9	-7.25	-7.77
1	2	9	-6.57	-7.07
1	3	9	5.47	5.14
1	6	9	-3.83	-3.44
4	2	9	-5.07	-4.28
0	2	10	6.11	5.88
0	8	10	-7.02	-7.65
1	0	10	13.48	13.49
1	2	10	10.54	11.36
1	3	10	-3.48	-3.71
2	0	10	-4.45	-4.49
2	1	10	-5.21	-4.98
3	0	10	4.01	3.97
3	2	10	-4.89	-4.23
5	0	10	5.55	5.89
5	1	10	5.98	6.24
0	6	11	6.10	6.62
1	1	11	-4.86	-4.64
2	1	11	5.13	5.07
3	3	11	7.00	7.43
4	3	11	-6.95	-7.16
0	4	12	5.01	5.77
1	1	12	4.72	5.19
1	5	12	6.53	6.93
1	6	12	4.89	6.43
3	3	12	-7.64	-7.43
3	4	12	-6.77	-7.29
4	0	12	-6.06	-6.94
4	2	12	-6.44	-6.78
0	4	13	6.07	6.13
2	5	13	7.20	7.19
3	4	13	7.26	7.25
4	1	13	-6.58	-6.80
1	3	14	6.05	6.34
1	4	14	4.24	4.56
1	6	14	4.37	5.52
2	4	14	6.88	8.04
3	0	14	-5.60	-6.96
0	2	15	4.89	5.06
1	3	15	4.75	6.09
1	4	15	8.17	9.45
3	1	15	-7.21	-7.41
1	3	16	5.34	4.85

The agreement between the corrected F_{obs} values for 120 reflexions common to both sets is 8·1%.

Structure analysis

According to Hengstenberg & Palacios the two parallel anthracene components are both bent by $2 \times 19^\circ$ out of their plane, away from each other. Some striking similarities in the intensity distribution of the *h*0*l* zones of dipara-anthracene and bi(anthracene-9,10-dimethylene) were observed and therefore a molecule bent in the way suggested by Hengstenberg & Palacios was placed in the unit cell so as to agree with our structure of bi(anthracene-9,10-dimethylene) (Ehrenberg, 1966), making allowance for the difference in the unit cells, *i.e.* for a rotation of -115° about [*b*]. The computing program for the Ferranti Pegasus computer for the calculation of structure factors and least squares (Milledge, 1962) allows the generation of molecular coordinates for specified rotation of the molecule about any axes, such as the crystal axes *a*, *b* and c^* or the molecular axes *L*, *M*, *N*. With this facility an attempt was made to improve the agreement between low-order calculated and observed structure factors by small rotations of the trial molecule only about the molecular axes, but it was not possible to reduce the discrepancy index below 30%. One least-squares refinement, however, of all reflexions with $\sin\theta < 0{\cdot}4$ reduced the *R* values to 17%.

Further refinements of the coordinates and isotropic temperature factors, different for each atom, with increasing numbers of reflexions, were made, accepting half shifts of the least-square recommendations in the case of the coordinates and quarter shifts for the temperature factors. Hydrogen contributions were added in the third least-squares refinement and in both cases the data were corrected for extinction when the *R* values were of the order of 10%, as mentioned above. The final *R* values, when isotropic temperature factors are used, are 6·9% for all observed reflexions with $I \geq 3$ in the first set, and 8·2% in the second set, which was refined from the same trial structure.

Table 3. *Comparison of bond lengths and bond angles*

	Isotropic refinements			Anisotropic refinements		
	1st set	2nd set	Combined data	1st set	2nd set	Combined data
C(1)–C(2)	1·38 Å	1·44 Å	1·40 Å	1·37 Å	1·44 Å	1·42 Å
C(2)–C(3)	1·40	1·41	1·39	1·39	1·40	1·39
C(3)–C(4)	1·43	1·42	1·40	1·42	1·41	1·38
C(5)–C(6)	1·41	1·39	1·38	1·39	1·37	1·37
C(6)–C(7)	1·38	1·39	1·36	1·38	1·37	1·37
C(7)–C(8)	1·43	1·44	1·42	1·43	1·44	1·42
C(1)–C(13)	1·39	1·36	1·37	1·39	1·36	1·37
C(4)–C(14)	1·41	1·42	1·44	1·41	1·43	1·45
C(5)–C(11)	1·43	1·45	1·42	1·43	1·46	1·42
C(8)–C(12)	1·41	1·36	1·38	1·40	1·35	1·38
C(9)–C(13)	1·49	1·53	1·52	1·48	1·53	1·53
C(9)–C(12)	1·54	1·49	1·54	1·55	1·49	1·54
C(10)–C(14)	1·54	1·49	1·51	1·54	1·49	1·51
C(10)–C(11)	1·54	1·49	1·51	1·53	1·50	1·52
C(11)–C(12)	1·40	1·39	1·40	1·39	1·39	1·40
C(13)–C(14)	1·42	1·41	1·42	1·44	1·42	1·42
C(9)–C(10′)	1·60	1·63	1·62	1·61	1·63	1·62
C(13)–C(1)–C(2)	119·0	120·4	118·2	119·1	118·9	117·5
C(1)–C(2)–C(3)	124·1	117·9	122·9	124·2	120·3	122·2
C(2)–C(3)–C(4)	117·1	120·3	118·7	118·3	119·4	120·0
C(3)–C(4)–C(14)	118·6	120·4	119·9	118·3	120·4	119·9
C(11)–C(5)–C(6)	113·7	119·9	117·6	114·1	119·5	117·0
C(5)–C(6)–C(7)	125·4	118·6	123·5	126·1	119·9	123·5
C(6)–C(7)–C(8)	119·4	121·8	119·9	118·9	121·5	119·6
C(7)–C(8)–C(12)	117·9	118·7	118·0	116·7	117·9	117·9
C(12)–C(9)–C(13)	107·3	106·0	108·2	107·9	107·2	108·5
C(8)–C(12)–C(9)	120·3	120·0	121·9	120·1	120·1	121·9
C(8)–C(12)–C(11)	121·1	121·1	121·7	122·7	122·4	122·1
C(9)–C(12)–C(11)	118·5	118·9	116·3	117·0	117·5	115·9
C(9)–C(13)–C(1)	122·3	120·8	122·3	123·2	121·3	121·8
C(9)–C(13)–C(14)	117·8	116·1	115·5	118·3	115·7	114·7
C(1)–C(13)–C(14)	119·9	123·3	122·2	118·6	123·0	123·5
C(11)–C(10)–C(14)	104·6	106·1	107·5	105·7	105·4	106·5
C(5)–C(11)–C(10)	119·8	122·2	122·6	120·0	122·6	122·0
C(5)–C(11)–C(12)	122·4	119·9	119·3	121·3	118·7	119·0
C(10)–C(11)–C(12)	117·8	117·9	118·1	118·7	118·6	118·8
C(10)–C(14)–C(4)	119·5	122·6	123·1	121·5	123·0	123·7
C(10)–C(14)–C(13)	119·0	119·7	118·9	116·7	119·0	119·4
C(4)–C(14)–C(13)	121·0	117·7	117·9	121·3	117·9	116·8
C(12)–C(9)–C(10′)	113·1	113·1	112·9	112·3	112·9	112·4

Both sets of data were then combined, taking the average values of common reflexions, and further calculations were made with 329 reflexions, giving an R index of 7·7%. Further refinements were calculated with anisotropic temperature factors in the three cases, and the following R values were obtained:

First set	$R=5·7\%$
Second set	$R=6·5\%$
Combined data	$R=6·5\%$

Table 1 gives the positional and thermal parameters for the combined data with the use of anisotropic temperature factors and Table 2 shows $F_{\rm obs}$ and $F_{\rm calc}$ values with the use of these parameters.

Discussion

Bond lengths and angles for the different sets of data are given in Table 3. The values are almost independent of the treatment of the thermal vibrations; any differences introduced in this way are small compared with the standard deviations of the bond lengths which are approximately 0·02 Å in all cases. Differences between values in the different sets are greater and amount in some cases to 0·06 Å; the r.m.s. differences are, however, very close to 0·02 Å. The value of 1·62 Å between the 9 and 10′ positions of the two anthracene components of the molecule exceeds the expected value of 1·54 Å by more than the experimental error. This may be due to the considerable forces arising from the close approach of the two half-molecules. The final values

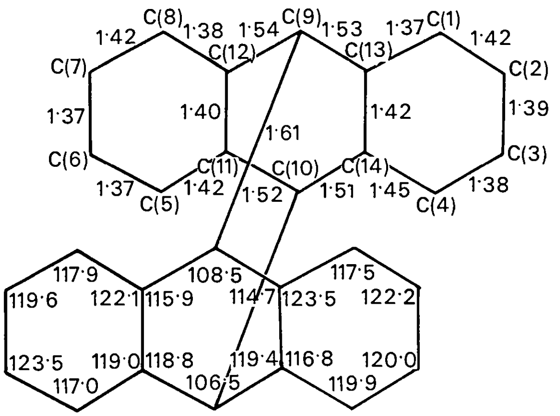

Fig. 1. Bond distances (Å) and angles (°).

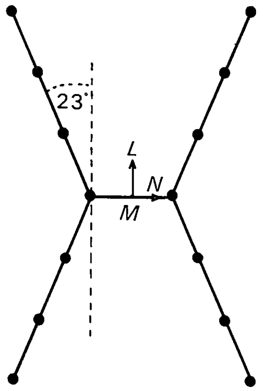

Fig. 2. Projection of molecule on a plane normal to the molecular axis M.

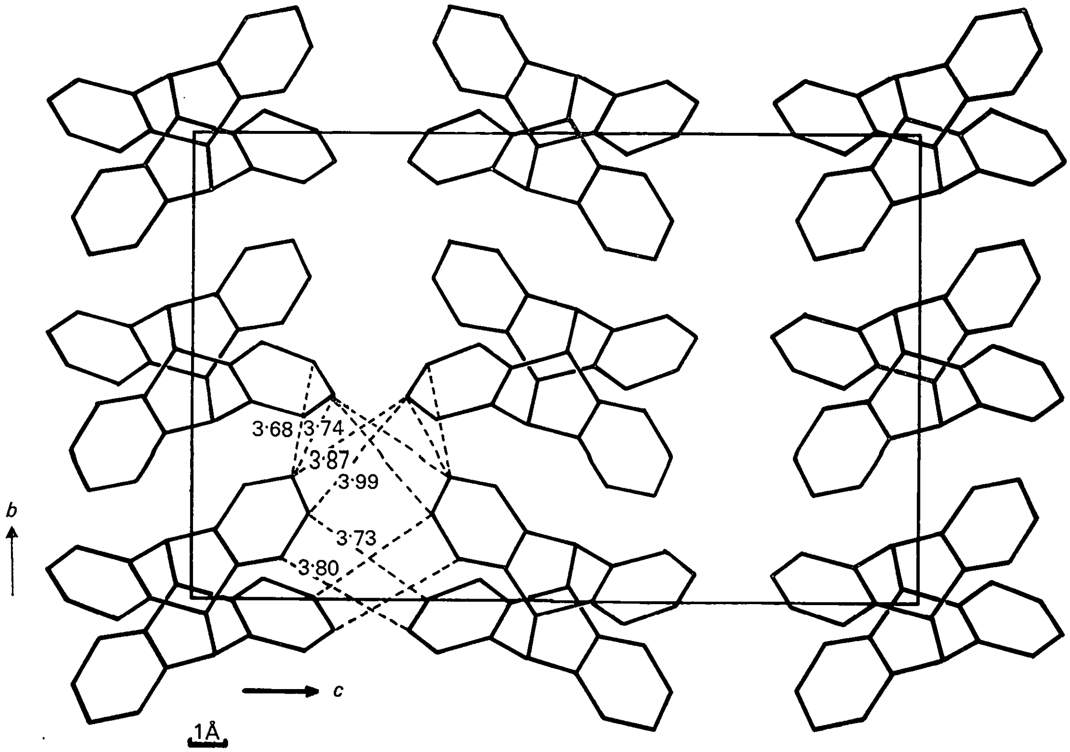

Fig. 3. Projection of structure along [a].

for bond lengths and angles derived from the combined set of data are shown in Fig. 1.

Hengstenberg & Palacios proposed a bending of 2 × 19° for each half-molecule, but this is found to be larger, having a value of 2 × 23° (Fig. 2). The molecular axis M makes an angle of 10° with the [111] direction, which agrees with their proposed orientation. The closest contacts between carbon atoms of neighbouring molecules are 3·67 and 3·73 Å parallel to the a axis. Further contacts are shown in Fig. 3.

The values of the isotropic temperature factors for the different atoms are given in Table 4. The values increase towards the outer parts of the molecule where greater freedom of movement may be expected. Again the three sets of data lead to substantially the same values. In order to compare the anisotropic temperature factors further analysis would be required, but this is not justified in view of the scarcity of data.

Table 4. *Isotropic temperature factors*

	1st set of data	2nd set of data	Combined data
	B	B	B
C(1)	2·7	3·7	3·2
C(2)	3·2	4·1	3·8
C(3)	3·3	3·7	3·6
C(4)	2·5	2·8	2·6
C(5)	2·9	3·7	3·2
C(6)	3·2	4·2	3·7
C(7)	3·2	3·5	3·5
C(8)	2·9	3·7	3·1
C(9)	2·5	2·9	2·8
C(10)	2·7	3·1	3·2
C(11)	2·5	2·7	2·6
C(12)	2·4	2·9	2·6
C(13)	2·5	2·8	2·6
C(14)	2·6	2·8	2·7
H(15)–H(24)	3·5	3·5	3·5
σ_B for all carbon atoms	0·4	0·4	0·3

In spite of the limited nature of the data it may be of interest to compare the different sets of data and the structures obtained. A discrepancy index between the common structure factors of the two sets can be defined as

$$R_1 = \frac{\Sigma||F_{\text{obs}\cdot 1}|-|F_{\text{obs}\cdot 2}||}{\frac{1}{2}(\Sigma|F_{\text{obs}\cdot 1}|+\Sigma|F_{\text{obs}\cdot 2}|)}.$$

where $F_{\text{obs}\cdot 1}$ and $F_{\text{obs}\cdot 2}$ are the observed structure factors of the first and second sets respectively. This and other discrepancy indices are listed in Table 5. In the theory of errors it is assumed that the average of an infinite number of observations (carrying a random error only) equals the true value. On this basis one calculates the standard error of the average of a finite number of observations. In each set of our observations a number of intensities are measured and from these the best coordinates and corresponding theoretical structure factors are calculated. If the number of intensities measured was infinite (very large compared with the number of parameters) the results of the two attempts should be identical and represent the true parameters. As the number of intensities measured for each set is, however, comparatively small, some of the random errors of the observed structure factors are carried over as errors of the parameters and therefore different sets of measurements lead to different parameters, as indicated by R_2. The conventional R indices R_3 to R_7 represent that part of the error in measurement which refuses to be taken up by the calculated structure factors and only in the limiting case of an infinite number of measurements do these R indices represent the mean difference between the observed

Table 5. *R indices for* 120 *reflexions measured in both sets*

	Isotropic refinements	Anisotropic refinements	
$R_1 = \frac{\Sigma\lvert\lvert F_{\text{obs}\,1}\rvert-\lvert F_{\text{obs}\,2}\rvert\rvert}{\frac{1}{2}(\Sigma\lvert F_{\text{obs}\,1}\rvert+\Sigma\lvert F_{\text{obs}\,2}\rvert)} =$	8·1 %		
$R_2 = \frac{\Sigma\lvert\lvert F_{\text{calc}\,1}\rvert-\lvert F_{\text{calc}\,2}\rvert\rvert}{\frac{1}{2}(\Sigma\lvert F_{\text{calc}\,1}\rvert+\Sigma\lvert F_{\text{calc}\,2}\rvert)} =$	5·8 %	5·4 %	
$R_3 = \frac{\Sigma\lvert\lvert F_{\text{obs}\,1}\rvert-\lvert F_{\text{calc}\,1}\rvert\rvert}{\Sigma\lvert F_{\text{obs}\,1}\rvert} =$	6·6 %	5·3 %	
$R_4 = \frac{\Sigma\lvert\lvert F_{\text{obs}\,2}\rvert-\lvert F_{\text{calc}\,2}\rvert\rvert}{\Sigma\lvert F_{\text{obs}\,2}\rvert} =$	6·6 %	5·0 %	
R indices for all observed reflexions			
$R_5 = \frac{\Sigma\lvert\lvert F_{\text{obs}\,1}\rvert-\lvert F_{\text{calc}\,1}\rvert\rvert}{\Sigma\lvert F_{\text{obs}\,1}\rvert} =$	6·9 %	5·7 %	(190 reflexions)
$R_6 = \frac{\Sigma\lvert\lvert F_{\text{obs}\,2}\rvert-\lvert F_{\text{calc}\,2}\rvert\rvert}{\Sigma\lvert F_{\text{obs}\,2}\rvert} =$	8·2 %	6·5 %	(280 reflexions)
$R_7 = \frac{\Sigma\lvert\lvert F_{\text{obs}\,1+2}\rvert-\lvert F_{\text{calc}\,1+2}\rvert\rvert}{\Sigma\lvert F_{\text{obs}\,1+2}\rvert} =$	7·7 %	6·5 %	(329 reflexions)

and the true structure factors. Table 5 shows that all R indices are approximately the same, although the agreement between the two sets of data is very bad ($R_1 = 8{\cdot}1\%$).

It is instructive to see how small is the effect on the parameters of appreciable differences in observed intensities, or, alternatively, how sensitive the calculated F values are to small differences in the parameters.

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The Crystal Structure of Bi(anthracene-9,10-dimethylene) Photo-Isomer

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Bi(anthracene-9,10-dimethylene) exists in three modifications referred to as α and β forms and the photo-isomer. The structure of the photo-isomer has been determined and refined by least-squares with three-dimensional data. The crystals are monoclinic, space group $P2_1/a$, with cell dimensions $a = 8{\cdot}56$, $b = 12{\cdot}99$, $c = 9{\cdot}87$ Å, $\beta = 111^\circ\ 39'$.

The structure of the photo-isomer has been compared with preliminary structural information available for the β form.

Introduction

Bi(anthracene-9,10-dimethylene) exists in three modifications referred to as α and β forms and the photo-isomer (Golden, 1961). The modifications arise as follows: crystallization from solution in chloroform in the dark results in the α or β form. The photo-isomer is obtained from the α or β form by the action of visible light, or by recrystallization from chloroform in the presence of light. The photo-isomer changes back into the β form in the dark. Cell dimensions and space groups of the three modifications were determined by J.R.C. Duke and are given by Golden (1961). The object of this paper is to present a complete structure determination of the photo-isomer and some information about the structures of the α and β forms, which leads to a comparison of the three modifications.

Experimental

Crystal data

Bi(anthracene-9,10-dimethylene) photo-isomer
$(C_{16}H_{12})_2$.
M.W. 408·544.
Monoclinic
$a = 8{\cdot}56 \pm 0{\cdot}07$ Å
$b = 12{\cdot}99 \pm 0{\cdot}09$.
$c = 9{\cdot}87 \pm 0{\cdot}08$.
$\beta = 111^\circ\ 39'$.
Density, calculated, 1·333 g.cm^{-3}.
measured, 1·326 g.cm^{-3} (S.T.P.).
Total number of electrons per unit cell, $F(000) = 432$.
Systematic absences: hkl none.
$h0l$ $h = 2n+1$
$0k0$ $k = 2n+1$.
Space group $P2_1/a$.

Description of crystals

Crystals of bi(anthracene-9,10-dimethylene) were supplied by Dr J.H. Golden, Ministry of Aviation, E.R.D.E. They are sparingly soluble in benzene and chloroform and crystals suitable for X-ray work were obtained by recrystallization from chloroform in daylight. The crystals are pale yellow with {010}, {001} and {110} faces. The dimensions of the two crystals used for collecting intensity data were $0{\cdot}45 \times 0{\cdot}42 \times 0{\cdot}32$ mm^3 for the b-axis data and $0{\cdot}42 \times 0{\cdot}30 \times 0{\cdot}20$ mm^3 for the a-axis data. The density was determined by flotation in an aqueous potassium iodide solution at S.T.P.

X-ray data

The unit-cell dimensions were redetermined from oscillation photographs about the b axis, using the layer line separation to determine b, and a number of high order reflexions to refine values for a, c and β. Space group absences were found from Weissenberg