Crystal and Molecular Structure of 6,12-Dimethyldibenzo[*def,mno*]-chrysene (6,12-Dimethylanthanthrene)

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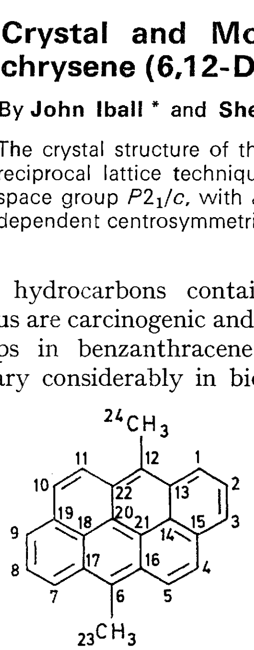
The crystal structure of the title compound (I) has been determined from diffractometer data by the weighted reciprocal lattice technique and refined to R 8·7% (for 1725 observed reflections). Crystals are monoclinic, space group $P2_1/c$, with a = 22·17(2), b = 5·229(3), c = 13·458(7) Å, β = 105·21°(10), Z = 4. The two independent centrosymmetrical molecules in the unit cell are planar and do not differ significantly.

MANY aromatic hydrocarbons containing the benzanthracene nucleus are carcinogenic and the introduction of methyl groups in benzanthracene produces compounds which vary considerably in biological activity.



(I)

6,12-Dimethyldibenzo[*def,mno*]chrysene (I) is one of the largest aromatic hydrocarbons known to possess carcinogenic activity,[1] although the unsubstituted compound has no such activity.[2]

EXPERIMENTAL

Crystals of (I) were thin orange laths.[3] The numbering system adopted is shown in (I). Unit-cell dimensions were determined from rotation and Weissenberg photographs taken with Cu-K_α radiation and confirmed by measurements made on a Wooster four-circle diffractometer. The crystals belong to the monoclinic system and with the most convenient unit-cell axes the systematic absences were hkl when $(h + l)$ odd and $(h0l)$ when h or l odd. The space group is therefore $B2_1/c$. This is not the conventional space group but we continued to use it throughout the analysis. Crystal data, atomic parameters, and structure-factor tables refer however to the space group $P2_1/c$ [the values of hkl in $B2_1/c$ become $-(h + l)/2,k,l$ in space group $P2_1/c$]. The intensities of the reflections were measured on a Wooster four-circle diffractometer (Cu-K_α) for crystals mounted on the b and c axes respectively. Intensity data were placed on a common scale and converted to structure factors in the usual way. As the crystals were small absorption corrections were neglected.

Crystal Data.—$C_{24}H_{16}$, M = 304·39. Monoclinic, a = 22·17(2), b = 5·229(3), c = 13·458(7) Å, β = 105·21(10)°, U = 1505 Å^3, D_m = 1·334, Z = 4, D_c = 1·341, $F(000)$ = 640, Cu-K_α radiation, λ = 1·5418 Å; μ(Cu-K_α) = 6·99 cm^{-1}. Space group (from absences) $P2_1/c$. [In the space group $B2_1/c$ the unit-cell dimensions are, a = 42·82(2), b = 5·229(3), c = 13·458(7) Å, β = 92·45°.]

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[1] A. Lacassagne, N. P. Buu-Hoï, and F. Zajdela, *Compt. rend.*, 1958, **246**, 1477.

[2] G. M. Badger, J. W. Cook, C. L. Hewett, E. L. Kennoway, N. M. Kennoway, R. H. Martin, and A. M. Robinson, *Proc. Roy. Soc.*, 1940, *B*, **129**, 439.

[3] N. P. Buu-Hoï and D. Lavit, *Rec. Trav. chim.*, 1957, **76**, 202.

Structure Determination.—The weighted reciprocal lattice technique has proved useful in the solution of the structures of many polycyclic hydrocarbons similar to (I) and so this method was used here. Examination of the $h0l$ weighted reciprocal lattice showed that there were two sets of peaks which could indicate the orientations of the benzene rings. The presence of two sets of peaks on the weighted reciprocal lattice implied that there were two differently oriented molecules in the $h0l$ projection of the unit cell. This was reinforced by the fact that reflections 103 and $10\bar{3}$ (in space group $B2_1/c$) had the highest $h0l$ structure factors and that there was a group of high-index $h0l$ planes with high structure-factors which could only be satisfied by two differently oriented molecules. After numerous false starts one molecule, designated molecule (1), with its maximum dimension parallel to the (103) plane, was placed at 0,0,0 and a second molecule, designated molecule (2), similarly arranged with respect to the $(10\bar{3})$ plane was placed at $\frac{1}{4}$,0,$\frac{1}{4}$ (in $B2_1/c$). A two-dimensional $h0l$ structure factor calculation had R 0·300 and four cycles of isotropic refinement using an overall temperature factor of 3·5 Å^2 reduced this to 0·170. The scattering factors used were taken from ref. 4.

TABLE 1

Atomic co-ordinates ($\times 10^4$) and anisotropic thermal parameters * ($\times 10^5$) with estimated standard deviations in parentheses

(*a*) Molecule (1)

Atom	x/a	y/b	z/c	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
C(1)	−1815(4)	314(21)	−1323(7)	271(24)	334(195)	203(61)	4491(471)	483(315)	730(62)
C(2)	−1977(5)	−1537(23)	−2080(8)	282(27)	107(222)	70(76)	4910(517)	176(366)	907(76)
C(3)	−1529(5)	−3248(21)	−2278(8)	315(27)	156(210)	196(67)	4382(468)	494(323)	731(65)
C(4)	−446(4)	−4740(20)	−1921(6)	295(22)	201(178)	350(51)	3813(415)	300(266)	589(51)
C(5)	152(4)	−4539(17)	−1397(6)	264(20)	156(151)	326(45)	2735(332)	102(225)	482(42)
C(6)	1004(4)	−2376(18)	−79(6)	284(21)	386(160)	417(49)	3292(383)	547(240)	592(48)
C(13)	−1181(4)	547(17)	−726(6)	242(19)	223(157)	288(48)	2896(346)	760(240)	584(48)
C(14)	−723(4)	−1139(17)	−947(6)	245(19)	139(155)	258(45)	2854(340)	546(230)	485(44)
C(15)	−910(4)	−3026(19)	−1722(6)	247(21)	−29(171)	239(52)	3710(389)	600(261)	561(50)
C(16)	370(4)	−2639(18)	−610(6)	263(20)	179(155)	327(47)	3369(383)	262(229)	489(46)
C(21)	−81(4)	−966(16)	−378(6)	210(18)	92(145)	178(45)	2429(302)	499(205)	441(42)
C(23)	1482(4)	−4088(21)	−318(7)	265(21)	657(183)	505(55)	4340(444)	−180(325)	986(65)

(*b*) Molecule (2)

Atom	x/a	y/b	z/c	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
C(1′)	6848(5)	596(23)	761(8)	285(25)	−117(220)	217(66)	5347(529)	846(351)	812(65)
C(2′)	7089(5)	−1188(24)	231(8)	284(25)	374(231)	326(69)	5935(582)	715(388)	966(75)
C(3′)	6710(5)	−2859(25)	−471(8)	294(26)	434(227)	396(65)	6900(646)	1050(370)	852(69)
C(4′)	5675(5)	−4519(21)	−1337(7)	303(25)	51(203)	190(59)	4412(460)	329(309)	604(55)
C(5′)	5042(5)	−4411(19)	−1507(7)	392(29)	−33(203)	164(65)	3113(381)	−35(280)	538(53)
C(6′)	4086(5)	−2514(19)	−1176(7)	302(25)	−504(181)	138(60)	3946(422)	459(268)	570(55)
C(13′)	6175(4)	714(19)	610(6)	276(22)	122(178)	234(52)	3570(387)	1034(258)	557(50)
C(14′)	5801(4)	−1018(18)	−99(6)	256(21)	−358(162)	161(52)	2933(349)	614(245)	549(49)
C(15′)	6068(5)	−2818(21)	−640(7)	322(25)	323(199)	344(59)	4700(485)	608(298)	659(57)
C(16′)	4749(5)	−2629(19)	−996(6)	343(25)	−22(181)	215(56)	3607(410)	167(243)	407(47)
C(21′)	5124(4)	−900(17)	−269(6)	229(20)	5(150)	193(47)	2490(320)	501(223)	529(47)
C(23′)	3678(5)	−4280(22)	−1916(7)	306(26)	−902(209)	46(70)	5044(493)	−93(339)	709(65)

* In the form: $T = \exp[-(h^2b_{11} + k^2b_{22} + l^2b_{33} + hkb_{12} + hlb_{13} + klb_{23})]$.

The y co-ordinates for the molecules were found from consideration of the foreshortening of the benzene rings, depicted on the weighted reciprocal lattice and then tilting the molecules about a line through the middle of each molecule parallel to a and placing the centre of each at $b = 0$. One problem which had yet to be resolved was the positions of the two independent molecules in the unit cell. Because they have different orientations they must be placed at the correct centres of symmetry. For example, the molecule which is inclined in the $h0l$ projection to the (103) plane can be at 0,0,0 or $\frac{1}{4}$,0,$\frac{1}{4}$ and likewise for the molecule which is inclined in the $h0l$ projection to the $(10\bar{3})$ plane. The possible situations were tested and the correct choice is with the molecule inclined to the (103) plane placed at 0,0,0 and the molecule inclined to the $(10\bar{3})$ plane placed at $\frac{1}{4}$,0,$\frac{1}{4}$. A structure-factor calculation with all the hkl data included had R 0·410.

Refinement.—Refinement of atomic co-ordinates and temperature factors was by the block-diagonal least-squares method. Initially, isotropic temperature factors were used and after three cycles R fell to 0·310. Further refinement reduced R to 0·249. Ring hydrogen atom positions were calculated and included in the structure-factor calculations. Methyl hydrogen atoms were included as six half-hydrogen atoms, assuming the actual hydrogen atoms lie on a ring whose plane is perpendicular to the line from the methyl-carbon atom to the ring-carbon atom to which it is attached. Three cycles of isotropic refinement reduced R to 0·178. Anisotropic temperature factors were then employed for the carbon atoms. A structure-factor calculation, with carbon atoms only, was followed by a difference-Fourier synthesis. The ring-hydrogen atom positions were readily found, but although there were rings of density where one might expect the methyl hydrogen atoms to be, there were no discrete peaks and so the methyl-hydrogen atoms continued to be included in the refinement as six half-hydrogen atoms. Three cycles of refinement with anisotropic temperature factors and the weighting scheme $w = 1/\{1 + [(|F_0| - F^*)/G^*]^2\}$, where $F^* = 25$ and $G^* = 15$, reduced R to 0·087 for 1725 reflections, unobserved reflections omitted. As the shifts in the atomic parameters were now much less than their σ, refinement was terminated. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21123 (6 pp.).†

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† See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1973, Index issue.

[4] 'International Tables for *X*-Ray Crystallography,' vol. II, Kynoch Press, Birmingham, 1959, p. 213.

DISCUSSION

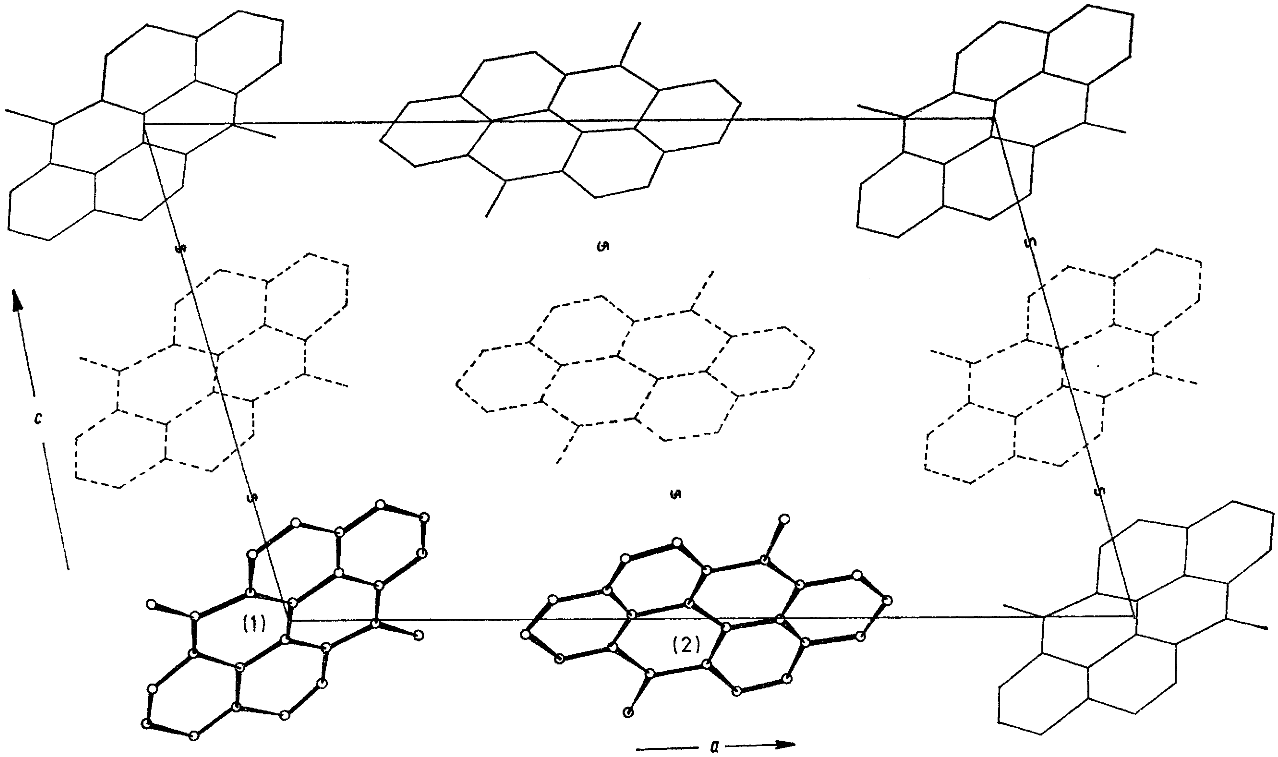
Final co-ordinates and temperature factors of the carbon atoms are in Table 1, together with their estimated standard deviations. Hydrogen-atom co-ordinates are listed in Table 2. Bond lengths and bond angles in the independent molecules are given in Tables 3 and 4. The corresponding bond lengths of the independent molecules are not significantly different but variations between bond lengths within each molecule are significant. In molecule (1) the shortest bond is 1·332 Å and in molecule (2) the shortest bond is 1·361 Å. These are the so-called '*K* regions' of the phenanthrene nucleus of each molecule.[5] Examination of the possible Kekulé structures for 6,12-dimethyldibenzo[*def,mno*]-chrysene show that this bond has more 'double-bond character' than any other in the molecule.

TABLE 2

Atomic co-ordinates for the hydrogen atoms ($\times 10^3$). A fixed isotropic temperature factor (B) of 6·00 was used

	Molecule (1)			Molecule (2)		
Atom	x/a	y/b	z/c	x/a	y/b	z/c
H(1)	−214	154	−116	716	184	131
H(2)	−244	−167	−251	758	−124	33
H(3)	−166	−470	−284	692	−422	−87
H(4)	−58	−618	−248	588	−588	−175
H(5)	46	−582	−157	476	−570	−192
HH(23,1)	146	−614	−31	334	−535	−173
HH(23,2)	134	−516	−98	316	−284	−202
HH(23,3)	146	−366	−104	338	−282	−248
HH(23,4)	178	−263	−48	374	−384	−263
HH(23,5)	192	−366	−19	392	−535	−233
HH(23,6)	174	−516	−24	370	−633	−189

HH denotes half-hydrogen atom.



Contents of the unit cell projected on the *ac* plane (dotted lines indicate molecules at *b*/2). Molecule (1) is at 0,0,0 and molecule (2) at *a*/2,0,0

TABLE 3

Bond lengths (Å), with standard deviations in parentheses

Distance	Molecule (1)	Molecule (2)	Mean
C(1)–C(2)	1·382(15)	1·365(17)	1·374(12)
C(1)–C(13)	1·429(12)	1·454(14)	1·442(10)
C(2)–C(3)	1·412(16)	1·395(15)	1·404(11)
C(3)–C(15)	1·385(12)	1·381(15)	1·383(11)
C(4)–C(5)	1·332(11)	1·361(14)	1·347(10)
C(4)–C(15)	1·441(14)	1·415(13)	1·428(10)
C(5)–C(16)	1·441(11)	1·414(15)	1·428(11)
C(6)–C(6)	1·405(12)	1·426(14)	1·416(10)
C(6)–C(23)	1·487(14)	1·480(13)	1·484(10)
C(13)–C(14)	1·432(13)	1·415(12)	1·424(9)
C(14)–C(15)	1·417(12)	1·412(15)	1·415(11)
C(14)–C(21)	1·432(11)	1·460(12)	1·446(8)
C(16)–C(21)	1·423(13)	1·428(12)	1·426(0)
C(20)–C(21)	1·412(15)	1·385(18)	1·399(13)

Equations of the least-squares mean planes of the two independent molecules are:

$$(1)\ 0{\cdot}34589X + 0{\cdot}65157Y - 0{\cdot}67514Z = 0$$

$$(2)\ 0{\cdot}14054X + 0{\cdot}66508Y - 0{\cdot}73342Z = 1{\cdot}5576$$

where X is parallel to a, Y is parallel to b, and Z is parallel to c^*. The carbon atoms in molecule (1) have deviations from the mean plane of from 0·004 to 0·061 Å; the latter value refers to the methyl group and is almost a significant deviation. In molecule (2), on the other hand, the maximum deviation from the mean plane is 0·022 Å which is not significant.

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[5] A. Pullman and B. Pullman, *Adv. Cancer Res.*, 1955, **3**, **117**.

An interesting feature of the structure is that with such a symmetrical arrangement in the molecule, two independent half molecules are required in the asymmetric unit. This has been observed in dibenzo-[*def,mno*]chrysene-6,12-dione [6] where three independent molecules are required in the unit cell. Two symmetry-unrelated molecules are also required in dinaphtho-[1,2,3-*cd*:3′,2′,1′-*lm*]perylene-5,10-dione,[7] dinaphtho-[1,2,3-*cd*:1′,2′,3′-*lm*]perylene-9,18-dione,[8] and pyranthrene-8,16-dione.[9]

TABLE 4

Bond angles (deg.), with standard deviations in parentheses

Angle	Molecule (1)	Molecule (2)	Mean
C(1)–C(2)–C(3)	121·6(9)	122·2(9)	121·9(6)
C(1)–C(13)–C(14)	118·5(8)	117·7(9)	118·1(6)
C(2)–C(1)–C(13)	120·1(9)	118·9(9)	119·5(6)
C(2)–C(3)–C(15)	119·4(9)	121·0(11)	120·2(8)
C(3)–C(15)–C(4)	120·1(8)	121·9(10)	121·0(7)
C(3)–C(15)–C(14)	120·9(9)	118·6(9)	119·8(9)
C(4)–C(5)–C(16)	122·7(8)	122·0(8)	122·4(6)
C(4)–C(15)–C(14)	119·1(7)	119·5(9)	119·3(6)
C(5)–C(4)–C(15)	120·8(8)	121·0(10)	120·9(7)
C(5)–C(16)–C(21)	117·7(7)	119·5(9)	118·6(6)
C(5)–C(16)–C(6)	122·7(8)	122·0(8)	122·4(6)
C(6)–C(16)–C(21)	119·6(7)	118·5(9)	119·1(6)
C(13)–C(14)–C(15)	119·7(7)	121·6(8)	120·7(6)
C(13)–C(14)–C(21)	120·7(7)	118·4(8)	119·6(6)
C(14)–C(21)–C(16)	120·1(7)	118·0(8)	119·1(6)
C(15)–C(14)–C(21)	119·7(8)	120·0(8)	119·9(6)
C(16)–C(6)–C(23)	120·3(8)	120·6(9)	120·5(6)

Short intermolecular distances are listed in Table 5. There are no very short intermolecular contacts between the two independent molecules. Each type of molecule is arranged in stacks of parallel molecules along the *b* axis. In the case of type (1) (at 0,0,0) there are very short intermolecular contacts, *e.g.* 3·385 Å, but in the case of type (2) (at *a*/2,0,0) there are no intermolecular contacts of <3·5 Å. On the other hand, the atoms involved in the shortest intermolecular distances are the same in both stacks of molecules. The separation of the mean planes is 3·407 Å for type (1) and 3·478 Å for type (2).

TABLE 5

Short intermolecular contacts (Å), with standard deviations in parentheses

C(7) · · · C(2′)	3·683(16)	C(11′) · · · $\mathrm{C}(21'^{\mathrm{I}})$	3·510(13)
C(11) · · · $\mathrm{C}(21^{\mathrm{I}})$	3·385(12)	C(12′) · · · $\mathrm{C}(15'^{\mathrm{I}})$	3·534
C(12) · · · $\mathrm{C}(15^{\mathrm{I}})$	3·488(13)		

Primed atoms are in molecule (2), unprimed in molecule (1); Roman numeral superscript I denotes molecule at *x*, 1 + *y*, *z*.

The Figure illustrates the packing in the unit cell.

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[6] I. A. S. Edwards and H. P. Stadler, *Acta Cryst.*, 1971, **B27**, 946.

[7] W. Bolton and H. P. Stadler, *Acta Cryst.*, 1964, **17**, 1015.

[8] W. Bolton, *Acta Cryst.*, 1964, **17**, 1020.

[9] H. P. Stadler, *Solid-State Phys. ' Bussei,'* 1964, **5**, 659.