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An X-ray Determination of the Crystal Structure of 1,12-Dimethylbenz[*a*]anthracene

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$C_{20}H_{16}$ is monoclinic, space group $P2_1$, with $Z = 2$, $a = 8{\cdot}432\ (14)$, $b = 8{\cdot}328\ (16)$, $c = 9{\cdot}963\ (14)$ Å, $\beta = 96{\cdot}65\ (15)$°. Intensities collected from different single crystals on two different automatic diffractometers have been refined independently: set *A* to $R = 0{\cdot}081$ for 1164 reflexions, set *B* to 0·010 for 1457 reflexions. Half-normal probability plots for the two data sets suggest that apparent standard deviations for C atom positions, $\sigma_A = 0{\cdot}008$, $\sigma_B = 0{\cdot}010$ Å, are underestimated by a factor of two. As in other benz[*a*]anthracenes, the *K*-region bond C(5)–C(6) is short (1·33 Å), and the bond in the bay is long, C(13)–C(18) = 1·50 Å. In this novel bay region (with one methyl buttressed by a *peri* H atom), the methyl C atoms are 3·0 Å apart, with the 1-methyl C atom 0·4 Å below ring *A* and the 12-methyl C atom 0·5 Å above ring *C*. Individually, the benzene rings are fairly planar but overall molecular distortion is closer to that in the 5,6-epoxide of the highly carcinogenic 7,12-DMBA than to distortions in the 1- and 12-methylbenz[*a*]anthracenes.

Introduction

Although 1,12-dimethylbenz[*a*]anthracene (1,12-DMBA) is not thought to be carcinogenic, it is related to several carcinogenically active methylated benz[*a*]anthracenes: 1-methylbenz[*a*]anthracene (1-MBA) (Jones & Sowden, 1975), 12-methylbenz[*a*]anthracene (12-MBA) (Jones & Sowden, 1976), and the highly active 7,12-dimethylbenz[*a*]anthracene (7,12-DMBA), previously designated 9,10-dimethyl-1,2-benzanthracene (Iball, 1964). An arrangement with two bay (Bartle & Jones, 1967) methyl groups, 1 and 12, in which one of them is buttressed by a *peri* H atom on C(11), might be expected to cause molecular distortion in solution and in the solid state; this arrangement has not previously received crystallographic study.

Experimental

Crystal data

1,12-DMBA, $C_{20}H_{16}$, m.p. 135 °C, monoclinic, space group $P2_1$, $a = 8{\cdot}432\ (14)$, $b = 8{\cdot}328\ (16)$, $c = 9{\cdot}963\ (14)$ Å, $\beta = 96{\cdot}65\ (15)°$, $V = 695$ Å^3, $M_r = 256$, $F(000) = 272$, $Z = 2$, $D_o = 1{\cdot}24 \pm 0{\cdot}01$ (NaI flotation), $D_c = 1{\cdot}22$ g cm^{-3}, μ(Cu $K\alpha$) = 4·9 cm^{-1}. The cell dimensions are weighted means of those from data sets *A* and *B* (Table 1).

The crystals, donated by Mr M. S. Newman, had a diamond-shaped prismatic habit, unusual for monoclinic hydrocarbon crystals, with *b* along the shorter diagonal.

Two independent sets of intensities, *A* and *B*, were collected from separate crystals on different diffractometers (Table 1) with Cu $K\alpha$ radiation. Corrections were applied for Lorentz and polarization effects, and application of a statistical analysis (Wilson, 1942) to *A* gave a scale factor for $|F_o|$ of 1·10 and a mean isotropic temperature factor of 6·6 Å^2.

Structure determination

The structure was solved by direct methods with *A*. Following calculation of normalized structure factors with *SYMBAD* (Danielsen, 1969), the 363 *E* values > 1·0 were fed into an early version of *MULTAN* (Germain, Main & Woolfson, 1971) to generate three-phase structure invariants ($\sum_2$ relations; no acceptable $\sum_1$ relations were found). Tangent refinement yielded eight pairs of phase sets. An *E* map calculated with *JIMDAP* from the phase sets of highest AFOM, lowest residual, and highest $\sum_\alpha$ contained plausible C atom positions.

Fourier and isotropic least-squares refinement with *LINUS* (Coppens & Hamilton, 1970) only took *R* to 0·30 and left discrepant 001, 101 and $10\bar{1}$ reflexions as well as unacceptably close intermolecular approaches. The whole molecule was shifted by half the vector C(7)—C(6); this is nearly perpendicular to *b* and occurs with multiplicity 26 in the cell. Isotropic refinement then gave $R = 0{\cdot}18$.

When, subsequently, the new *MULTAN* suite (Main, Woolfson, Lessinger, Germain & Declercq, 1974) was applied to *A*, the most favourable (in terms of composite combined FOM, derived from combination of AFOM, ψ_0-FOM, and Karle residual) eight out of 64 sets of phases gave molecular fragments in the correct position in the cell. The advantage of the CFOM with a ψ_0 contribution was underlined by calculating CFOM's with the ψ_0 contribution removed; the set with highest

Table 1. *Comparison of crystal data, collection procedures, and structure refinements for two sets A and B*

	Data set *A* (from 12 reflexions)	Data set *B* (from 25 reflexions)
Crystal data		
a (Å)	8·430 (15)	8·440 (32)
b (Å)	8·325 (18)	8·337 (32)
c (Å)	9·971 (17)	9·947 (26)
β (°)	96·67 (16)	96·41 (53)
V (Å^3)	695·0	695·5
Crystal dimensions (mm)	0·6 × 0·5 × 0·4	0·15× 0·15 × 0·15
Crystal mounting	*b*	$b \parallel \varphi$
Data collection		
Diffractometer	Computer-controlled Hilger & Watts Y290	Computer-controlled Enraf–Nonius CAD-4
Scan mode	$\omega/2\theta$	Moving-crystal, moving-counter
Radiation	Cu $K\alpha$; Ni filter	Cu $K\alpha$; graphite monochromator
θ range(s)	0·9–30·1 °; 70 steps of 1 s in peak 29·9–65·1 °; 75 steps of 1 s in peak Background count time 30 s on each side	2·5–72 ° Scan width (3·0 + 0·5 tan θ)° Counter aperture (3·0 + 0·87 tan θ)° Time for maximum counts: 60 s
Standard reflexions (recorded every 50)	400, 006	104
Internal agreements (SD) of standard reflexions	1·3%, 1·9% ($R = 0{\cdot}11$ over 188 pairs)	1·0%
Collection rate (reflexions h^{-1})	20	40
Total number of reflexions measured	1290 (1 octant)	2888 (1 hemisphere)
Rejection criterion	$I < 3\sigma(I)$	$I < 3\sigma(I)$
Number of independent reflexions	1164	1457
Number of zero-intensity reflexions included	145	69
Internal agreement factor, *R*, between 1180 reflexions measured in different octants	–	0·068
Absorption correction	None	None

CFOM was no longer one of the correct solutions and its phases resembled those of the earlier highest-AFOM set.

Structure refinement

Set A

Full-matrix least-squares anisotropic refinement reduced R to 0·11 for 1164 reflexions, with maximum coordinate shifts of 0·006 Å and e.s.d.'s < 0·015 Å. H-atom location from a difference map was unsatisfactory; inclusion of H atoms at positions corresponding to C—H = 1 Å enabled R to drop to 0·081 with e.s.d.'s of 0·008 Å for C positions, 0·011 Å for C—C lengths and 0·7° for bond angles at C.

Set B

With the previous C-atom positions as a starting point, anisotropic least-squares refinement was performed with B and a weighting scheme $w = 1/(2{\cdot}0 + 0{\cdot}017|F_o|^2)$ to yield $R = 0{\cdot}14$ over all 1457 reflexions. A difference map revealed plausible sites for all non-methyl H atoms but, even after further refinement, with $w = 1/(2{\cdot}0 + 0{\cdot}017|F_o|^2 + 0{\cdot}0004|F_o|^3)$, a difference map failed to reveal methyl H atoms unambiguously. The most satisfactory distribution of $w\Delta^2$ was achieved with $w = 1/(3{\cdot}0 + 0{\cdot}021|F_o|^2 + 0{\cdot}003|F_o|^3)$. After refinement* to $R = 0{\cdot}10$ (weighted $R = 0{\cdot}16$), with positional e.s.d.'s about 0·010 Å, σ(C—C) = 0·014 Å, and σ(bond angles) = 0·9°, a final difference map revealed no peaks >0·25 e Å^{-3}.

Table 2. *Fractional atomic coordinates* ($\times 10^4$) *with the significant figures of apparent e.s.d.'s in parentheses* (*set B above, set A below*)

	x	y	z		x	y	z
C(1)	5434 (9)	256	5443 (8)	C(19)	3662 (9)	−244 (16)	5556 (8)
	5395 (9)	256	5454 (7)		3688 (7)	−251 (12)	5501 (6)
C(2)	6282 (11)	779 (15)	6614 (8)	C(20)	3083 (9)	1608 (14)	3014 (9)
	6304 (10)	804 (11)	6598 (7)		3041 (8)	1603 (11)	3014 (6)
C(3)	7932 (12)	1039 (16)	6683 (11)	H(2)	5732	971	7409
	7957 (10)	1055 (12)	6681 (8)		5952	890	7669
C(4)	8710 (12)	596 (17)	5640 (14)	H(3)	8534	1541	7468
	8788 (9)	501 (12)	5621 (8)		8835	1074	7812
C(5)	8668 (10)	−794 (16)	3395 (13)	H(4)	9880	695	5698
	8763 (9)	−833 (11)	3419 (8)		10065	214	6305
C(6)	7887 (10)	−1505 (16)	2335 (12)	H(5)	9857	−783	3506
	7949 (10)	−1544 (11)	2358 (8)		10172	−1097	4226
C(7)	5483 (13)	−1929 (15)	829 (10)	H(6)	8499	−2170	1768
	5503 (12)	−1953 (10)	822 (8)		8817	−2464	1550
C(8)	3116 (14)	−2170 (17)	−798 (9)	H(7)	6093	−2621	291
	3109 (12)	−2197 (12)	−818 (8)		6279	−2436	65
C(9)	1576 (17)	−1792 (20)	−1262 (9)	H(8)	3701	−2918	−1367
	1565 (11)	−1814 (13)	−1267 (8)		3352	−3179	−1515
C(10)	687 (11)	−704 (18)	−501 (9)	H(9)	1062	−2279	−2134
	672 (9)	−699 (11)	−506 (7)		748	−2416	−2413
C(11)	1431 (10)	−41 (16)	693 (8)	H(10)	−438	−491	−810
	1454 (9)	−43 (11)	691 (7)		−775	−401	−516
C(12)	3839 (8)	140 (14)	2408 (6)	H(11)	885	761	1215
	3824 (8)	86 (11)	2419 (6)		485	813	1193
C(13)	6167 (8)	−4 (13)	4281 (7)	H(191)	3676	−1129	6235
	6165 (9)	−55 (11)	4259 (7)		2585	−928	4700
C(14)	7852 (9)	−20 (14)	4436 (10)	H(192)	3095	710	5881
	7896 (9)	−41 (11)	4431 (7)		2858	701	5813
C(15)	6237 (9)	−1326 (14)	2024 (8)	H(193)	3042	−626	4700
	6244 (9)	−1384 (11)	2021 (7)		3630	−875	6314
C(16)	3873 (11)	−1568 (14)	396 (8)	H(201)	3042	2489	2329
	3884 (10)	−1621 (11)	374 (8)		3692	1883	3967
C(17)	3083 (8)	−482 (14)	1186 (6)	H(202)	1971	1302	3169
	3038 (9)	−488 (11)	1179 (6)		1706	1507	3082
C(18)	5325 (9)	−418 (13)	2897 (9)	H(203)	3620	2050	3883
	5335 (8)	−419 (11)	2896 (7)		2737	2331	2104

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* Lists of structure factors, anisotropic thermal parameters and the r.m.s. components along principal axes of thermal ellipsoids for both data sets have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33686 (36 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

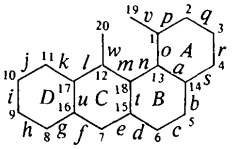
Parameters derived from refinements of A and B

Table 2 lists the atomic coordinates, and Tables 3 and 4 list the bond lengths and angles. The weighted average values are calculated from $\langle l\rangle = (\sum_i l_i/\sigma_i^2)/(\sum_i 1/\sigma_i^2)$ and the variances from $\sigma^2(\langle l\rangle) = (\sum_i 1/\sigma_i^2)^{-1}$.

Comparison of results from the two data sets

For the 1164 reflexions common to *A* and *B*, the linear scale factor $s = \sum |F_A|/\sum |F_B| = 0{\cdot}443$, for which the internal consistency index $R_c = 100(\sum |F_A - sF_B|)/\sum |F_A| = 20{\cdot}3\%$. Regression analysis of *B* on *A* gave a least-squares gradient, $s = [\sum(|F_A|.|F_B|) - (\sum |F_A|).(\sum |F_B|)/1164].[\sum |F_A|^2 - (\sum |F_A|)^2/1164]^{-1} = 0{\cdot}545$, from which the corresponding $R_c = 26{\cdot}3\%$. Despite a correlation coefficient of 0·95 on the basis of a linear relation, the R_c indicates that agreement is only fair; in particular, linear scaling underscales the larger $|F_{\rm rel}|$, *i.e.* higher-order reflexions appear to have been measured at lower intensities in *A* than *B*.

Table 3. C–C *bond lengths* (Å) *with the significant figures of e.s.d.'s in parentheses*



	Bond	Experimental set *B*	Experimental set *A*	Weighted mean	Theoretical*
a	C(13)–C(14)	1·411 (13)	1·450 (11)	1·434 (8)	1·411
b	C(14)–C(5)	1·459 (15)	1·469 (12)	1·465 (9)	1·450
c	C(5)–C(6)	1·319 (16)	1·331 (12)	1·326 (10)	1·345
d	C(6)–C(15)	1·398 (14)	1·445 (11)	1·427 (9)	1·451
e	C(15)–C(7)	1·378 (14)	1·367 (12)	1·372 (9)	1·393
f	C(7)–C(16)	1·408 (14)	1·413 (12)	1·411 (9)	1·412
g	C(16)–C(8)	1·378 (15)	1·374 (12)	1·375 (9)	1·430
h	C(8)–C(9)	1·364 (17)	1·366 (13)	1·365 (10)	1·364
i	C(9)–C(10)	1·445 (17)	1·462 (12)	1·457 (10)	1·416
j	C(10)–C(11)	1·393 (15)	1·404 (11)	1·400 (9)	1·364
k	C(11)–C(17)	1·469 (13)	1·417 (11)	1·438 (8)	1·429
l	C(17)–C(12)	1·406 (12)	1·416 (11)	1·412 (8)	1·413
m	C(12)–C(18)	1·372 (12)	1·374 (10)	1·373 (8)	1·390
n	C(18)–C(13)	1·516 (12)	1·485 (10)	1·498 (8)	1·460
o	C(13)–C(1)	1·391 (10)	1·444 (9)	1·420 (7)	1·409
p	C(1)–C(2)	1·367 (12)	1·376 (10)	1·372 (8)	1·378
q	C(2)–C(3)	1·402 (15)	1·403 (12)	1·402 (9)	1·401
r	C(3)–C(4)	1·343 (17)	1·411 (12)	1·388 (10)	1·377
s	C(4)–C(14)	1·423 (16)	1·403 (12)	1·410 (10)	1·411
t	C(15)–C(18)	1·440 (13)	1·466 (11)	1·455 (8)	1·428
u	C(16)–C(17)	1·415 (13)	1·475 (11)	1·450 (8)	1·426
v	C(1)–C(19)	1·568 (11)	1·506 (9)	1·531 (7)	–
w	C(12)–C(20)	1·534 (12)	1·573 (10)	1·557 (8)	–

* Calculated from SCF bond orders.

Accordingly, a graph analogous to a Wilson (1942) plot was computed, with $\ln S = \ln(\sum |F_B|^2/\sum |F_A|^2)$. Successive shells of $\langle\sin^2\theta/\lambda^2\rangle$ up to 0·275 Å^{-2} gave a good straight line (correlation coefficient 0·99), corresponding to $|F_A| = 0{\cdot}58|F_B| \exp(-1{\cdot}81 \sin^2\theta/\lambda^2)$.

While the apparent overall temperature factor applicable to *A* up to moderate $\sin\theta/\lambda$ (and also the higher attenuation of *A* at the highest $\sin\theta/\lambda$) may be partly attributed to slight misalignment, molecular dimensions from *B* were not quite as close to those in 1-MBA as expected; some crystal variability or other systematic effect is not excluded.

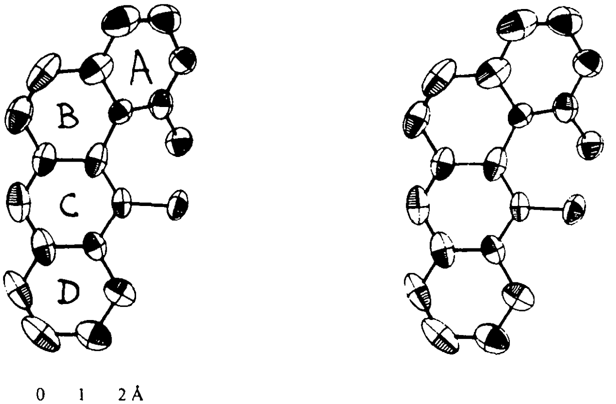


Fig. 1. Thermal ellipsoids of C atoms in a molecule of 1,12-dimethylbenz[*a*]anthracene.

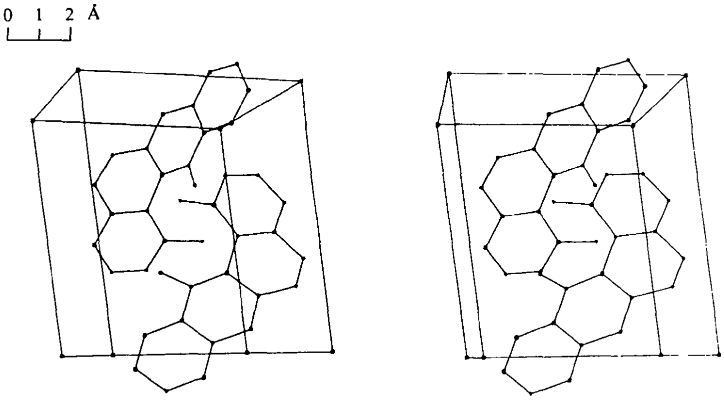


Fig. 2. Stereographic projection down *b* showing the packing of the molecules.

Half-normal probability plots (Abrahams & Keve, 1971) for the differences between the derived positional and other parameters were as linear as those from comparable structures (Abrahams & Keve, 1971; Mullen, 1974) with small intercepts (around −0·2) and with gradients about 2 for atomic coordinates, bond lengths, and angles, and 3·2 for temperature parameters. Evidently, the e.s.d.'s of positional coordinates (and bond lengths and angles) are underestimated by a factor of two, and of temperature factors by a factor of three. Taking into account also a signed structure-factor normal-probability analysis, systematic errors may be about as large as random errors.

Discussion

An individual molecule of 1,12-DMBA is shown in Fig. 1; the crystal packing is shown in Fig. 2. Comparison of bond lengths for data sets *A* and *B* (Table 3) shows that five [C(13)–C(1), C(16)–C(17), C(1)–C(19), C(3)–C(4), and C(11)–C(17)] differ by more than 3σ. In the remaining discussion only the weighted mean values will be considered.

Individually, the rings *A*, *B*, and *C* in 1,12-DMBA all deviate slightly (average 0·05 and 0·04 Å for *A* and *C*) from planarity. The 1-methyl C atom is displaced by 0·38 Å from ring *A* and the 12-methyl C atom by 0·48 Å from ring *C*. Angles between pairs of rings *A*, *B*, *C*, and *D* for 1,12-DMBA and relevant analogues are shown in Table 5. The major bending of the molecule is about ring *B* (with the *BCD* anthracene fragment remaining closely planar) and is comparable with that in 5,6-epoxy-7,12-DMBA (Glusker, Carrell & Zacharias, 1974), in which ring *B* is no longer aromatic; distortion is greater than in monomethylbenz[*a*]anthracenes (Jones & Sowden, 1976). From the best plane through all 18 C atoms in the parent BA nucleus, the r.m.s. deviation is 0·24 Å in 1,12-DMBA; the largest deviations are for the extranuclear methyl atoms: 0·98 Å for C(20) and −1·28 Å for C(19). Torsion angles (Table 6) around the bay region,

Table 4. *Bond angles (°) with e.s.d.'s in parentheses*

See Table 3 for bond labelling.

	Set *B*	Set *A*	Weighted mean		Set *B*	Set *A*	Weighted mean
vp	115·6 (7)	120·6 (6)	118·5 (5)	*ao*	116·7 (7)	116·3 (7)	116·5 (5)
vo	122·5 (6)	119·9 (6)	121·2 (4)	*an*	117·2 (8)	118·1 (7)	117·7 (5)
op	121·4 (7)	118·8 (6)	119·9 (5)	*bs*	121·5 (9)	117·7 (7)	119·1 (6)
pq	120·6 (9)	123·6 (7)	122·5 (6)	*as*	119·7 (9)	122·5 (7)	121·4 (6)
qr	119·4 (11)	118·9 (8)	119·1 (6)	*ab*	118·5 (9)	119·3 (7)	119·0 (6)
rs	120·3 (11)	118·3 (8)	119·0 (6)	*de*	120·0 (9)	120·9 (7)	120·6 (6)
bc	122·3 (10)	119·6 (8)	120·6 (6)	*dt*	120·6 (9)	119·1 (7)	119·7 (6)
cd	121·4 (10)	123·5 (7)	122·8 (6)	*et*	119·2 (9)	119·5 (7)	119·4 (6)
ef	121·3 (9)	122·4 (8)	121·9 (6)	*fg*	121·4 (9)	123·3 (8)	122·5 (6)
gh	122·4 (11)	122·8 (8)	122·7 (6)	*fu*	117·7 (9)	117·6 (7)	117·7 (6)
hi	119·9 (11)	120·5 (8)	120·3 (6)	*gu*	120·8 (9)	118·8 (8)	119·7 (6)
ij	119·1 (10)	117·9 (7)	118·3 (6)	*kl*	121·0 (8)	122·6 (7)	121·9 (5)
jk	120·1 (9)	121·4 (7)	120·9 (6)	*ku*	117·6 (8)	118·5 (7)	118·1 (5)
lm	119·1 (8)	121·4 (7)	120·4 (5)	*lu*	121·4 (8)	118·9 (7)	120·0 (5)
lw	117·8 (7)	115·2 (6)	116·3 (5)	*mn*	123·9 (8)	125·0 (7)	124·6 (5)
mw	122·3 (8)	121·9 (7)	122·1 (5)	*mt*	119·5 (8)	119·3 (7)	119·4 (5)
no	125·9 (7)	125·5 (6)	125·7 (5)	*nt*	116·2 (7)	115·6 (6)	115·9 (5)

Table 5. *Mutual inclinations (°) between pairs of ring planes (A, B, C, and D) in* 1,12-*DMBA and related benz*[*a*]*anthracenes*

Ring pairs	1,12-DMBA(a)	BA complex(b)	1-MBA(c)	12-MBA(d)	7,12-DMBA(e)	5,6-Epoxy-7,12-DMBA(f)
A/B	15·0	2·2	8·9	10·7	10·9	14·2
A/C	27·9	2·9	18·7	19·2	21·2	28·6
B/C	13·3	1·2	10·2	8·7	10·5	15·1
A/D	29·6	1·4	21·8	20·1	24·0	34·8
B/D	14·7	1·6	13·0	9·5	13·2	20·9
C/D	2·8	1·8	4·5	3·7	5·0	6·4

References: (*a*) Present work, (*b*) Foster, Iball, Scrimgeour & Williams (1976), (*c*) Jones & Sowden (1975), (*d*) Jones & Sowden (1976), (*e*) Iball (1964), (*f*) Glusker *et al.* (1974).

Table 6. *Torsion angles* (°) *for sequences of* C–C *bonds*

The sign refers to the convention of Klyne & Prelog (1960); the angle is positive when the rotation is clockwise from the front substituent to the rear. E.s.d.'s are 1–2°. See Table 3 for bond labelling.

	Set *B*	Set *A*		Set *B*	Set *A*
nab	−15	−18	*mlu*	−5	−1
nas	170	171	*lmn*	−172	−172
oab	160	161	*lmt*	15	9
oas	−15	−11	*fed*	−171	−171
anm	−152	−154	*fet*	5	1
ant	22	26	*efg*	−180	−179
onm	34	27	*efu*	4	6
ont	−153	−153	*dtn*	−13	−16
aop	12	11	*dtm*	161	163
nop	−173	−171	*etn*	171	171
abc	−1	0	*etm*	−15	−9
sbc	173	172	*guk*	1	0
asr	7	0	*gul*	180	179
bsr	−168	−171	*fuk*	177	175
bcd	11	10	*ful*	−4	−6
cde	173	171	*opq*	−1	−1
cdt	−3	−1	*pqr*	−8	−10
ghi	1	2	*qrs*	5	10
hgf	−178	−177	*vpq*	171	170
hgu	−2	−3	*von*	15	19
hij	1	0	*voa*	−159	−160
ijk	−2	−2	*wlk*	−16	−17
jkl	−178	−177	*wlu*	165	165
jku	1	2	*wmn*	19	23
klm	174	177	*wmt*	−155	−156

C(19)–C(1)–C(13)–C(18) (*von*) = 17°, C(1)–C(13)–C(18)–C(12) (*onm*) = 30°, and C(13)–C(18)–C(12)–C(20) (*wmn*) = 21°, are larger in 1,12-DMBA than in other BA compounds. The methyl bond angles are C(19)–C(1)–C(13) = 121° and C(20)–C(12)–C(18) = 122° in 1,12-DMBA. C(1)–C(19) is at 75·8° to the ring *A* normal (83·8° in 1-MBA), and C(12)–C(20) is at 72·0° to the ring *C* normal (78·3° in 12-MBA).

By comparison with the mean BA lengths (Jones & Sowden, 1976), the most discrepant lengths determined in 1,12-DMBA are (mean BA length followed by 1,12-DMBA length): C(16)–C(8) 1·43, 1·38 Å; C(10)–C(11) 1·36, 1·40 Å; C(16)–C(17) 1·42, 1·45 Å; C(9)–C(10) 1·43, 1·46 Å. Of the bond angles in 1,12-DMBA, only the bay angle C(1)–C(13)–C(18) at 126° differs significantly from the corresponding mean for the methylbenz[*a*]anthracenes. As in all these methylbenz[*a*]anthracenes {and in 7-chloromethylbenz[*a*]anthracene (Zacharias, 1977)}, the *K*-region bond C(5)–C(6) is the shortest (here 1·33 Å), while the dihedral angle of 10° around it, C(14)–C(5)–C(6)–C(15), is rather larger in 1,12-DMBA than the value of 8° typical of the methylbenz[*a*]anthracenes. The longest C–C bond within the BA nucleus in 1,12-DMBA is that at the beach of the bay, C(18)–C(13) = 1·50 Å. The two methyl C atoms are separated across the bay by 2·96 Å, rather less than the 3·25 Å in 1,12-dimethylbenzophenanthrene (Hirshfeld, Sandler & Schmidt, 1963).

The closest non-bonded intermolecular C···C contacts (e.s.d. 0·01 Å), listed under the generating symmetry elements, are:

$1+x, y, 1+z$	
C(3)–C(10)	3·71 Å
$1+x, y, z$	
C(6)–C(11)	3·77
$2-x, y+\frac{1}{2}, 1-z$	
C(4)–C(5)	3·77
$1-x, y+\frac{1}{2}, -z$	
C(18)–C(8)	3·73
C(15)–C(8)	3·74
$1-x, y+\frac{1}{2}, 1-z$	
C(2)–C(7)	3·65 Å
C(2)–C(12)	3·73
C(20)–C(1)	3·58
C(20)–C(2)	3·55
C(2)–C(15)	3·57
C(2)–C(18)	3·48
C(3)–C(17)	3·74
C(2)–C(16)	3·72
$-x, y+\frac{1}{2}, -z$	
C(9)–C(11)	3·79.

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