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3,9-Dimethylbenz[*a*]anthracene: a Carcinogenically Inactive and Nearly Planar Hydrocarbon

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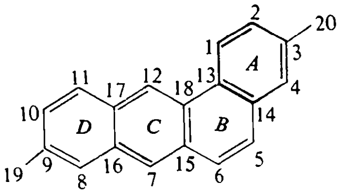
Abstract. $C_{20}H_{16}$, $M_r = 256{\cdot}3$, monoclinic, $P2_1/n$, $a = 14{\cdot}069\,(2)$, $b = 7{\cdot}664\,(1)$, $c = 25{\cdot}871\,(4)$ Å, $\beta = 101{\cdot}23\,(2)°$, $V = 2736{\cdot}0$ Å^3, $Z = 8$, $D_m = 1{\cdot}24\,(1)$ (NaI flotation), $D_x = 1{\cdot}24$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}35$ cm^{-1}, $F(000) = 1088$, $T = 298$ K, final $R = 0{\cdot}039$ for 2087 observed reflections. The two independent molecules (I and II) are almost parallel and r.m.s. differences between corresponding C—C bond lengths and C—C—C angles are 0·006 Å and 0·7°, respectively. Deviations from planarity are larger than in other methylbenz[*a*]anthracenes lacking a 1- or 12-(bay) substituent and amount to a bowing along the lengths of the molecules, greater in molecule (I) than (II) such that mutual inclinations of the outermost rings *A*/*D* are 8·6 and 5·1°. The shortest mean C—C bonds are C(5)—C(6) = 1·334 (3) Å (K-region) and C(10)—C(11) = 1·354 (3) Å; in the bay region, the beach bond C(13)—C(18) = 1·462 (3) Å and the beach angles C(13)—C(18)—C(12) and C(18)—C(13)—C(1) are both 123·2 (3)°. Methyl H atoms appear to be disordered between two sets of positions, almost equally populated for three methyl groups and dominated by one orientation in the fourth.

Introduction. The dimethylbenz[*a*]anthracenes (DMBA's), like the monomethylbenz[*a*]anthracenes (MBA's), embrace a wide range of carcinogenic activity (Newman, 1976; Jones & Matthews, 1974) from the extremely potent 7,12-DMBA (Iball, 1964) to the almost inactive 1,12-DMBA (Jones & Shaw, 1985, unpublished measurements; Jones, Sowden, Hazell & Hazell, 1978). Both these DMBA's contain at least one substituent in the bay region (Bartle & Jones, 1967) so that steric interaction buckles them into a type-II molecular shape (Briant, Jones & Shaw, 1985). The title compound (3,9-DMBA, formerly designated 3′,6-dimethylbenz-1:2-anthracene) is almost inactive (Wislocki, Fiorentini, Fu, Yang & Lu, 1982) and is the first type-I (nearly planar) DMBA to have its crystal and molecular structure determined (Briant & Jones, 1983).



3,9-DMBA

Experimental. Powder sample (provided by Professor M. S. Newman) recrystallized from ethanol to yield thin plates. Single crystal of dimensions 0·5 × 0·3 × 0·2 mm used to confirm photographically determined cell dimensions (25 reflections, $10 < \theta < 15°$) and for intensity-data collection with graphite-monochromatized Mo $K\alpha$ radiation on an Enraf–Nonius CAD-4*F* diffractometer (Rothamstead). Collection details: $\omega/2\theta$ scan, variable scan width $(0{\cdot}70 + 0{\cdot}35\tan\theta)°$, variable aperture width $(1{\cdot}40 + 3{\cdot}00\tan\theta)$ mm, θ range 1·5–22·5°, index ranges h 0/16, k 0/8, l −28/28; no significant changes in intensities of standard reflections $21\bar{3}$ and 204 (remeasured at 2 h intervals) or orientation-control reflections $\bar{2},\bar{1},10$, 427, 5,0,11 (remeasured every 150 reflections). 3852 measured reflections yielded 3564 unique reflections ($R_{\text{int}} = 0{\cdot}030$) utilized in direct-methods structure solution by *MULTAN*77 (Main, Lessinger, Woolfson, Germain & Declercq, 1977). Among the highest CFOM solutions from the highest 300 of the E values [distribution, and that of $N(z)$, close to hypercentric; $E_{\max}$ for 12,1,10] was one from which the two independent 3,9-DMBA moieties could be discerned from the hexagonal networks. Unsatisfactory refinement was attributed, as with some other MBA's (Jones *et al.*, 1978; Walker, Briant, Jones & Shaw, 1985, unpublished measurements), to incorrect positioning of correctly orientated molecules. Constrained refinements of rigid molecules (I) and (II) (defined by moiety positions and Euler orientation angles) with *KONSLS* (Pawley, 1971) after a series of vector shifts of one or both molecules gave a lowest $R = 0{\cdot}33$ for $z = +0{\cdot}25$ *meta* shifts [*e.g.*

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C(16)→C(15)] to both fragments. Isotropic full-matrix least-squares refinement with *SHELX*76 (Sheldrick, 1976) to $R = 0{\cdot}214$ was followed by anisotropic blocked-matrix refinement and location of all aromatic H atoms by Fourier difference synthesis. Slant-plane ΔF sections in *CRYSTALS* (Carruthers, 1975) through the expected methyl-H planes first gave H positions for a single predominant orientation of methyl group C(119) on C(9) in molecule (II) but with rings of electron density for H atoms of the other three methyls. This was attributed, as with 2-MBA (Briant & Jones, 1985), to pairs of C—C(methyl) rotamer orientations at each methyl group (revealed in later slant-plane ΔF sections), initially with equal occupancy but ultimately refined to occupation factors: H(19 1–3) 0·58 (3), H(19 4–6) 0·42 (3); H(20 1–3) 0·56 (3), H(20 4–6) 0·44 (3); H(119 1–3) 0·74 (4), H(119 4–6) 0·26 (4); H(120 1–3) 0·44 (3), H(120 4–6) 0·56 (3). After final stages of least-squares anisotropic refinement on F (separate common $U_{\rm iso}$ for aromatic H's and for each of the four methyl H trios) with Chebyshev (Carruthers & Watkin, 1979) weighting coefficients 25·84, 32·89, 8·30 to $R = 0{\cdot}039$ ($wR = 0{\cdot}043$) over 2087 reflections ($|F_o| > 3\sigma|F_o|$) and 503 variables, a ΔF synthesis showed only random peaks $\leq 0{\cdot}15$ e Å^{-3}. $(\Delta/\sigma)_{\rm max} = 0{\cdot}3$. Scattering factors from Stewart, Davidson & Simpson (1965) for H and Cromer & Mann (1968) for C. No correction for absorption or secondary extinction. Corrections for rigid-body motion typically lengthen C—C bond lengths by ~0·003 Å.

Discussion. Final fractional coordinates of C atoms are in Table 1,* C—C bond lengths in Table 2 and C—C—C bond angles in Table 3. The two crystallographically independent 3,9-DMBA molecules have similar but not identical shapes, approximating to the type-I or nearly planar methylbenz[*a*]anthracenes (Briant, Jones & Shaw, 1985); they are less planar than 2-MBA and 11-MBA (Briant & Jones, 1984) and are slightly arched along the length of the molecule [*i.e.* C(3) to C(9)]. Individual benzene rings are planar; only rings *B* and *C* have r.m.s. deviations from the mean planes as high as 0·1 Å. The inclination between extreme rings *A* and *D* is 8·6 (3)° for molecule (I) and 5·1 (3)° for molecule (II). Although the most deviant C atom from the 18-atom BA mean plane, C(9), is only 0·15 Å (molecule I) and 0·09 Å (II) away, C(12) (in ring *C*) and C(9) differ in height above and below the mean molecular plane by 0·30 (2) Å [0·18 (2) Å in (II)], while the methyl C atoms attached to C(9) and C(3) have separations from C(12) of 0·43 (2) and 0·35 (2) Å

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* (Å^2 $\times 10^2$) *with e.s.d.'s in parentheses*

$$U_{\rm eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	$U_{\rm eq}$
Molecule (I)				
C(1)	4484 (2)	6653 (4)	8739 (1)	54 (2)
C(2)	4034 (3)	6560 (4)	9163 (1)	60 (2)
C(3)	4485 (2)	7119 (4)	9665 (1)	57 (2)
C(4)	5403 (3)	7777 (4)	9717 (1)	57 (2)
C(5)	6858 (2)	8572 (4)	9369 (1)	56 (2)
C(6)	7321 (2)	8775 (4)	8970 (1)	52 (2)
C(7)	7340 (2)	8577 (4)	8022 (1)	49 (2)
C(8)	7352 (2)	8534 (4)	7070 (1)	51 (2)
C(9)	6924 (2)	8112 (4)	6564 (1)	54 (2)
C(10)	6013 (2)	7268 (4)	6486 (1)	56 (2)
C(11)	5555 (2)	6872 (4)	6886 (1)	51 (2)
C(12)	5522 (2)	7004 (4)	7837 (1)	45 (2)
C(13)	5428 (2)	7312 (4)	8792 (1)	46 (2)
C(14)	5893 (2)	7879 (4)	9297 (1)	49 (2)
C(15)	6869 (2)	8273 (3)	8441 (1)	43 (2)
C(16)	6907 (2)	8143 (3)	7506 (1)	46 (2)
C(17)	5983 (2)	7323 (4)	7411 (1)	44 (2)
C(18)	5929 (2)	7493 (3)	8350 (1)	43 (2)
C(19)	7409 (3)	8541 (5)	6109 (1)	66 (2)
C(20)	3966 (3)	6972 (5)	10122 (1)	70 (2)
Molecule (II)				
C(101)	7293 (2)	1417 (4)	2696 (1)	51 (2)
C(102)	6833 (2)	1343 (4)	3121 (1)	54 (2)
C(103)	7297 (2)	1897 (4)	3620 (1)	52 (2)
C(104)	8224 (2)	2528 (4)	3672 (1)	54 (2)
C(105)	9687 (2)	3260 (4)	3320 (1)	54 (2)
C(106)	10165 (2)	3350 (4)	2923 (1)	51 (2)
C(107)	10189 (2)	3042 (4)	1983 (1)	48 (2)
C(108)	10229 (2)	2855 (4)	1028 (1)	55 (2)
C(109)	9794 (2)	2419 (4)	527 (1)	58 (2)
C(110)	8845 (3)	1721 (4)	440 (1)	59 (2)
C(111)	8374 (3)	1461 (4)	842 (1)	54 (2)
C(112)	8323 (2)	1676 (4)	1794 (1)	46 (2)
C(113)	8242 (2)	2032 (3)	2746 (1)	43 (2)
C(114)	8711 (2)	2616 (4)	3249 (1)	46 (2)
C(115)	9712 (2)	2831 (3)	2398 (1)	44 (2)
C(116)	9758 (2)	2614 (4)	1464 (1)	46 (2)
C(117)	8811 (2)	1895 (4)	1373 (1)	46 (2)
C(118)	8748 (2)	2145 (3)	2305 (1)	42 (2)
C(119)	10310 (3)	2661 (5)	73 (1)	73 (2)
C(120)	6803 (3)	1744 (5)	4085 (1)	65 (2)

Table 2. *Bond lengths* (Å) *for* C—C *bonds, uncorrected and corrected for rigid-body thermal motion, with e.s.d.'s in parentheses*

	Molecule (I)		Molecule (II)		Mean
	Uncorrected	Corrected	Uncorrected	Corrected	Uncorrected
C(13)—C(14)	1·411 (4)	1·414	1·412 (4)	1·415	1·411
C(5)—C(14)	1·436 (4)	1·440	1·436 (4)	1·440	1·436
C(5)—C(6)	1·332 (4)	1·333	1·335 (4)	1·337	1·334
C(6)—C(15)	1·446 (4)	1·449	1·439 (4)	1·442	1·443
C(7)—C(15)	1·394 (4)	1·396	1·382 (4)	1·384	1·388
C(7)—C(16)	1·395 (4)	1·398	1·399 (4)	1·402	1·397
C(8)—C(16)	1·426 (4)	1·428	1·427 (4)	1·428	1·427
C(8)—C(9)	1·367 (4)	1·370	1·364 (4)	1·367	1·366
C(9)—C(10)	1·414 (4)	1·417	1·415 (4)	1·419	1·415
C(10)—C(11)	1·356 (4)	1·358	1·352 (4)	1·353	1·354
C(11)—C(17)	1·417 (4)	1·419	1·432 (4)	1·435	1·424
C(12)—C(17)	1·405 (4)	1·407	1·405 (4)	1·407	1·405
C(12)—C(18)	1·390 (4)	1·393	1·389 (4)	1·392	1·389
C(13)—C(18)	1·463 (4)	1·464	1·461 (4)	1·463	1·462
C(1)—C(13)	1·403 (4)	1·406	1·398 (4)	1·402	1·400
C(1)—C(2)	1·372 (4)	1·374	1·379 (4)	1·381	1·376
C(2)—C(3)	1·396 (4)	1·399	1·397 (4)	1·400	1·397
C(3)—C(4)	1·368 (4)	1·372	1·372 (4)	1·376	1·370
C(4)—C(14)	1·396 (4)	1·397	1·402 (4)	1·404	1·399
C(15)—C(18)	1·429 (4)	1·432	1·432 (4)	1·435	1·430
C(16)—C(17)	1·422 (4)	1·425	1·419 (4)	1·422	1·420
C(9)—C(19)	1·509 (4)	1·511	1·508 (4)	1·509	1·509
C(3)—C(20)	1·510 (5)	1·512	1·505 (4)	1·507	1·508

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* Lists of structure factors, anisotropic thermal parameters, parameters of H atoms and intermolecular contacts have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42800 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(molecule I) and 0·23 (2) and 0·16 (2) Å (molecule (II), respectively, perpendicular to the molecular plane. Within the unit cell (Fig. 1), the independent 3,9-DMBA molecules lie in almost parallel (3° mutual inclination) layers, ~3·5 Å apart, although screw-related molecules have a mutual inclination of ~30°; $|F(020)|$ is almost one-half $F(000)$. As in the 2-MBA structure, there is very little overlap of adjacent ring systems but some $H_{\text{ring}}\cdots H_{\text{methyl}}$ intermolecular approaches are closer [*i.e.* 2·4 (1) – 2·8 (1) Å] than in the 2-MBA or 11-MBA structures. It appears that the comparatively large bowing in crystalline 3,9-DMBA is a consequence of crystal packing forces.

Table 3. *Bond angles* (°)

E.s.d.'s are 0·3° for all C—C—C bond angles.

	Molecule (I)	Molecule (II)	Mean
C(13)—C(14)—C(5)	119·3	119·4	119·3
C(3)—C(4)—C(14)	123·0	122·7	122·9
C(14)—C(5)—C(6)	122·4	122·2	122·3
C(4)—C(14)—C(5)	121·2	121·2	121·2
C(5)—C(6)—C(15)	120·8	121·0	120·9
C(4)—C(14)—C(13)	119·5	119·5	119·5
C(6)—C(15)—C(7)	120·2	120·6	120·4
C(6)—C(15)—C(18)	119·3	119·4	119·3
C(15)—C(7)—C(16)	121·2	122·2	121·7
C(7)—C(15)—C(18)	120·5	120·0	120·3
C(7)—C(16)—C(8)	122·0	123·1	122·6
C(7)—C(16)—C(17)	119·1	117·9	118·5
C(16)—C(8)—C(9)	121·9	121·9	121·9
C(8)—C(16)—C(17)	118·9	119·0	118·9
C(8)—C(9)—C(10)	117·7	118·6	118·1
C(11)—C(17)—C(16)	118·5	117·6	118·1
C(9)—C(10)—C(11)	122·9	121·5	122·2
C(12)—C(17)—C(16)	119·1	120·2	119·6
C(10)—C(11)—C(17)	120·1	121·4	120·8
C(12)—C(18)—C(15)	117·7	118·2	118·0
C(11)—C(17)—C(12)	122·4	122·2	122·3
C(13)—C(18)—C(15)	118·9	118·7	118·8
C(17)—C(12)—C(18)	122·4	121·5	121·9
C(18)—C(13)—C(14)	119·3	119·3	119·3
C(12)—C(18)—C(13)	123·4	123·0	123·2
C(1)—C(13)—C(14)	117·5	117·3	117·4
C(1)—C(13)—C(18)	123·2	123·2	123·3
C(8)—C(9)—C(19)	120·9	121·1	121·0
C(13)—C(1)—C(2)	121·0	121·9	121·4
C(10)—C(9)—C(19)	121·5	120·4	121·0
C(1)—C(2)—C(3)	122·1	121·1	121·6
C(2)—C(3)—C(20)	120·2	120·6	120·4
C(2)—C(3)—C(4)	117·0	117·6	117·3
C(4)—C(3)—C(20)	122·8	121·8	122·3

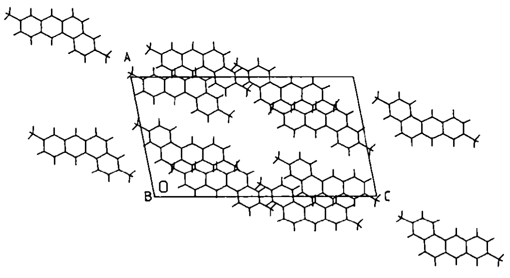

Fig. 1. View down the *b* axis of the molecular packing of 3,9-DMBA in one unit cell of the crystal structure.

As a test of the significance of small differences between corresponding bond lengths and angles in molecules (I) and (II), half-normal probability plots (Abrahams & Keve, 1971; Hamilton & Abrahams, 1972) for 23 bonds, 34 angles and 108 interatomic distances were fairly linear and suggestive of an increase of e.s.d.'s by about 50%. Such enhanced e.s.d.'s would formally deprive intermolecular differences of any significance but discrepancies between molecular dimensions around ring *D* may be just on the edge of significance. Application in *GEOM* (Davies, 1980) of a best-match analysis program based on a Watkin (1980) algorithm confirms that there are small genuine overall molecular-shape differences between the independent molecules, principally in the coordinates perpendicular to the molecular plane. Most large r.m.s. deviations from the best-fit 18-atom and 20-atom C mean planes are near substitution points, around 0·05 Å for C(3), C(8) and C(9); the methyl C atoms have an r.m.s. deviation of about 0·13 Å from the 20-atom plane.

Corresponding C—C bonds (Table 2) in the 3,9-DMBA molecules have remarkably similar lengths [only C(11)—C(17) has a relatively large difference of 0·015 Å] and there is very close agreement (if allowance is made for slight lengthening adjacent to substitution points) of mean lengths within the BA framework with corresponding ones in other type-I MBA's: 2-MBA, 8-MBA and 11-MBA. As usual, the K-region bond C(5)—C(5) = 1·334 (3) Å is shortest [with a $^1H\cdots{}^1H$ NMR coupling constant (Jones & Mokoena, 1982) of 9·0 Hz], with C(10)—C(11) = 1·354 (3) Å next shortest. At the bay region, the beach bond C(13)—C(18) = 1·462 (3) Å is long and the beach angles C(13)—C(18)—C(12) and C(18)—C(13)—C(1) are extended to 123·2 (3)°, even without bay substituents. The analysis of 3,9-DMBA also provides unequivocal examples of the reduction by about 2° of the C—C—C bond angles at substituent points 3 and 9, and the corresponding enhancements by 2–3° in angles at the β positions 2, 4, 8 and 9.

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Structures of Two Derivatives of 1,2,4-Trioxane

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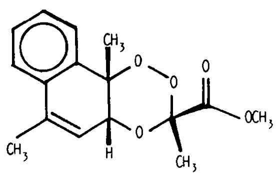
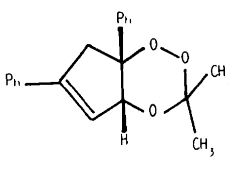
Abstract. (I): *cis*-4a,10b-Dihydro-3,6,10b-trimethylnaphtho[2,1-*e*][1,2,4]trioxin-3-carboxylic acid methyl ester, $C_{16}H_{18}O_5$, $M_r = 290{\cdot}3$, monoclinic, $P2_1/a$, $a = 24{\cdot}474\ (4)$, $b = 7{\cdot}798\ (8)$, $c = 8{\cdot}150\ (8)$ Å, $\beta = 106{\cdot}95\ (2)°$, $U = 1487{\cdot}8\ (3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}30$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}54178$ Å, $\mu = 0{\cdot}710$ mm^{-1}, $F(000) = 616$, $T = 293$ K, final $R = 0{\cdot}047$ for 2367 unique diffractometer data $[F_o > 3\sigma(F_o)]$. (II): *cis*-4a,7a-Dihydro-3,3-dimethyl-6,7a-diphenyl-7*H*-cyclopenta[1,2,4]trioxin, $C_{20}H_{20}O_3$, $M_r = 308{\cdot}4$, monoclinic, $P2_1/c$, $a = 17{\cdot}144\ (4)$, $b = 5{\cdot}771\ (1)$, $c = 17{\cdot}720\ (4)$ Å, $\beta = 110{\cdot}64\ (2)°$, $U = 1640{\cdot}7\ (6)$ Å^3, $Z = 4$, $D_x = 1{\cdot}25$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}54178$ Å, $\mu = 0{\cdot}584$ mm^{-1}, $F(000) = 656$, $T = 293$ K, final $R = 0{\cdot}042$ for 2577 unique diffractometer data $[F_o > 3\sigma(F_o)]$. *cis*-Fusion of 1,2,4-trioxane [to cyclohexadiene in (I) and cyclopentene in (II)] is confirmed. The heterocycle adopts a chair conformation in (I) and a twist-boat form in (II). The C—O bond lengths in (I) and (II) cover a wide range [1·401 (1)–1·444 (1) Å], as is found in other trioxanes.

Introduction. The 1,2,4-trioxane ring is the key substructural feature of the antimalarial *Qinghaosu* [Qinghaosu Antimalarial Coordinating Research Group, 1979; crystal structure: Academica Sinica Qingahaosu Research Group (hereinafter ASQRG), 1980]. There is considerable current pharmaceutical and structural interest in this unusual heterocycle, for which few reliable synthetic routes were previously known. Recently, however, Jefford and co-workers have shown that high yields of 1,2,4-trioxanes are produced *via* catalytic reactions of ketones and aldehydes with 1,2-dioxetanes (Jefford, Boukouvalas & Kohmoto, 1983), 1,4-endoperoxides (Jefford, Jaggi, Boukouvalas & Kohmoto, 1983), and allylic hydroperoxides (Jefford, Jaggi, Kohmoto, Boukouvalas & Bernardinelli, 1984). Here we present X-ray results for two derivatives (I, II) prepared *via* the second of these synthetic routes.



(I)



(II)

Experimental. (I): Colourless needles, crystal 0·15 × 0·20 × 0·43 mm, Nicolet $P2_1$ diffractometer, unit-cell parameters derived from 15 reflections with $36 < 2\theta < 85°$, $\omega/2\theta$ scan mode with variable scan rate (3–29·3° min^{-1}), 3355 reflections measured in two

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