

The glycosidic angle is in the *anti* domain, with a value of $142.1(4)^\circ$. This is in contrast with the *syn* conformation typical of formycin salts (McKenna, Neidle & Serafinowski, 1987; Koyama, Umezawa & Iitaka, 1974), with an intramolecular hydrogen bond between O(5') and N(3) stabilizing the arrangement, which has been found in 3'-deoxyformycin A (McKenna, Neidle & Serafinowski, 1987) and 2',3'-dideoxyformycin A (Neidle, Urpi, Serafinowski & Whitby, 1989) when they are hydrochloride salts. In the former case a proton was located attached to the N(3) atom; the analysis of 2',3'-dideoxyformycin hydrochloride was of insufficient accuracy for it to be found. Formycin A 5'-monophosphate is similarly protonated at N(3) (Giranda, Berman & Schramm, 1988). The replacement of O(5') by a Cl atom in the present structure renders such an interaction unlikely in the absence of protonation at N(3).

Conversely, the protonated form of 5'-chloro-3',5'-dideoxyformycin A is likely to have a *syn* conformation in view of the high electronegativity of the Cl atom.

The conformation about the C(4')—C(5') bond is *trans* with a Cl—C(5')—C(4')—C(3') torsion angle of $175.6(3)^\circ$. It is possible that the increased size of the Cl atom, compared with a hydroxyl O atom in a normal nucleoside, is responsible for this *trans* arrangement.

The water molecule is, unusually, at close hydrogen-bonding distance to the deoxyribose sugar ring O atom [OW...O(4') 2.809(3) Å].

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References

- ALTONA, C. & SUNDARALINGAM, M. (1972). *J. Am. Chem. Soc.* **94**, 8205–8212.
 FRENZ, B. A. (1980). *Enraf-Nonius Structure Determination Package*. Enraf-Nonius, Delft, The Netherlands.
 GIRANDA, V. L., BERMAN, H. M. & SCHRAMM, V. L. (1988). *Biochemistry*, **27**, 5813–5818.
 KOYAMA, G., UMEZAWA, H. & IITAKA, Y. (1974). *Acta Cryst.* **B30**, 1511–1516.
 MCKENNA, R., NEIDLE, S. & SERAFINOWSKI, P. (1987). *Acta Cryst.* **C43**, 2358–2361.
 NEIDLE, S., URPI, L., SERAFINOWSKI, P. & WHITBY, D. (1989). *Biochem. Biophys. Res. Commun.* **161**, 910–916.
 PRUSINER, P., BRENNAN, T. & SUNDARALINGAM, M. (1973). *Biochemistry*, **12**, 1196–1202.
 SERAFINOWSKI, P. (1987). *Synthesis*, **10**, 873–884.
 SHELDRICK, G. M. (1984). *SHELX84*. Program for crystal structure determination. Univ. of Göttingen, Federal Republic of Germany.
 SUHADOLNIK, R. J. (1979). *Nucleosides as Biological Probes*. New York: John Wiley.
 TAYLOR, R. & KENNARD, O. (1982). *J. Mol. Struct.* **78**, 1–28.
 WALKER, N. L. & STUART, D. I. (1983). *Acta Cryst.* **A39**, 158–166.

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5-Methylbenz[a]anthracene: a Mildly Carcinogenic Planar Polycyclic Hydrocarbon

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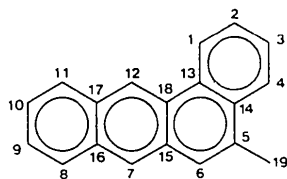
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Abstract. C₁₉H₁₄, *M_r* = 242.3, monoclinic, *P*2₁/*c*, *a* = 5.994(1), *b* = 23.482(6), *c* = 18.367(2) Å, β = 90.57(1)°, *V* = 2585.0(2) Å³, *Z* = 8, *D_m* = 1.23(1) (NaI flotation), *D_x* = 1.25 g cm⁻³, $\lambda(\text{Cu K}\alpha)$ = 1.5418 Å, μ = 5.6 cm⁻¹, *F*(000) = 1024, *T* = 298 K, final *R* = 0.053 for 2618 observed reflections. The two independent molecules have different orientations within the cell and are nearly planar (r.m.s. deviations of C atoms 0.055 and 0.041 Å), but the dihedral angles of 3.4 and 6.2° between the outermost *A* and *D* rings are larger than in most benz[a]anthracenes unsubstituted in the bay position. The shortest mean C—C bonds are C5—C6 = 1.324(4)

(*K* region), C10—C11 = 1.357(4), C8—C9 = 1.355(4) and C2—C3 = 1.360(4) Å. In the bay region, the beach bond is 1.471(4) Å with beach angles C12—C18—C13 = 122.2(4) and C18—C13—C1 = 121.4(4)°.

Introduction. Isomeric monomethylbenz[a]anthracenes (MBA's) encompass a wide range of carcinogenic activities (Wislocki, Fiorentini, Fu, Yang & Lu, 1982). They, and the dimethylbenz[a]anthracenes (DMBA's), vary in shape from the appreciably distorted or type II (Briant, Jones & Shaw, 1985) when either or each of the bay sites 1 and 12 carries a

substituent (Jones & Shaw, 1987), to the almost planar, with methyl substituted at a non-bay site as in 11-MBA (Briant & Jones, 1984). 5-MBA is one of the less carcinogenically active MBA's and determination of its crystal and molecular structure is of especial interest in that substitution is at the phenanthrenic *K* region, directly opposite the bay.



5-Methylbenz[a]anthracene

Experimental. Fine needles (Professor M. S. Newman) recrystallized from benzene/alcohol in a sealed tube to yield colourless prisms. Absences from photographic measurements indicated space group $P2_1/c$. Crystal of dimensions $0.5 \times 0.3 \times 0.2$ mm used to refine cell dimensions (24 reflections, $35 < 2\theta < 60^\circ$) and for intensity-data collection on an Enraf-Nonius CAD-4 diffractometer with Cu $K\alpha$ radiation. Collection details: $\omega/2\theta$ scan, variable scan width $(0.9 + 0.14 \tan \theta)^\circ$, fixed aperture width (3.5 mm), θ range $1.5\text{--}65^\circ$, index range $h - 1\text{--}7$, $k - 1\text{--}27$, $l - 21\text{--}21$. Intensity standards $\bar{1}85$, $\bar{3}31$, $1, 12, 1$, checked hourly, showed no systematic variation. 6129 measured reflections yielded 2618 unique reflections with $|F| > 3\sigma(|F|)$. Merging $R = 0.015$.

With a statistically (rather than normally) weighted tangent formula, structure solution by *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) generated *E* maps with two complete MBA ring systems. Following isotropic least-squares refinement on *F* of C atoms in *CRYSTALS* (Carruthers, 1978) to $R = 0.139$, and anisotropic refinement to $R = 0.108$, difference Fourier syntheses revealed sites for all H atoms, which were included in subsequent least-squares calculations with isotropic temperature factors. For the final stages (with variables separated into two groups which were adjusted in successive refinement cycles because of their number), with Chebyshev weighting (Carruthers & Watkin, 1979), two terms with coefficients 41.93 and 32.96, refinement converged to $R = 0.053$ ($wR = 0.058$) over 2618 unique reflections; a ΔF synthesis showed only randomly distributed peaks $< |0.15| e \text{ \AA}^{-3}$. Scattering factors from Stewart, Davidson & Simpson (1965) for H atoms and Cromer & Mann (1968) for C atoms. No correction for absorption or secondary extinction.

Discussion. Final fractional coordinates of C atoms with equivalent isotropic temperature factors are in

Table 1. Fractional atomic positional coordinates ($\times 10^4$) and average U ($\text{\AA}^2 \times 10^3$) with e.s.d.'s in parentheses

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

| | <i>x</i> | <i>y</i> | <i>z</i> | U_{eq} |
|------|-----------|----------|----------|----------|
| C101 | 1434 (6) | 3454 (2) | 1222 (2) | 68 (2) |
| C102 | 1173 (7) | 4024 (2) | 1458 (2) | 79 (3) |
| C103 | 2613 (8) | 4434 (2) | 1226 (2) | 87 (3) |
| C104 | 4384 (7) | 4295 (2) | 759 (2) | 79 (3) |
| C105 | 6526 (6) | 3572 (2) | 61 (2) | 69 (2) |
| C106 | 6833 (6) | 3032 (2) | -129 (2) | 71 (2) |
| C107 | 5682 (6) | 2026 (2) | -128 (2) | 68 (2) |
| C108 | 4556 (6) | 1013 (2) | -180 (2) | 73 (3) |
| C109 | 3033 (7) | 607 (2) | -21 (2) | 75 (3) |
| C110 | 1138 (7) | 733 (2) | 376 (2) | 72 (2) |
| C111 | 758 (6) | 1272 (2) | 615 (2) | 64 (2) |
| C112 | 1935 (6) | 2282 (1) | 698 (2) | 60 (2) |
| C113 | 3147 (6) | 3304 (1) | 762 (2) | 63 (2) |
| C114 | 4665 (5) | 3733 (1) | 536 (2) | 59 (2) |
| C115 | 5324 (5) | 2574 (2) | 93 (2) | 60 (2) |
| C116 | 4215 (5) | 1592 (1) | 50 (2) | 58 (2) |
| C117 | 2277 (5) | 1718 (1) | 461 (2) | 53 (2) |
| C118 | 3454 (5) | 2714 (1) | 524 (2) | 58 (2) |
| C119 | 8099 (8) | 4029 (2) | -210 (3) | 87 (3) |
| C201 | 6344 (6) | 1435 (2) | 2020 (2) | 69 (2) |
| C202 | 6014 (7) | 873 (2) | 1776 (2) | 74 (3) |
| C203 | 7458 (7) | 457 (2) | 1980 (2) | 84 (3) |
| C204 | 9288 (7) | 577 (2) | 2447 (2) | 77 (3) |
| C205 | 11503 (6) | 1270 (2) | 3170 (2) | 72 (2) |
| C206 | 11895 (6) | 1800 (2) | 3373 (2) | 75 (3) |
| C207 | 10842 (6) | 2818 (2) | 3383 (2) | 69 (2) |
| C208 | 9848 (7) | 3828 (2) | 3464 (2) | 73 (3) |
| C209 | 8401 (8) | 4255 (2) | 3301 (2) | 85 (3) |
| C210 | 6490 (8) | 4155 (2) | 2872 (2) | 85 (3) |
| C211 | 6030 (7) | 3625 (2) | 2622 (2) | 74 (3) |
| C212 | 7058 (6) | 2601 (2) | 2538 (2) | 62 (2) |
| C213 | 8130 (6) | 1571 (1) | 2468 (2) | 61 (2) |
| C214 | 9602 (5) | 1136 (1) | 2690 (2) | 57 (2) |
| C215 | 10415 (5) | 2275 (2) | 3149 (2) | 63 (2) |
| C216 | 9412 (5) | 3269 (1) | 3207 (2) | 57 (2) |
| C217 | 7465 (5) | 3168 (1) | 2783 (2) | 57 (2) |
| C218 | 8530 (6) | 2160 (1) | 2718 (2) | 56 (2) |
| C219 | 12982 (8) | 804 (2) | 3449 (3) | 96 (3) |

Table 1,* selected bond lengths and angles in Table 2. The two independent molecules (Fig. 1) are appreciably inclined to one another but, as in 8-MBA (Walker, Briant, Jones & Shaw, 1986), where different molecules were found to have angles *A/D* 5.1 and 2.4° between extreme rings, the molecules in 5-MBA have similar but not identical overall shapes (angles *A/D* = 6.2 and 3.4°). These correspond to the type I nearly planar (Briant, Jones & Shaw, 1985) MBA's with rather greater distortions than in 6-MBA (Jones, Briant & Shaw, 1988). In each MBA molecule, there are deviations (Johnson, Jones & Shaw, 1990) approaching 0.1 Å of C7 and C8 from one side of the mean carbon plane and of C10, C11 and the methyl carbon from the other side. In 5-MBA, C—C bonds derived for the two independent molecules differ by as much as 3σ for the sequence C15—C18—C13—C14 adjoining the beach in ring *B* but

* Lists of structure factors, anisotropic thermal parameters, parameters of the H atoms, C—H lengths and C—H angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53338 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. C—C bond lengths (Å) and C—C—C angles (°) with e.s.d.'s in parentheses

All C—C—C angles have e.s.d.'s of 0.4°.

| | Molecule 1 | Molecule 2 |
|-------------|------------|------------|
| C13—C14 | 1.422 (4) | 1.407 (4) |
| C14—C5 | 1.472 (5) | 1.468 (5) |
| C5—C6 | 1.328 (5) | 1.320 (5) |
| C6—C15 | 1.466 (5) | 1.481 (5) |
| C15—C7 | 1.367 (5) | 1.369 (5) |
| C7—C16 | 1.387 (5) | 1.398 (5) |
| C16—C8 | 1.439 (5) | 1.418 (5) |
| C8—C9 | 1.354 (5) | 1.357 (5) |
| C9—C10 | 1.388 (6) | 1.404 (5) |
| C10—C11 | 1.360 (5) | 1.354 (5) |
| C11—C17 | 1.418 (5) | 1.405 (4) |
| C17—C12 | 1.410 (5) | 1.426 (4) |
| C12—C18 | 1.402 (5) | 1.398 (4) |
| C18—C13 | 1.465 (4) | 1.476 (4) |
| C13—C1 | 1.382 (5) | 1.381 (5) |
| C1—C2 | 1.416 (5) | 1.407 (5) |
| C2—C3 | 1.364 (5) | 1.355 (6) |
| C3—C4 | 1.410 (6) | 1.414 (6) |
| C4—C14 | 1.393 (5) | 1.399 (5) |
| C15—C18 | 1.417 (4) | 1.399 (4) |
| C16—C17 | 1.423 (4) | 1.417 (4) |
| C5—C19 | 1.516 (5) | 1.496 (5) |
| | | |
| C13—C14—C5 | 118.8 | 119.9 |
| C14—C13—C18 | 120.0 | 119.4 |
| C14—C13—C1 | 118.6 | 119.0 |
| C13—C14—C1 | 120.4 | 120.4 |
| C14—C5—C6 | 120.6 | 120.5 |
| C5—C14—C4 | 120.8 | 119.6 |
| C14—C5—C19 | 119.4 | 120.2 |
| C5—C6—C15 | 122.7 | 121.8 |
| C6—C5—C19 | 120.1 | 119.3 |
| C6—C15—C7 | 120.6 | 120.3 |
| C6—C15—C18 | 118.6 | 119.3 |
| C15—C7—C16 | 121.3 | 121.4 |
| C7—C15—C18 | 120.8 | 120.3 |
| C7—C16—C8 | 122.2 | 120.9 |
| C7—C16—C17 | 119.7 | 120.0 |
| C16—C8—C9 | 120.3 | 119.7 |
| C8—C16—C17 | 118.1 | 119.1 |
| C8—C9—C10 | 121.4 | 121.1 |
| C9—C10—C11 | 120.6 | 120.4 |
| C10—C11—C17 | 120.9 | 120.6 |
| C11—C17—C12 | 122.5 | 123.0 |
| C11—C17—C16 | 118.8 | 119.2 |
| C17—C12—C18 | 120.8 | 120.8 |
| C12—C17—C16 | 118.8 | 117.9 |
| C12—C18—C13 | 122.2 | 121.4 |
| C12—C18—C15 | 118.6 | 119.7 |
| C18—C13—C1 | 121.3 | 121.6 |
| C13—C18—C15 | 119.2 | 119.0 |
| C13—C1—C2 | 120.9 | 120.8 |
| C1—C2—C3 | 120.0 | 120.0 |
| C2—C3—C4 | 120.6 | 120.9 |
| C3—C4—C14 | 119.5 | 118.8 |

otherwise generally by $\leq 2\sigma$. Bonds C1—C2 and C3—C4 (*N* and *M* regions) in 5-MBA are longer than in all other MBA's studied. The *K*-region bond C5—C6 [1.324 (4) Å] is short despite the presence of a substituent (which usually lengthens the bond by 0.01 Å), while three others, C2—C3 (shorter than in any other MBA studied), C8—C9 and C10—C11 are close to 1.360 Å. The long beach bond C18—C13 = 1.471 (4) Å is typical of a type I MBA with bay beach C—C—C angles enlarged to 121–122°. Whereas interior bond angles at substituent points in other MBA's are 1–2° below 120° (Briant, Jones & Shaw, 1985), in 5-MBA C14—C5—C6 slightly exceeds 120°, as does the analogous C5—C6—C15 angle in 6-MBA (Jones & Shaw, 1990). In solution,

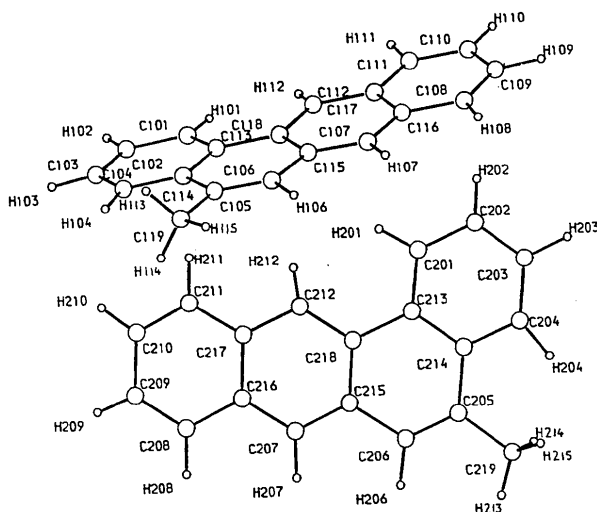


Fig. 1. Projection of the two independent (but approximately screw-related along a) molecules of 5-MBA.

220 MHz ^1H NMR spectra (Jones & Mokoena, 1982) indicate that the 5-methyl substituent shields H8 to H12.

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References

- BRIANT, C. E. & JONES, D. W. (1984). *Carcinogenesis*, **5**, 363–365.
- BRIANT, C. E., JONES, D. W. & SHAW, J. D. (1985). *J. Mol. Struct.* **130**, 167–176.
- CARRUTHERS, J. R. (1978). *Crystals User Manual*. Oxford Univ. Computing Laboratory, England.
- CARRUTHERS, J. R. & WATKIN, D. J. (1979). *Acta Cryst.* **A35**, 698–699.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- JOHNSON, O., JONES, D. W. & SHAW, J. D. (1990). *Polycyclic Aromatic Hydrocarbons*, edited by M. COOKE, E. MAY & K. LOENING. Chelsea, MI: Lewis. In the press.
- JONES, D. W., BRIANT, C. E. & SHAW, J. D. (1988). *Molecular Structure and Biological Activity*, edited by J. J. STEZOWSKI, J.-L. HUANG & M.-C. SHAO, pp. 221–229. Oxford Univ. Press.
- JONES, D. W. & MOKOENA, T. T. (1982). *Spectrochim. Acta*, **A38**, 491–498.
- JONES, D. W. & SHAW, J. D. (1987). *Carcinogenesis*, **8**, 1323–1326.
- JONES, D. W. & SHAW, J. D. (1990). *Cancer Biochem. Biophys.* **11**, 1–6.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCO, J.-P. & WOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- WALKER, N. P. C., BRIANT, C. E., JONES, D. W. & SHAW, J. D. (1986). *Acta Cryst.* **C42**, 1392–1395.
- WISLOCKI, P. G., FIORENTINI, K. M., FU, P. P., YANG, S. K. & LU, A. Y. H. (1982). *Carcinogenesis*, **3**, 215–217.