Fig. 3. (a) Bond lengths (Å), (b) bond angles (°), and (c) torsion angles (°) for (1). E.s.d.'s are 0·033 Å for bond lengths, 1·9° for bond angles and 2·0° for torsion angles. The ranges of bond lengths and angles involving H are C—H 0·886–0·952 Å, H—C—C 114·4–124·5°.

than is typical for unconjugated acyloxy groups [1·212 (4) Å] (Allen, 1981). The C=C bond lengths are close to the average for a cinnamoyl group. The overall picture is thus of strong conjugative interaction between the phenyl groups and their adjacent C=C bonds, but there seems to be little extension of the conjugation to the carbonyl groups despite the planarity.

In trans-cinnamoyl peroxide the α,β-unsaturated carbonyl group adopts the s-cis conformation. A review of gas-phase electron diffraction studies has led to the conclusion that the s-trans (or antiplanar) conformation is favoured for sterically unhindered compounds at normal temperatures (Bohn, 1977), and this is also the case in almost half of the α,β-unsaturated acids for which crystal structures have been scrutinized (Einspahr & Donohue, 1973). Nevertheless, the s-cis conformation occurs in the majority of cases, especially in cinnamoyl compounds (see, for example, Hanson, 1975). In the present case there seems to be no obvious steric reason for the preference, and, in the absence of through conjugation, no strong electrostatic interaction either.

torsion angle about the O—O bond is 87·1°, a value close to that observed in five of the eight diacyl peroxide structures listed in the Cambridge Structural Database (1983) with $R \leq 0.14$. The O—O bond length 1·42 (2) Å is somewhat shorter than the average for these eight compounds (1·458 Å).

We call attention to two other features of the present structure, namely the bond lengths in and the conformation of the α,β-unsaturated acyloxy groups. The carbonyl bond length is substantially shorter [mean value 1·15 (2) Å] than the average for the 13 compounds containing the cinnamoyl moiety for which structures having $R < 0.10$ are available [1·228 (25) Å]. On the other hand it is little less than the average for the eight diacyl peroxides [1·186 (28) Å] which is itself less

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7-Methoxymethyl-12-methylbenz[a]anthracene, C21H18O

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Abstract. $M_r = 286.4$, monoclinic, $P2_1/a$, $a = 7.899$ (1), $b = 17.041$ (3), $c = 11.388$ (3) Å, $\beta = 99.44$ (4)°, $V = 1512.1$ Å³, $Z = 4$, $D_m = 1.2$, $D_x = 1.26$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.069$ mm⁻¹, $F(000) = 608$, $T = 298$ K, final $R = 0.037$ for 1550 observed reflections. The planar anthracene skeleton is distorted around the attachment of the methyl group. The K region, C(5)—C(6), shows

the expected shortening with a bond length of 1·364 (3) Å. Hückel molecular-orbital calculations of bond order agree well with observed values except in the vicinity of the methyl and methoxy substituents.

Introduction. The title compound (I) is a carcinogen, and is important in the study of polyaromatic hydrocarbon carcinogens. Of special interest are the bay-region distortions, and the bonds with a high bond order.

(I)
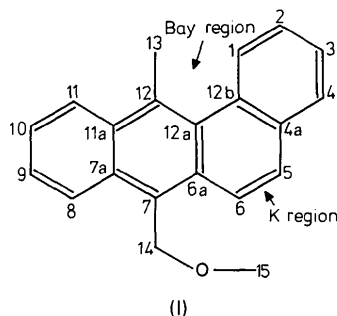
Experimental. D_m by flotation. Crystal dimensions $0.3 \times 0.2 \times 0.2$ mm. CAD-4 diffractometer. 25 reflections with $\theta > 12°$ used to measure lattice parameters. No absorption corrections. $\omega/2\theta$ scan to $\theta = 25°$; index range $h\,0/9$, $k\,0/21$, $l\,-14/14$. Two standards, no significant drift. 3212 reflections measured; 223 of these were duplicates and merged with $R_{int} = 0.021$; 1550 with $I > 2.0\sigma(I)$ deemed observed. Solution by direct methods with *MITHRIL* (Gilmore, 1984). Refinement by least squares on F with weights from counting statistics with an instability correction term of $0.02I^2$. H atoms located by Fourier methods, and refined isotropically. Other atoms refined anisotropically. Convergence at $R = 0.037$, $R_w = 0.044$. Max. $\Delta/\sigma = 0.04$, mean = 0.01. Max. and min. values on final difference Fourier synthesis 0.10 and -0.13 e Å^{-3}. No correction for secondary extinction. Scattering factors from *International Tables for X-ray Crystallography* (1974). All calculations on a Gould SEL 32/27 computer using Glasgow GX package.
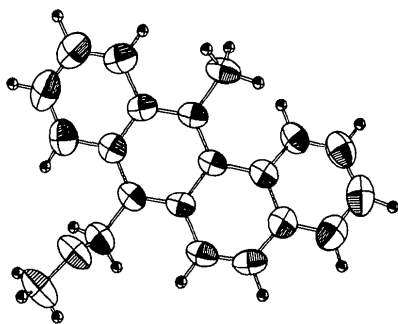

Fig. 1. Projection of the molecule showing 50% probability ellipsoids. H atoms have 0·2 Å radii.

Table 1. *Fractional atomic coordinates and isotropic temperature factors with e.s.d.'s in parentheses*

For non-hydrogen atoms temperature factors are equivalent isotropic values, where $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

	x	y	z	U_{eq} or U_{iso}(Å^2)
C(1)	0·8644 (3)	0·2129 (1)	1·2355 (2)	0·064 (2)
C(2)	0·8340 (4)	0·2051 (2)	1·3511 (2)	0·084 (2)
C(3)	0·7433 (4)	0·1432 (2)	1·3898 (3)	0·095 (2)
C(4)	0·6866 (4)	0·0858 (2)	1·3107 (3)	0·085 (2)
C(4a)	0·7194 (3)	0·0913 (1)	1·1916 (2)	0·062 (1)
C(5)	0·6820 (3)	0·0271 (1)	1·1121 (2)	0·067 (2)
C(6)	0·7411 (3)	0·0254 (1)	1·0060 (2)	0·062 (2)
C(6a)	0·8278 (2)	0·0908 (1)	0·9583 (2)	0·051 (1)
C(7)	0·8902 (2)	0·0881 (1)	0·8470 (2)	0·054 (1)
C(7a)	0·9516 (2)	0·1571 (1)	0·7679 (2)	0·057 (1)
C(8)	1·0233 (3)	0·1576 (2)	0·6853 (2)	0·077 (2)
C(9)	1·0741 (3)	0·2259 (2)	0·6368 (3)	0·092 (3)
C(10)	1·0553 (3)	0·2973 (2)	0·6933 (3)	0·086 (2)
C(11)	0·9886 (3)	0·2992 (2)	0·7987 (2)	0·069 (2)
C(11a)	0·9358 (2)	0·2299 (1)	0·8560 (2)	0·055 (1)
C(12)	0·8723 (2)	0·2329 (1)	0·9696 (2)	0·050 (1)
C(12a)	0·8368 (2)	0·1628 (1)	1·0261 (2)	0·047 (1)
C(12b)	0·8035 (2)	0·1575 (1)	1·1509 (2)	0·052 (1)
C(13)	0·8318 (3)	0·3118 (1)	1·0186 (2)	0·063 (2)
C(14)	0·8932 (3)	0·0124 (1)	0·7796 (2)	0·069 (2)
C(15)	0·7642 (5)	−0·0563 (2)	0·6187 (4)	0·106 (3)
O	0·75415 (19)	0·01021 (8)	0·69204 (13)	0·075 (1)
H(1)	0·937 (3)	0·257 (1)	1·211 (2)	0·077 (7)
H(2)	0·880 (3)	0·246 (2)	1·408 (2)	0·099 (8)
H(3)	0·714 (3)	0·133 (2)	1·470 (3)	0·116 (9)
H(4)	0·634 (3)	0·040 (1)	1·333 (2)	0·085 (8)
H(5)	0·617 (3)	−0·015 (1)	1·136 (2)	0·080 (7)
H(6)	0·721 (3)	−0·021 (1)	0·957 (2)	0·078 (7)
H(8)	1·035 (3)	0·104 (1)	0·650 (2)	0·080 (7)
H(9)	1·125 (3)	0·225 (1)	0·561 (2)	0·11 (1)
H(10)	1·098 (3)	0·344 (2)	0·652 (2)	0·110 (9)
H(11)	0·973 (3)	0·347 (1)	0·842 (2)	0·070 (7)
H(131)	0·778 (3)	0·346 (1)	0·954 (2)	0·087 (7)
H(132)	0·753 (3)	0·307 (1)	1·085 (2)	0·065 (6)
H(133)	0·930 (3)	0·341 (1)	1·051 (2)	0·081 (7)
H(141)	1·002 (3)	0·010 (1)	0·732 (2)	0·091 (8)
H(142)	0·887 (3)	−0·034 (1)	0·831 (2)	0·079 (7)
H(151)	0·756 (4)	−0·101 (2)	0·669 (3)	0·12 (1)
H(152)	0·662 (4)	−0·053 (2)	0·560 (3)	0·13 (1)
H(153)	0·876 (5)	−0·055 (2)	0·580 (3)	0·14 (1)

Discussion. Coordinates are in Table 1,* with bond angles and bond lengths in Table 2. Fig. 1 is a perspective drawing of the molecule.

The molecule is not planar. The greatest distortions occur around the bay region where the following torsion angles are found: C(1)–C(12b)–C(12a)–C(12) −24·5 (2); C(4a)–C(12b)–C(12a)–C(6a) −17·6 (2); C(12b)–C(12a)–C(6a)–C(6) 16·6 (2); C(6a)–C(12a)–C(12)–C(11a) −13·5 (2)°. All other ring torsion angles are less than 10°. Bond angles, in contrast, show maximum deviations of only 5° from ideality. This accords with observations on 7,12-dimethylbenz[a]anthracene (Sayre & Friedlander, 1960; Iball, 1964), the monomethylbenz[a]anthracenes (Jones & Sowden, 1975), and 7-chloro-12-methylbenz[a]anthracene (Glusker, Zacharias & Carrell, 1976). The distortion is due to overcrowding of the

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* Lists of structure factors, anisotropic thermal parameters, torsion angles and bond lengths and angles involving H atoms, and intermolecular contacts less than the sum of the van der Waals radii have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39517 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å), *calculated bond lengths from Hückel calculations, and bond angles* (°) *for the nonhydrogen atoms*

The errors are derived from the full inverse matrix.

	Experimental	Hückel		Experimental	Hückel
C(1)–C(2)	1·382 (4)	1·38	C(1)–C(12b)	1·379 (3)	1·40
C(2)–C(3)	1·387 (4)	1·39	C(3)–C(4)	1·355 (5)	1·38
C(4)–C(4a)	1·425 (4)	1·41	C(4a)–C(5)	1·420 (3)	1·44
C(4a)–C(12b)	1·424 (3)	1·42	C(5)–C(6)	1·364 (3)	1·38
C(6)–C(6a)	1·458 (3)	1·44	C(6a)–C(7)	1·435 (3)	1·39
C(6a)–C(12a)	1·444 (3)	1·44	C(7)–C(7a)	1·426 (3)	1·40
C(7)–C(14)	1·504 (3)		C(7a)–C(8)	1·474 (4)	1·42
C(7a)–C(11a)	1·426 (3)	1·44	C(8)–C(9)	1·377 (4)	1·38
C(9)–C(10)	1·395 (4)	1·40	C(10)–C(11)	1·389 (4)	1·38
C(11)–C(11a)	1·442 (3)	1·42	C(11a)–C(12)	1·463 (3)	1·41
C(12)–C(12a)	1·407 (3)	1·39	C(12)–C(13)	1·510 (3)	
C(12a)–C(12b)	1·490 (4)	1·46	C(14)–O	1·358 (3)	
C(15)–O	1·418 (4)				

Mean C—H distance 0·99 (3) Å.

C(2)–C(1)–C(12b)	120·2 (3)		C(1)–C(2)–C(3)	123·8 (3)
C(2)–C(3)–C(4)	117·9 (3)		C(3)–C(4)–C(4a)	119·6 (3)
C(4)–C(4a)–C(5)	120·4 (3)		C(4)–C(4a)–C(12b)	121·9 (3)
C(5)–C(4a)–C(12b)	117·5 (3)		C(4a)–C(5)–C(6)	121·0 (3)
C(5)–C(6)–C(6a)	124·3 (2)		C(6)–C(6a)–C(7)	123·7 (2)
C(6)–C(6a)–C(12a)	115·8 (2)		C(7)–C(6a)–C(12a)	120·4 (2)
C(6a)–C(7)–C(7a)	121·0 (2)		C(6a)–C(7)–C(14)	121·0 (3)
C(7a)–C(7)–C(14)	118·0 (3)		C(7)–C(7a)–C(8)	123·6 (3)
C(7)–C(7a)–C(11a)	117·9 (2)		C(8)–C(7a)–C(11a)	118·5 (3)
C(7a)–C(8)–C(9)	121·9 (3)		C(8)–C(9)–C(10)	119·5 (3)
C(9)–C(10)–C(11)	120·2 (3)		C(10)–C(11)–C(11a)	123·4 (3)
C(7a)–C(11a)–C(11)	116·4 (3)		C(7a)–C(11a)–C(12)	121·0 (2)
C(11)–C(11a)–C(12)	122·6 (3)		C(11a)–C(12)–C(12a)	119·9 (2)
C(11a)–C(12)–C(13)	118·8 (2)		C(12a)–C(12)–C(13)	121·1 (2)
C(6a)–C(12a)–C(12)	118·2 (2)		C(6a)–C(12a)–C(12b)	117·2 (2)
C(12)–C(12a)–C(12b)	124·6 (2)		C(1)–C(12b)–C(4a)	116·3 (3)
C(1)–C(12b)–C(12a)	121·9 (2)		C(4a)–C(12b)–C(12a)	121·6 (2)
C(7)–C(14)–O	108·6 (2)		C(14)–O–C(15)	109·7 (3)

methyl H atoms on C(13) with those on C(1). The shortest contact distance is H(1)···H(132) at 2·05 (4) Å. For a planar molecule this would be *ca* 1·8 Å. The bay-region distortion seems to increase polyaromatic hydrocarbon carcinogenic activity (Glusker, 1982).

The K-region bond length, C(5)—C(6), is 1·364 (3) Å. Short bonds are also found between C(3)—C(4), 1·355 (5) Å, and C(8)—C(9), 1·377 (4) Å. Presumably these are preferred sites for hydroxyl and epoxide group addition which is a postulated intermediate step in the interaction between DNA and the hydrocarbon.

Simple Hückel MO theory calculations were performed for the unsubstituted benz[a]anthracene skeleton assuming planarity. Bond lengths (d) were calculated from bond orders (b) via:

$$d = 1·37 + 0·04(0·8-b) + 0·6(0·8-b)^2$$

and these are included in Table 2. The agreement is good with an r.m.s. deviation of 0·02 Å confirming that torsion alone is sufficient to reduce overcrowding in the bay region without significantly reducing π-orbital delocalization. The positions of the shortest bonds also correspond to experimental results. Three deviations exceed 0·03 Å. This is due to the substitution of the skeleton by the methyl and methoxymethyl groups.

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SHORT COMMUNICATIONS

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Concerning a second polymorph of the HMX–DMF complex.* By RICHARD E. MARSH, *Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California* 91125, *USA*

Abstract

The monoclinic phase recently reported for the 1:1 complex between octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine

(HMX) and *N,N*-dimethylformamide is almost certainly identical with the rhombohedral phase reported earlier, and should be described in space group $R\bar{3}c$ rather than $C2/c$.

Recently, Haller, Rheingold & Brill (1983; HRB) described the crystal structure of a second monoclinic polymorph of the 1:1 complex between octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and *N,N*-dimethylformamide (DMF).