

The metabolizing enzyme acts on 5-methylchryse-
ne to give a diol epoxide. The carcinogenically active
species is 3,4-epoxy-1,2,3,4-tetrahydro-5-methyl-1,2-
chrysenediol rather than the 9,10-epoxy-7,8,9,10-
tetrahydro-7,8-diol (Melikian, LaVoie, Hecht &
Hoffmann, 1982, 1983). This fact must be related to the
location of the 5-methyl group which either aids in
orienting 5-methylchryse-
ne in the active site of the
metabolizing enzyme or else causes more distortion in
the resulting diol epoxide, thus enhancing its car-
cinogenic activity.

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Structure of 1,4,5,8-Tetramethylnaphthalene, C₁₄H₁₆

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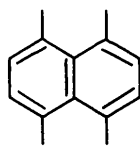
Abstract. $M_r = 184.28$, $P2_1/n$, $a = 7.962$ (3), $b = 5.205$ (1), $c = 12.922$ (4) Å, $\beta = 104.98$ (2)°, $V = 517.3$ (2) Å³, $Z = 2$, $D_x = 1.18$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.62$ cm⁻¹, $F(000) = 200$, 300 K, final

conventional $R = 0.045$ for 607 unique reflections and 96 parameters. The carbon framework is planar, relieving short intramolecular contacts between the methyl groups by in-plane distortions of the bond angles and bond lengths. The structure is compared with those of related compounds.

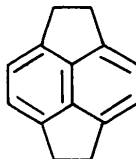
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Introduction. *Peri* strain, the result of repulsive nonbonded interactions between substituents at C(1) and C(8) in naphthalene derivatives, can cause both in-plane and out-of-plane deviations from the molecular geometry of naphthalene (for leading references, see Hull & Gladfelter, 1982). The relative importance of out-of-plane distortions is variable and difficult to predict. In some structures the *peri* substituents and all ring carbons are co-planar. At the other extreme, the naphthalene nucleus itself can be significantly distorted from planarity. An intermediate structural type involves a planar naphthalene skeleton with the *peri* substituents displaced above and below the ring plane.

The structure of 1,4,5,8-tetramethylnaphthalene (IUPAC numbering) (I), in which two methyl/methyl *peri* interactions are present, has not previously been determined. Comparison with related structures permits no clear prediction of the likelihood of out-of-plane distortions. The carbon skeleton of 1,8-dimethylnaphthalene is planar (White, Carnduff, Guy & Bovill, 1977; Bright, Maxwell & de Boer, 1973), whereas in octamethylnaphthalene the ring system is severely distorted from planarity (Hull & Gladfelter, 1982). Pyracene (II), in which the pairs of *peri* substituents are covalently linked, has a planar carbon framework (Simmons & Lingafelter, 1961). Fluorescence studies of 1,4,5,8-tetramethylnaphthalene have suggested that the naphthalene skeleton is non-planar (Reiser & Wright, 1973). Enthalpies of combustion of the 1,8-dimethyl and 1,4,5,8-tetramethyl compounds indicate that the respective *peri* strain energies are *ca* 25 and 63 kJ mol⁻¹ (Mansson, 1974).

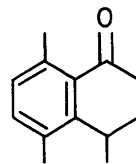


(I)

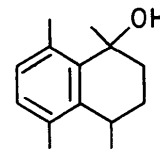


(II)

Experimental. 1,4,5,8-Tetramethylnaphthalene was synthesized *via* a modification of Mosby's approach. The known (Mosby, 1952) ketone (III) was treated with 1.0 equivalents of methyllithium in ether at 253 K, followed by two cycles of methanol quenching and addition of a further 1.0 equivalents of methyllithium. The alcohol (IV), obtained in 90% yield in this fashion, was used without purification. 1,4,5,8-Tetramethylnaphthalene then was generated in a single step by reaction of (IV) with two equivalents of triphenylmethanol in trifluoroacetic acid at 298 K (Fu & Harvey, 1974). The product was obtained in 70% yield after flash chromatography, and after recrystallization from 95% ethanol had m.p. 405–406.6 K [lit. (Mosby, 1952) 405–406 K].



(III)



(IV)

Compound recrystallized from chloroform-*d*, colorless needles, fragment approximately 0.2 × 0.2 × 0.4 mm cut from a larger crystal, Nicolet P1 diffractometer; Mo K α radiation, graphite-crystal monochromator; unit-cell parameters by least-squares adjustment to the setting angles of 28 carefully selected reflections with $30 < 2\theta < 34^\circ$; systematic absences $h0l$ $h + l = 2n$, $0k0$ $k = 2n$; 3288 reflections (the full sphere) with $2\theta < 49^\circ$ measured, fixed scan speed 6° min^{-1} , ω - 2θ scan; intensity control reflections, measured after every 50 reflections, showed no significant decay; no correction for absorption; after averaging of symmetry-related reflections (R_{int} from merging = 0.036), 866 independent reflections obtained, 607 with $I > 3\sigma(I)$, $\sigma(I)$ based on counting statistics; Lorentz and polarization corrections, intensity data reduced to $|F_{\text{obs}}|$ values; structure solved with *SHELX* direct-methods procedure (*EEES*) (Sheldrick, 1976), $R = 0.12$ in 3 cycles of isotropic full-matrix least-squares refinement on F ; difference Fourier synthesis at this stage clearly showed all H atoms as peaks of 0.3 to 0.5 e \AA^{-3} ; continued full-matrix least-squares refinement of atomic coordinates, anisotropic thermal parameters for C atoms, isotropic thermal parameters for H atoms, $w = (\sigma_c^2 + 0.001F_o^2)^{-1}$, final $R = 0.045$ ($R_w = 0.072$) for 607 reflections and 96 parameters; max. Δ in last least-squares cycle $< 0.3\sigma$; final difference map showed no $\Delta\rho$ excursions $> 0.14 \text{ e } \text{\AA}^{-3}$; calculations performed with *SHELX* package (Sheldrick, 1976); atomic scattering factors and anomalous-dispersion corrections those of *SHELX*.*

Discussion. Final positional and thermal parameters are given in Table 1. Table 2 contains the bond angles and selected torsion angles. Fig. 1 gives the atomic numbering scheme and the carbon-carbon bond lengths, and Fig. 2 shows a stereoview of the molecular packing.

A least-squares plane calculated through the atoms C(1) through C(5) shows that the carbon skeleton is almost perfectly planar; the largest deviation from the least-squares plane is 0.009 (3) \AA . Although the

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39003 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates and (equivalent) isotropic thermal parameters (e.s.d.'s in parentheses)

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

	x	y	z	$U_{eq}/U_{iso}(\text{\AA}^2)$
C(1)	0.5475 (3)	0.1006 (4)	0.5360 (2)	0.0413 (7)
C(2)	0.4758 (3)	0.1951 (5)	0.6199 (2)	0.0469 (8)
C(3)	0.7091 (3)	0.1909 (5)	0.5200 (2)	0.0477 (8)
C(4)	0.7672 (3)	0.0928 (5)	0.4377 (2)	0.0576 (10)
C(5)	0.3230 (3)	0.0938 (5)	0.6307 (2)	0.0590 (10)
C(6)	0.5524 (4)	0.4071 (6)	0.6984 (2)	0.0612 (11)
C(7)	0.8244 (4)	0.3949 (6)	0.5868 (3)	0.0644 (12)
H(1)	0.672 (4)	0.342 (5)	0.743 (3)	0.074 (8)
H(2)	0.567 (3)	0.557 (6)	0.669 (2)	0.066 (8)
H(3)	0.465 (3)	0.458 (5)	0.742 (2)	0.072 (8)
H(4)	0.774 (4)	0.558 (6)	0.581 (3)	0.072 (9)
H(5)	0.853 (4)	0.359 (5)	0.659 (3)	0.075 (9)
H(6)	0.938 (6)	0.381 (6)	0.566 (3)	0.109 (11)
H(7)	0.278 (3)	0.190 (5)	0.687 (2)	0.064 (7)
H(8)	0.881 (4)	0.166 (5)	0.428 (2)	0.071 (8)

Table 2. Bond angles ($^\circ$) and selected torsion angles ($^\circ$) with e.s.d.'s in parentheses

C(1A)—C(1)—C(2)	118.7 (3)	C(1)—C(3)—C(7)	125.4 (2)
C(1A)—C(1)—C(3)	118.4 (3)	C(4)—C(3)—C(7)	115.4 (2)
C(2)—C(1)—C(3)	122.9 (2)	H(8)—C(4)—C(3)	117 (2)
C(1)—C(2)—C(5)	118.9 (2)	H(7)—C(5)—C(2)	112 (2)
C(1)—C(2)—C(6)	125.8 (2)	C(5A)—C(4)—C(3)	122.5 (3)
C(5)—C(2)—C(6)	115.3 (2)	C(4A)—C(5)—C(2)	122.3 (3)
C(1)—C(3)—C(4)	119.2 (2)		

Bond angles involving methyl H's are in the range 102–116 (3°).

C(3)—C(1)—C(2)—C(6)	3.2 (4)
C(1A)—C(1)—C(2)—C(6)	−177.8 (2)
C(4A)—C(5)—C(2)—C(6)	177.1 (2)
C(3)—C(1)—C(2)—C(5)	−178.5 (2)
C(1)—C(2)—C(5)—C(4A)	−1.4 (4)
C(1A)—C(1)—C(3)—C(4)	1.6 (3)

All other torsion angles in the carbon skeleton are either 0 or 180° within experimental error.

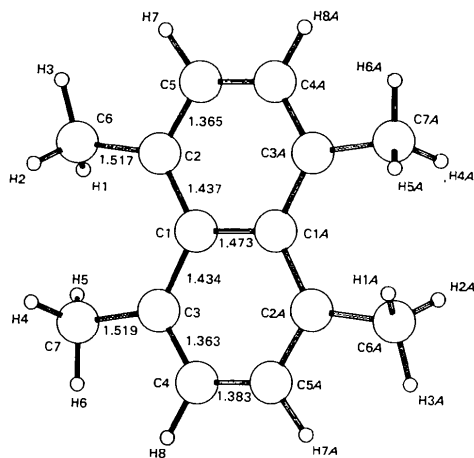


Fig. 1. Atomic numbering scheme and carbon-carbon bond lengths. E.s.d.'s are $\sim 0.003 \text{ \AA}$.

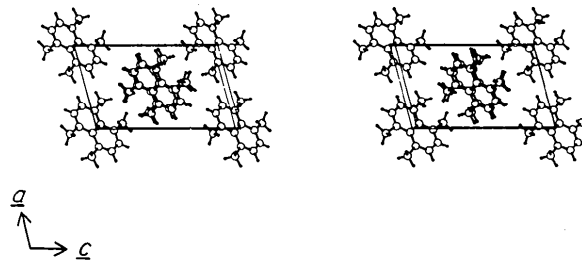


Fig. 2. Stereoview of the packing viewed along the b axis.

deviation for the methyl carbon atom C(6) is significantly larger [$-0.067 (3) \text{ \AA}$; $0.012 (3) \text{ \AA}$ for C(7)], the total out-of-plane displacement of each *peri* methyl pair ($|\delta_1| + |\delta_8|$) is no greater than in 1,8-dimethylnaphthalenes (White *et al.*, 1977; Bright *et al.*, 1973). The molecule reduces the steric interaction of the methyl groups primarily by an in-plane splaying of the ring-methyl bonds of about 6° , thus increasing the C(6)···C(7) distance by about 0.4 \AA to $2.896 (3) \text{ \AA}$. The corresponding distance in 1,8-dimethylnaphthalene is 2.932 \AA (Bright *et al.*, 1973). The outward splaying of the methyl groups results in significant distortions of the bond angles and bond lengths of the naphthalene nucleus, as expected. The carbon-hydrogen bond lengths are in the range $0.89\text{--}1.04 (3) \text{ \AA}$. The fixed orientation of the methyl hydrogens (Fig. 1) is the same as in 1,8-dimethylnaphthalene (Bright *et al.*, 1973).

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