Crystal Structure of 1,5-Dimethylnaphthalene: a Neutron Diffraction Study

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The crystal structure of the title compound has been examined at room temperature by neutron diffraction. Three-dimensional least-squares refinement of positional and anisotropic temperature parameters for all atoms gave *R* 0·041 over 437 independent neutron reflections. Aromatic bond lengths and angles are essentially the same as for the unsubstituted compound and C(methyl) atoms do not deviate significantly from the plane of the rings. The H(methyl) atoms are locked in fixed orientations in which one hydrogen of each is in the ring plane; closest approaches of out-of-plane H(methyl) atoms to adjacent α-hydrogen atoms are 2·35(4)—2·40(4) Å. Aromatic C–H and methyl C–H bond lengths do not differ significantly from their means (1·05 and 1·06 Å).

THE crystal structure of naphthalene, one of the first organic crystals to be studied by *X*-ray diffraction, has been carefully re-investigated by *X*-ray [1] and, in deuteriated form, by neutron diffraction.[2] However, for few naphthalene derivatives have the hydrogen atom positions in their crystal structures been determined accurately. With methyl substitution, inductive effects can enhance charges on *ortho*- and *para*-carbon atoms in the naphthalene nucleus. In α,α'-dimethylnaphthalene solutions, these changes influence partial rate factors for hydrogen–deuterium exchange [3] and also the ^{1}H n.m.r. chemical shifts of ring protons.[4] Indications of slight steric distortion of 1,5-dimethylnaphthalene (I) in the solid state came from an *X*-ray crystal-structure analysis,[5] based on visually-estimated photographic intensities. Least-squares refinement of the (*yz*) and (*xz*) projections to *R*-values of 0·09 and 0·14, respectively, led to σ for carbon-atom positions of 0·008 and 0·022 Å. In view of uncertainties in the hydrogen-atom positions derived from the *X*-ray analysis, a three-dimensional neutron-diffraction investigation was undertaken. It forms part of a wider spectroscopic [6-11] and diffraction [12,13] study of

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[1] D. W. J. Cruickshank, *Acta Cryst.*, 1957, **10**, 504.

[2] G. S. Pawley and E. A. Yeats, *Acta Cryst.*, 1969, *B*25, 2009.

[3] G. Dallinga, P. J. Smit, and E. L. Mackor, *Mol. Phys.*, 1960, **3**, 130.

[4] C. MacLean and E. L. Mackor, *Mol. Phys.*, 1960, **3**, 223.

[5] J. Beintema, *Acta Cryst.*, 1965, **18**, 647.

[6] K. D. Bartle and D. W. Jones, *J. Chem. Soc.* (*A*), 1969, 437.

[7] K. D. Bartle and D. W. Jones, *J. Mol. Spec.*, 1969, **32**, 353.

[8] K. D. Bartle and D. W. Jones, *J. Phys. Chem.*, 1969, **73**, 293.

[9] K. D. Bartle, R. S. Matthews, and D. W. Jones, *J. Chem. Soc.* (*A*), 1969, 876.

[10] K. D. Bartle, R. S. Matthews, and D. W. Jones, *Tetrahedron*, 1969, **25**, 2701.

[11] K. D. Bartle, R. S. Matthews, and D. W. Jones, *Rev. Pure Appl. Chem.*, 1969, **19**, 191.

[12] J. Yerkess, D. W. Jones, and W. A. Denne, *Acta Cryst.*, 1969, *B*25, 2649.

[13] D. W. Jones and J. Yerkess, *J. Cryst. Mol. Struct.*, 1971, **1**, 17.

the structural implications for carcinogenesis [14,15] of steric hindrance in polycyclic hydrocarbons and their derivatives and analogues.

EXPERIMENTAL

Crystal Data.[5]—Monoclinic, $C_{12}H_{12}$, $M = 156$, $a = 6{\cdot}18 \pm 0{\cdot}01$, $b = 8{\cdot}91 \pm 0{\cdot}01$, $c = 16{\cdot}77 \pm 0{\cdot}02$ Å, $\beta = 101{\cdot}4_0 \pm 0{\cdot}0_5$°, $z = 4$, $D_c = 1{\cdot}14_5$ g cm^{-3}. Space group $P2_1/c$ (No. 14, C^5_{2h}).

A roughly prismatic single crystal, 9·0 (a-axis) × 6·5 × 3·5 mm, grown by slow evaporation from acetone solution, was enclosed in a soda-glass cover (sealed with plasticine) to minimise evaporation loss. Success in this was confirmed by the constancy over ten days of the intensity of a standard reflection (002, for which $\phi = 0°$, $\chi = 0°$, $\theta = 4{\cdot}08°$) measured every 3 h. Neutron intensity data for the hkl and $\bar{h}kl$ octants were collected at a wavelength monochromatised to 1·170 Å with the a-axis along the ϕ-rotation axis of the Ferranti Mark II (left-handed) automatic single-crystal diffractometer at the DIDO reactor, A.E.R.E., Harwell. Diffractometer control tapes were punched with an ATLAS programme written by Curry from setting angles on cards derived by the ATLAS version of a programme written by Powell. For each reflection, counts were recorded with an ω–2θ step-scan in 22 steps of 0·08° in ω over 3·5° in 2θ, together with five steps of 0·04° in ω covering 0·4° (in 2θ) for background on each side of the peak. At each point, the counting time was controlled by a fission chamber which monitored the intensity of the incident beam. A monitor count of 4×10^4 was used for the timing of both peak counts and background counts; the total measurement time was about 10 min per reflection. Integrated intensities ranged from 123,000 ± 400 counts (precision 0·3%) for 021 down to 270 ± 170 counts for the weakest reflections. Although all 807 unique reflections (including systematic absences) within the limit $2\theta < 70°$ were recorded, only 54% had intensities significantly above the background. The high percentage of 'accidentally absent' reflections was attributed to thermal motion, and to the high background from incoherent neutron scattering by the hydrogen atoms in the crystal (which is 50 atomic % hydrogen) and the glass cover. An ATLAS programme written by Curry converted the punched-tape diffractometer output to a set of punched cards listing structure factors and their estimated standard deviations based on counting statistics.

In view of the large size of the crystal, the linear absorption coefficient (μ) was calculated from mass absorption coefficients.[16] With $\mu = 0{\cdot}11$ cm^{-1}, $\lambda = 1{\cdot}17$ Å, and detailed dimensions of the crystal measured by microscope, transmission factors were computed by the ABSCOR programme of the '*X*-RAY '63' system [17a] on the Chilton ATLAS to be between 0·963 and 0·975, an insignificant spread. Since a further test with μ set at 2·3 cm^{-1}, in an effort to make some allowance for incoherent hydrogen scatter,[17b] gave an increased R, this artificial absorption correction was not made.

Structure Refinement.—Structure factors calculated from the carbon atomic positional co-ordinates found in ref. 5, and with an overall isotropic temperature factor of 3·2 Å^2, led to an initial R-value of 0·19. A difference Fourier synthesis gave negative peaks within 0·3 Å of the hydrogen-atom sites given in ref. 5. Neutron scattering lengths used were: C $0{\cdot}661 \times 10^{-12}$, and H $-0{\cdot}378 \times 10^{-12}$ cm. The first cycle of full-matrix least-squares refinement with the ORFLS programme [18] utilized a $1/\sigma$ weighting scheme (where σ is the estimated standard deviation of the structure factor, based on counting statistics). Refinement of the individual isotropic temperature factors (which increased to *ca.* 5·0 Å^2 for aromatic hydrogens and about 6·4 Å^2 for methyl hydrogens) and positional co-ordinates for just the hydrogen atoms reduced R to 0·14; two further cycles, in which the positional and isotropic temperature factors for all atoms were varied, reduced R to 0·115. Since subsequent refinement with the $1/\sigma$ weighting scheme gave no further improvement, all reflections were now weighted equally and four cycles reduced R to 0·072; at this stage, all shifts were $<\sigma$. In two further cycles, the positional and anisotropic temperature factors for the methyl hydrogen atoms only were varied, and R was reduced to 0·067. Finally all atoms were refined anisotropically. With concurrent refinement of the extinction parameter,[19] g, from a zero starting value, R was reduced to 0·041, and g increased to $0{\cdot}0034 \times 10^{24}$ cm^{-2}. Since all shifts were now $<\sigma$ refinement was judged to be complete. A difference Fourier synthesis showed only random ripples with extrema $\pm 0{\cdot}04 \times 10^{-12}$ cm Å^{-3}; observed and calculated structure amplitudes are listed in Supplementary Publication No. SUP 20402 (4 pp., 1 microfiche).*

RESULTS AND DISCUSSION

Tables 1 and 2 give the final atomic-positional and thermal parameters, together with their estimated standard deviations; those for the x co-ordinates of the carbon atoms are *ca.* $\frac{1}{2}$ to $\frac{1}{3}$ of those quoted by Beintema,[5] while those for the y and z co-ordinates are much the same as for the X-ray analysis. Table 3 lists the carbon–carbon and Table 4 the carbon–hydrogen bond lengths; interatomic angles are shown in the Figure. Estimated standard deviations for the C–C bond lengths and C–C–C angles are 30—50% smaller than those from the X-ray analysis. Equations of least-squares planes through the molecule are given in Table 5; Table 6 shows deviations of individual atoms from these planes, calculated by the method of Schomaker.[20] Table 7 gives the root-mean-square components of thermal vibration along the three principal axes of the thermal vibration ellipsoid for each

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

[14] K. D. Bartle, D. W. Jones, and R. S. Matthews, *J. Medic Chem.*, 1969, **12**, 1062.

[15] K. D. Bartle, D. W. Jones, and R. S. Matthews, *J. Theoret. Biol.*, 1970, **27**, 117.

[16] G. E. Bacon, 'Neutron Diffraction,' Oxford University Press, Oxford, 1962.

[17] (*a*) '*X*-Ray '63,' System, J. M. Stewart, University of Maryland Report TR 64 6; (*b*) J. A. K. Duckworth, B. T. M. Willis, and G. S. Pawley, *Acta Cryst.*, 1970, *A*26, 263.

[18] W. R. Busing, K. D. Martin, and H. A. Levy, 1962, ORFLS, a FORTRAN crystallographic least-squares programme, Oak Ridge National Laboratory, Tennessee, Report ORNL TM 305.

[19] A. C. Larson, 1970, in Crystallographic Computing: Proc. Internat. Summer School, Ottawa, eds. F. R. Ahmed, S. R. Hall, and C. P. Huber, Copenhagen, Munksgaard, p. 291.

[20] V. Schomaker, J. Waser, R. E. Marsh, and G. Bergman, *Acta Cryst.*, 1959, **12**, 600.

atom. For the hydrogen atoms, angles between these axes and the C–H bonds are given in Table 8.

While the estimated standard deviation of 0·026 Å for the apparent lengthening (in the neutron analysis as compared with the *X*-ray analysis) of the central C(9)–C(10) bond by 0·064 Å is not formally significant, it suggests a difference between the centres of nuclear and electronic charge. The shortest C · · · C intermolecular contact of 3·63 Å, between C(5) of one molecule and C(1′) of another, is not unusually short. Overall, the neutron results show up no significant differences between chemically equivalent bond lengths or bond angles, and they confirm the similarity of the rings with the

TABLE 1

Fractional atomic positional co-ordinates ($\times 10^4$ for carbon, $\times 10^3$ for hydrogen) with estimated standard deviations in parentheses

	x/*a*	*y*/*b*	*z*/*c*
C(1)	3744(12)	4062(8)	3249(5)
C(2)	2358(15)	3255(10)	3672(8)
C(3)	529(16)	2437(11)	3244(7)
C(4)	50(16)	2427(12)	2397(5)
C(5)	911(12)	3262(9)	1096(5)
C(6)	2271(14)	4077(9)	674(8)
C(7)	4139(14)	4862(11)	1108(5)
C(8)	4597(17)	4876(11)	1947(6)
C(9)	3276(11)	4073(8)	2392(5)
C(10)	1400(1)	3244(8)	1959(4)
C(1′)	5704(20)	4905(15)	3730(9)
C(5′)	$\overline{1034}$(20)	2416(16)	612(8)
H(2)	268(3)	325(2)	430(2)
H(3)	$\overline{50}$(4)	184(3)	357(1)
H(4)	$\overline{130}$(4)	180(2)	210(1)
H(6)	189(3)	409(2)	6(2)
H(7)	513(4)	550(3)	76(1)
H(8)	604(4)	548(2)	227(1)
H(1′,1)	577(4)	479(3)	435(2)
H(1′,2)	563(4)	611(3)	360(2)
H(1′,3)	718(5)	455(3)	360(2)
H(5′,1)	$\overline{107}$(4)	255(4)	$\overline{2}$(2)
H(5′,2)	$\overline{252}$(5)	281(3)	77(2)
H(5′,3)	$\overline{89}$(5)	120(3)	74(2)

TABLE 2

Anisotropic vibration coefficients, B_{ij}, in Å^2, with estimated standard deviations in parentheses

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	4·1(4)	2·8(4)	3·3(5)	0·0(4)	1·1(3)	0·1(5)
C(2)	5·1(5)	3·0(5)	5·2(5)	0·2(5)	1·1(4)	0·2(4)
C(3)	5·5(5)	3·3(4)	5·4(5)	$\overline{1{\cdot}2}$(5)	1·6(4)	1·0(4)
C(4)	4·8(5)	4·1(5)	3·3(5)	$\overline{0{\cdot}6}$(5)	1·4(4)	0·6(5)
C(5)	3·9(4)	2·9(4)	3·5(4)	$\overline{0{\cdot}4}$(4)	0·0(4)	$\overline{0{\cdot}1}$(4)
C(6)	5·0(5)	3·4(4)	4·7(5)	$\overline{0{\cdot}1}$(4)	1·4(4)	$\overline{0{\cdot}1}$(4)
C(7)	4·6(4)	4·6(5)	3·4(5)	$\overline{1{\cdot}1}$(4)	1·5(4)	$\overline{0{\cdot}5}$(4)
C(8)	4·1(5)	3·8(5)	5·2(5)	$\overline{0{\cdot}7}$(4)	1·5(4)	$\overline{0{\cdot}1}$(4)
C(9)	3·6(4)	2·3(4)	3·5(4)	$\overline{0{\cdot}2}$(4)	1·0(3)	0·3(3)
C(10)	2·9(4)	2·3(4)	3·4(4)	0·1(3)	1·4(3)	$\overline{0{\cdot}3}$(3)
C(1′)	4·7(6)	4·9(6)	4·6(6)	0·0(5)	0·0(5)	$\overline{0{\cdot}4}$(5)
C(5′)	5·7(6)	4·3(6)	5·6(6)	$\overline{1{\cdot}2}$(5)	0·3(5)	0·6(5)
H(2)	7·4(1·2)	5·2(1·0)	7·0(1·2)	$\overline{0{\cdot}6}$(0·8)	2·8(0·9)	1·0(0·9)
H(3)	11·3(1·2)	8·0(1·3)	4·7(0·9)	$\overline{1{\cdot}3}$(1·2)	2·5(1·1)	0·0(0·9)
H(4)	8·8(1·2)	5·6(1·0)	5·4(0·9)	$\overline{3{\cdot}4}$(1·0)	1·9(1·0)	0·1(0·8)
H(6)	8·5(1·1)	6·7(1·1)	3·9(0·9)	$\overline{1{\cdot}2}$(0·9)	1·8(0·8)	$\overline{0{\cdot}2}$(0·8)
H(7)	7·8(1·2)	9·2(1·4)	5·6(0·9)	$\overline{3{\cdot}2}$(1·1)	2·0(1·0)	1·3(1·0)
H(8)	6·2(1·1)	6·2(1·2)	8·6(1·3)	$\overline{1{\cdot}8}$(1·0)	2·6(1·0)	$\overline{0{\cdot}7}$(1·0)
H(1′,1)	8·8(1·5)	12·2(2·3)	7·2(1·6)	$\overline{3{\cdot}2}$(1·4)	0·5(1·1)	$\overline{0{\cdot}5}$(1·4)
H(1′,2)	6·9(1·1)	6·3(1·2)	9·7(1·4)	$\overline{1{\cdot}2}$(1·0)	2·1(0·9)	$\overline{0{\cdot}7}$(1·1)
H(1′,3)	7·8(1·6)	11·7(2·1)	10·5(1·8)	$\overline{3{\cdot}3}$(1·5)	0·9(1·4)	$\overline{3{\cdot}5}$(1·5)
H(5′,1)	9·2(1·7)	11·7(1·8)	7·4(1·7)	$\overline{1{\cdot}7}$(1·4)	$\overline{1{\cdot}0}$(1·2)	$\overline{1{\cdot}9}$(1·5)
H(5′,2)	7·4(1·4)	9·4(1·7)	10·8(1·8)	$\overline{0{\cdot}8}$(1·2)	1·2(1·3)	$\overline{2{\cdot}2}$(1·3)
H(5′,3)	14·7(1·9)	2·8(1·0)	11·6(1·8)	$\overline{1{\cdot}7}$(1·1)	$\overline{2{\cdot}3}$(1·4)	$\overline{0{\cdot}7}$(1·2)

TABLE 3

Comparison of C–C bond lengths (Å, with estimated standard deviations in parentheses) derived from the neutron analysis [columns (2) and (1)] and from ref. 5 [column (3)] of 1,5-dimethylnaphthalene with corresponding bonds in the parent hydrocarbon [columns (4) and (5)]. Entries in columns (2) and (3) are means between bonds which are equivalent if the molecule is centrosymmetrical

	1,5-Dimethylnaphthalene			$C_{10}H_8$	$C_{10}D_8$
	Neutron Present work		*X*-ray [a]	*X*-ray [b]	Neutron [c]
	(1)	(2)	(3)	(4)	(5)
C(1)–C(2)	1·413(14)	1·408(10)	1·361(13)	1·357(4)	1·372(5)
C(5)–C(6)	1·403(14)				
C(3)–C(4)	1·392(14)	1·386(10)	1·385(11)		
C(7)–C(8)	1·380(12)				
C(1)–C(9)	1·408(11)	1·413(8)	1·440(10)	1·420(3)	1·423(5)
C(5)–C(10)	1·418(10)				
C(8)–C(9)	1·402(44)	1·404(10)	1·438(13)		
C(4)–C(10)	1·406(13)				
C(2)–C(3)	1·416(13)	1·419(9)	1·425(21)	1·416(6)	1·401(7)
C(6)–C(7)	1·422(12)				
C(9)–C(10)	1·444(10)	1·444(10)	1·380(24)	1·405(6)	1·412(7)
C(1)–C(1′)	1·515(14)	1·514(9)	1·515(18)		
C(5)–C(5′)	1·513(14)				

[a] Ref. 5. [b] Ref. 1. [c] Ref. 2.

TABLE 4

Uncorrected C–H bond lengths (Å) with values corrected for thermal motion (hydrogen atom assumed to ride on carbon atom) in square brackets; estimated standard deviations in parentheses

C(2)–H(2)	1·03(3) [1·05]	C(1′)–H(1′,1)	1·03(4) [1·11]
C(3)–H(3)	1·05(3) [1·09]	C(1′)–H(1′,2)	1·10(3) [1·14]
C(4)–H(4)	1·05(2) [1·09]	C(1′)–H(1′,3)	1·03(3) [1·10]
C(6)–H(6)	1·01(3) [1·05]	C(5′)–H(5′,1)	1·06(4) [1·12]
C(7)–H(7)	1·08(3) [1·14]	C(5′)–H(5′,2)	1·06(3) [1·13]
C(8)–H(8)	1·09(2) [1·12]	C(5′)–H(5′,3)	1·10(3) [1·20]

TABLE 5

Equations of least-squares planes through the molecule in orthogonal co-ordinates (Å): X and Y coincide with the unit cell x and y axes, and Z is normal to x and y

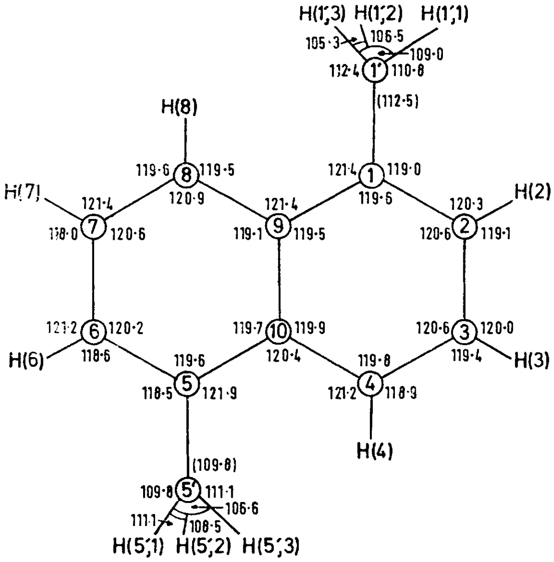
Plane (1): All carbon atoms
$-0{\cdot}5883X + 0{\cdot}8086Y + 0{\cdot}0083Z = 2{\cdot}242$

Plane (2): Aromatic carbon atoms
$-0{\cdot}5893X + 0{\cdot}8079Y + 0{\cdot}0073Z = 2{\cdot}236$

Plane (3): Aromatic carbon and aromatic hydrogen atoms
$-0{\cdot}5902X + 0{\cdot}8072Y + 0{\cdot}0076Z = 2{\cdot}235$

Plane (4): All carbon and aromatic hydrogen atoms, H(1′,1) and H(5′,1)
$-0{\cdot}5904X + 0{\cdot}8070Y + 0{\cdot}0070Z = 2{\cdot}231$

parent compound and the centrosymmetry of the molecule. Within experimental error, methyl-group angles are tetrahedral. Neither aromatic- nor ring-carbon atoms deviate significantly from the mean plane through the aromatic carbons [Table 5, plane (2)]. The difference-Fourier synthesis and subsequent successful least-squares refinements confirm that the methyl groups have a fixed orientation, each with one hydrogen in the molecular plane. Intramolecular steric interference between methyl-hydrogen atoms and the nearest α-hydrogen atoms of the aromatic nucleus is evidently sufficient to lock the methyl groups. The methyl C–H bonds (Table 4) are all close (σ 0·01 Å) to their mean length of 1·06 Å, as are aromatic C–H bonds to their mean of 1·05 Å (σ 0·01 Å). Shortest intramolecular H · · · H contacts between out-of-plane methyl-hydrogen atoms and adjacent α-hydrogen atoms are 2·35 and 2·40 Å (σ 0·04 Å), *i.e.* close to van der Waals contact distances.



Bond angles (deg.) in 1,5-dimethylnaphthalene, showing the atom numbering. Approximate estimated standard deviations are: C–C–C 0·8, C–C–H 1·6, and H–C–H 2·5°

TABLE 6

Deviations (Å × 10^4) of atoms from least-squares planes given in Table 5

Atom	Plane (1)	Plane (2)	Plane (3)	Plane (4)
C(1)	$\overline{12}$	16	30	36
C(2)	$\overline{117}$	$\overline{98}$	$\overline{100}$	$\overline{93}$
C(3)	19	16	3	2
C(4)	116	100	91	81
C(5)	$\overline{57}$	$\overline{80}$	$\overline{69}$	$\overline{88}$
C(6)	$\overline{82}$	$\overline{97}$	$\overline{70}$	$\overline{90}$
C(7)	127	134	171	159
C(8)	$\overline{61}$	$\overline{40}$	$\overline{7}$	$\overline{10}$
C(9)	$\overline{3}$	10	29	26
C(10)	49	40	47	36
C(1′)	40	91	117	131
C(5′)	$\overline{19}$	$\overline{66}$	$\overline{67}$	$\overline{94}$
H(2)	$\overline{210}$	$\overline{181}$	$\overline{185}$	$\overline{172}$
H(3)	$\overline{103}$	$\overline{112}$	$\overline{137}$	$\overline{137}$
H(4)	383	350	332	317
H(6)	$\overline{277}$	$\overline{303}$	$\overline{274}$	$\overline{300}$
H(7)	$\overline{141}$	$\overline{128}$	$\overline{78}$	$\overline{91}$
H(8)	137	174	217	219
H(1′,1)	$\overline{188}$	$\overline{130}$	$\overline{108}$	$\overline{88}$
H(1′,2)	$\overline{8703}$	$\overline{8647}$	$\overline{8613}$	$\overline{8598}$
H(1′,3)	8254	8310	8343	8358
H(5′,1)	239	185	189	156
H(5′,2)	$\overline{8570}$	$\overline{8621}$	$\overline{8629}$	$\overline{8657}$
H(5′,3)	8995	8943	8934	8960

TABLE 7

Root-mean-square components (Å) of thermal vibration along principal axes of thermal ellipsoid

	Axis (1)	Axis (2)	Axis (3)
C(1)	0·19	0·20	0·23
C(2)	0·19	0·25	0·26
C(3)	0·16	0·27	0·27
C(4)	0·18	0·23	0·26
C(5)	0·18	0·20	0·24
C(6)	0·20	0·23	0·26
C(7)	0·19	0·21	0·27
C(8)	0·20	0·23	0·26
C(9)	0·16	0·20	0·22
C(10)	0·15	0·18	0·22
C(1′)	0·22	0·25	0·28
C(5′)	0·21	0·26	0·30
H(2)	0·22	0·29	0·33
H(3)	0·23	0·31	0·39
H(4)	0·20	0·26	0·38
H(6)	0·21	0·28	0·34
H(7)	0·20	0·29	0·40
H(8)	0·23	0·30	0·35
H(1′,1)	0·29	0·32	0·43
H(1′,2)	0·26	0·30	0·36
H(1′,3)	0·25	0·36	0·44
H(5′,1)	0·25	0·39	0·40
H(5′,2)	0·29	0·32	0·40
H(5′,3)	0·17	0·34	0·50

TABLE 8

Angles (deg.) between C–H bond directions and principal axes (1), (2), and (3) of thermal vibration of hydrogen atoms

	(1)	(2)	(3)
C(2)–H(2)	119	59	135
C(3)–H(3)	134	128	69
C(4)–H(4)	47	130	70
C(6)–H(6)	14	97	77
C(7)–H(7)	5	85	89
C(8)–H(8)	149	81	119
C(1′)–H(1′,1)	125	35	93
C(1′)–H(1′,2)	139	57	69
C(1′)–H(1′,3)	113	147	113
C(5′)–H(5′,1)	50	127	118
C(5′)–H(5′,2)	66	26	101
C(5′)–H(5′,3)	23	67	90

TABLE 9

Evidence for methyl-group rotation in 1,5-dimethylnaphthalene

Temp./K	Crystalline state	Temp./K	Soln. in CCl_4
>290	Reorientating (^{1}H n.m.r.) [a]	298	Rotating (high-resolution ^{1}H n.m.r.[b,c] and polarised i.r. [a])
290	Fixed (*X*-ray [d] and N.D.)		
93—290	Fixed (polarised i.r. [a])	238	Reduced rotational freedom (polarised i.r. [a])

[a] Ref. 32. [b] Ref. 7. [c] Ref. 32. [d] Ref. 5.

Thus there is no evidence of intramolecular overcrowding or indication of the distortion suggested from the *X*-ray analysis.[5]

For the very few reported crystal structures of methyl-substituted polynuclear compounds, hydrogen atoms have not generally been located.[21-25] In *p,p'*-bitolyl[26] and durene,[27] however, the methyl substituents appear to be fixed, while in 1,12-dimethylbenzo[*c*]phenanthrene[28] the higher apparent thermal parameters for the methyl hydrogens are suggestive of some rotational freedom. As steric interaction increases from that in (I) to the *peri*-methyl–methyl interaction of 1,8-dimethyl-3-bromonaphthalene, there is already considerable in- and some out-of-plane distortion.[22] Successively greater interactions would be encountered in the bay[29] positions of phenanthrene[13] and fluoranthene, the buttressed bay of benz[*a*]anthracene, and the fjord[30] of benzo[*c*]phenanthrene.

In the analysis of the high-resolution ^{1}H n.m.r. spectrum[7] of (I), a methyl *peri* deshielding of $-0{\cdot}20$ p.p.m. for H(4) and H(8) relative to naphthalene was ascribed to a van der Waals effect; the present results show that what we have termed a primary,[29] rather than a secondary, effect is responsible. (A bond-anisotropic shielding of $+0{\cdot}082$ p.p.m. has been calculated[31] for a rotating-methyl-group model.) The single ^{1}H methyl n.m.r. peak of 1·6 Hz halfheight width for (I) in carbon tetrachloride solution was attributed[29] to a less static situation than occurs in the solid state.

Polarised single-crystal i.r. spectra of (I) enabled Forel and Fouassier[32] to assign the methyl stretching vibrations: $\nu_s = 2925$, $\nu'_s = 2971$, $\nu_a = 2948$ cm^{-1}, with harmonics $2\delta'_s = 2867$, $2\delta_a = 2898$ cm^{-1}; analogous absorptions were measured for the corresponding crystal in which the methyl groups are deuteriated. While the powder spectrum in the 3000 cm^{-1} region does not change much between 93 and 298 K, intensity changes occur in the solution spectra. It was suggested that, in substituted naphthalenes with small steric interaction, as in (I), one hydrogen of each methyl group is in the ring plane; where hindrance is greater, as in 1-methyl-8-bromonaphthalene, there is an appreciable contribution to the equilibrium in solution of the methyl conformation which has its mirror plane perpendicular to the ring plane. While the present neutron analysis confirms that, in the solid, the methyl groups are effectively fixed at room temperature, reduction of the ^{1}H n.m.r. second moment[33] in (I) has been interpreted in terms of reorientation of the methyl groups beginning above 290 K.

In summary, as indicated in Table 9, a consistent picture, derived from *X*-ray[5] and neutron diffraction, broad-line[33] and high-resolution ^{1}H n.m.r.,[7,34] and polarised i.r. spectroscopy[32] emerges for methyl-group rotation in (I). There is some analogy[30] with biphenyl, which is planar in the crystal but has rotation in the gas phase and in solution with mean angle of 40° between ring planes.

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[21] S. A. Chaudhury, *Acta Cryst.*, 1968, *B*24, 1222.

[22] M. B. Jameson and B. R. Penfold, *J. Chem. Soc.*, 1965, 528.

[23] C. J. Brown, *Acta Cryst.*, 1954, **7**, 97.

[24] J. Iball, *Nature*, 1964, **201**, 916.

[25] J. Iball and S. G. G. McDonald, *Z. Krist.*, 1960, **114**, 439.

[26] G. Casalone, C. Mariani, A. Mugnoli, and M. Simonetta, *Acta Cryst.*, 1969, *B*25, 1741.

[27] R. Riley, *Nature*, 1962, **193**, 162.

[28] F. L. Hirshfeld, S. Sandler, and G. M. J. Schmidt, *J. Chem. Soc.*, 1963, 2108.

[29] K. D. Bartle and D. W. Jones, *Trans. Faraday Soc.*, 1967, **63**, 2868.

[30] K. D. Bartle and D. W. Jones, *Adv. Org. Chem.*, 1972, **8**, 317.

[31] W. T. Raynes, *Mol. Phys.*, 1971, **20**, 321.

[32] M.-T. Forel and M. Fouassier, *Spectrochim. Acta*, 1968, **24***A*, 311.

[33] V. D. Agrawal, B. K. P. N. Singh, and R. C. Gupta, *Ind. J. Pure Appl. Phys.*, 1969, **7**, 740.

[34] P. M. E. Lewis, *Tetrahedron Letters*, 1971, **21**, 1859.