Another Look at the Structure of Octamethylnaphthalene

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Abstract. $C_{18}H_{24}$, $M_r = 240.39$, orthorhombic, *Ccca*, $a = 16.595$ (2), $b = 11.242$ (3), $c = 7.632$ (2) Å, $Z = 4$, $U = 1423.8$ Å^3, $D_c = 1.121$, $D_m = 1.089$ Mg m^{-3}, $F(000) = 528$, μ(Cu $K\alpha$) = 0.47 mm^{-1}. The crystal structure of octamethylnaphthalene has been redetermined by X-ray diffractometry (Cu $K\alpha$ radiation). Least-squares adjustment of the atomic parameters converged at $R = 0.045$ for 478 independent reflections. The carbon framework of the molecule is appreciably distorted from planarity.

Introduction. Octamethylnaphthalene was the subject of one of the earliest X-ray diffraction investigations of a notably strained aromatic compound (Donaldson, 1952; Donaldson & Robertson, 1953). The material crystallizes in the orthorhombic space group *Ccca*, with $Z = 4$, and the molecule displays D_2 symmetry in the crystal. Though the atoms were not fully resolved in electron-density projections, a detailed study of these maps led Donaldson & Robertson to conclude that the molecule is non-planar, with the α-methyl groups displaced from the mean plane by about 0.73 Å and the β-methyl groups displaced by a smaller amount, probably between 0.25 and 0.40 Å. They also suggested that the naphthalene nucleus may depart from planarity, to a lesser extent.

The geometries of several overcrowded naphthalene derivatives have been characterized by three-dimensional X-ray diffraction analyses in recent years. It seemed desirable to define the geometry of octamethylnaphthalene with like precision and the reinvestigation of the crystal structure by modern X-ray methods was undertaken as a contribution to the Symposium held to mark J. M. Robertson's 80th birthday. Structural results for strained hydrocarbons are of prime importance for the calibration of the empirical force fields used in molecular-mechanics calculations, since such compounds are free from the complexities associated with the presence of hetero atoms.

Cell dimensions were derived from least-squares treatment of the setting angles for 25 reflections measured on an Enraf–Nonius CAD-4 diffractometer with Cu $K\alpha$ radiation from a graphite monochromator. For intensity measurements octants hkl and $hk\bar{l}$ were surveyed in the range $\theta \leq 72°$ and 923 reflections

satisfied the criterion $I > 2.5\sigma(I)$. Equivalent reflections were merged to give 478 unique reflections and this process gave $R_{merge} = 0.047$. A small crystal of dimensions $0.4 \times 0.2 \times 0.1$ mm was used and no absorption correction was applied.

Ambiguities arise when the two-dimensional coordinates obtained by Donaldson & Robertson are converted to a three-dimensional set. Accordingly, the crystal structure was solved by a version of *MULTAN* (Germain, Main & Woolfson, 1971) adapted for the Glasgow University ICL 2976 computer by Dr C. J. Gilmore.

The coordinates and thermal parameters of the C atoms were submitted to full-matrix least-squares calculations with unit weights and convergence was reached at $R = 0.11$. The H atoms were then located in difference electron-density maps and when these atoms were included in the least-squares calculations with isotropic thermal parameters, and the weighting scheme was changed to $w = 1/\sigma^2(F)$, R converged to 0.058, R_w 0.057. Finally, the H atoms were assigned anisotropic thermal parameters and R decreased to 0.045, R_w 0.042. The coordinates from this procedure differed only slightly from those given by the calculation with isotropic H, but the decrease in R is highly significant. It is uncommon to obtain meaningful anisotropic thermal parameters for H atoms in an X-ray study and the success in the present case can be attributed both to accurate intensity measurements and to the circumstance that the H atoms contribute 22% of the electrons in the molecule.

Fourier and least-squares calculations were performed with *SHELX* (Sheldrick, 1976).*

Discussion. The atomic coordinates, bond lengths and angles, torsion angles, and intramolecular non-bonded separations are listed in Table 1–5. A stereoscopic view of the molecular structure is shown in Fig. 1 and the numbering system and deviations from the mean plane of the molecule are shown in Fig. 2. Since the molecule

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Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* [$U_{eq}=\frac{1}{3}(U_{11} + U_{22} + U_{33})$] *with e.s.d.'s in parentheses*

	x	y	z	U_{eq} (Å^2)
C(1)	0·4168 (1)	0·1392 (2)	0·2807 (2)	0·071 (1)
C(2)	0·4586 (1)	0·0343 (1)	0·2712 (2)	0·079 (1)
C(9)	0·4571 (1)	0·2500	0·2500	0·052 (1)
C(11)	0·3301 (2)	0·1386 (4)	0·3459 (4)	0·112 (2)
C(12)	0·4176 (3)	−0·0847 (3)	0·2999 (5)	0·123 (3)
H(11₁)	0·3231 (15)	0·077 (3)	0·440 (5)	0·15 (3)
H(11₂)	0·3142 (12)	0·222 (3)	0·401 (4)	0·14 (2)
H(11₃)	0·2879 (16)	0·120 (3)	0·249 (4)	0·15 (2)
H(12₁)	0·360 (3)	−0·063 (4)	0·309 (9)	0·23 (5)
H(12₂)	0·435 (3)	−0·129 (3)	0·402 (5)	0·21 (4)
H(12₃)	0·422 (3)	−0·139 (3)	0·205 (4)	0·18 (3)

Fig. 1. Stereoscopic view of the molecular structure.

Table 2. *Bond lengths* (Å) *with e.s.d.'s in parentheses*

C(1)–C(2)	1·370 (2)	C(11)–H(11₁)	1·01 (4)
C(1)–C(9)	1·433 (2)	C(11)–H(11₂)	1·06 (3)
C(1)–C(11)	1·522 (3)	C(11)–H(11₃)	1·04 (3)
C(2)–C(3)	1·411 (4)	C(12)–H(12₁)	0·99 (4)
C(2)–C(12)	1·517 (3)	C(12)–H(12₂)	0·97 (4)
C(9)–C(10)	1·423 (3)	C(12)–H(12₃)	0·95 (3)

Table 3. *Bond angles* (°) *with e.s.d.'s in parentheses*

C(9)–C(1)–C(2)	120·2 (1)	C(1)–C(9)–C(10)	117·8 (2)
C(9)–C(1)–C(11)	119·9 (2)	C(1)–C(11)–H(11₁)	110·3 (16)
C(2)–C(1)–C(11)	119·4 (2)	C(1)–C(11)–H(11₂)	111·1 (12)
C(1)–C(2)–C(3)	120·3 (1)	C(1)–C(11)–H(11₃)	114·0 (15)
C(1)–C(2)–C(12)	121·6 (2)	C(2)–C(12)–H(12₁)	103·3 (27)
C(3)–C(2)–C(12)	118·0 (2)	C(2)–C(12)–H(12₂)	115·8 (25)
C(1)–C(9)–C(8)	124·3 (3)	C(2)–C(12)–H(12₃)	115·3 (22)

Fig. 2. Numbering system and deviations (Å) of the atoms from the mean molecular plane. E.s.d.'s of the displacements are ≤0·004 Å.

Table 4. *Torsion angles* (°) *with e.s.d.'s in parentheses*

C(9)–C(1)–C(2)–C(3)	−0·9 (2)	C(12)–C(2)–C(3)–C(13)	4·9 (5)
C(11)–C(1)–C(2)–C(12)	8·6 (3)	C(1)–C(2)–C(3)–C(4)	8·6 (5)
C(2)–C(1)–C(9)–C(10)	−14·1 (4)	C(1)–C(9)–C(10)–C(4)	21·3 (4)
C(11)–C(1)–C(9)–C(8)	−21·7 (5)		

Table 5. *Intramolecular non-bonded separations* (Å)

C(11)···C(18)	2·90 (1)	H(11₂)···H(18₃)	2·16 (4)
C(11)···C(12)	2·92 (1)	H(11₂)···H(18₂)	2·39 (6)
C(12)···C(13)	2·84 (1)	H(12₂)···H(13₃)	2·51 (5)
H(11₁)···H(12₁)	1·96 (4)		

has D_2 symmetry successive pairs of α- and β-methyl C atoms are displaced alternately above and below the mean plane.

The serious repulsive interactions between methyl groups result in considerable distortions of the molecular framework. The out-of-plane deviations shown in Fig. 2 demonstrate that the naphthalene nucleus buckles in response to the displacements of the α- and β-methyl C atoms. An enlargement of the angle C(1)—C(9)—C(8) to 124·3 (3)° from the value of 121·5° in naphthalene (Cruickshank, 1957) also

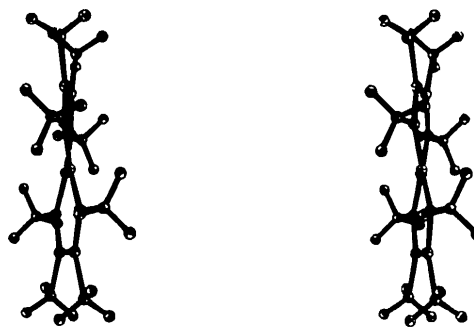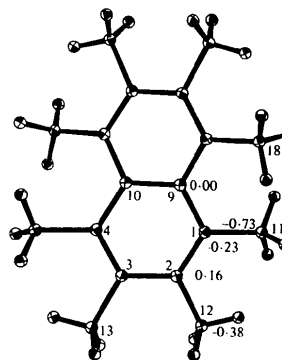contributes to the separation of the methyl groups at the *peri* positions. As a result of these distortions, the methyl C···C separations are ca 2·9 Å and only one of the H···H separations is shorter than 2 Å.

The distortions from planarity have little effect on the bond lengths in the naphthalene nucleus; they differ from those in naphthalene itself only by ca 0·01 Å.

Among related compounds, 1,8-dimethylnaphthalene retains a planar carbon skeleton and the C···C α-methyl separation of 2·93 Å is obtained by in-plane bond-angle distortions at C(1), C(9) and C(8) (Bright, Maxwell & de Boer, 1973). In contrast, 1,3,6,8-tetra-*tert*-butylnaphthalene exhibits massive departures from planarity, with the central C atoms of the *tert*-butyl groups at positions 1 and 8 displaced by 1·22 Å above and below the mean plane of the molecule (Handal, White, Franck, Yuh & Allinger, 1977).

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3-Dimethylamino-1-phenyl-1-propanone Hydrochloride Monohydrate

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Abstract. $C_{11}H_{16}NO^+.Cl^-.H_2O$, orthorhombic, *Pbca*, $a = 7.342$ (2), $b = 11.043$ (2), $c = 30.440$ (4) Å, $Z = 8$, $D_x = 1.301$ (1) Mg m^{-3}, $T = 295$ K, Mo $K\alpha$ ($\lambda = 0.7107$ Å). The structure was solved by direct methods and refined by full-matrix least-squares methods to a conventional R of 0.044 for the 1477 reflections with intensities above 2σ. The structure consists of a quarternary ammonium cation, a chloride anion, and a water of hydration. The single H atom on the N atom of the quaternary ammonium ion is hydrogen bonded to the chloride ion. The water of hydration is weakly hydrogen bonded to a symmetry-related water and also hydrogen bonded to the chloride ion. Distances and angles in the quaternary ammonium cation are normal. Except for one methyl C atom on the amine N, the non-H atoms are essentially coplanar.

Introduction. 3-Dimethylamino-1-phenyl-1-propanone hydrochloride monohydrate was prepared from acetophenone *via* the Mannich reaction (Maxwell, 1955). Crystals were obtained from a water–ethanol–acetone mixture. A crystal of approximate dimensions $0.3 \times 0.4 \times 0.4$ mm was chosen for the X-ray studies. The crystal system, cell dimensions and space group were determined using an Enraf–Nonius CAD-4 automated diffractometer.

All computations were performed on a PDP 11/34 computer using the Enraf–Nonius *SDP* software. A total of 2894 reflections were measured to a maximum 2θ of 47° using the θ–2θ step scan technique with a variable speed to enhance the uniformity of the counting statistics from reflection to reflection. Three standard reflections measured after approximately every 150 reflections indicated no crystal decomposition. The data were corrected for background and

Lorentz–polarization effects. The empirical absorption-correction method (ψ scans) was applied giving a range of transmission of 0.948 to 0.998.

Table 1. *Positional and thermal parameters with e.s.d.'s in parentheses*

	x	y	z	B_{eq}^* (Å^2)
Cl	0.7729 (1)	0.35272 (8)	0.08475 (2)	5.19 (4)
O	0.0153 (3)	−0.0381 (1)	0.32732 (5)	4.55 (9)
O(W)	0.9344 (5)	0.0836 (3)	0.04494 (12)	12.8 (3)
N	0.9145 (3)	0.2148 (2)	0.42569 (6)	3.82 (9)
C(1)	0.8699 (3)	0.0862 (2)	0.26595 (7)	3.12 (9)
C(2)	0.9164 (3)	0.1983 (2)	0.24931 (9)	3.7 (1)
C(3)	0.9256 (4)	0.2166 (2)	0.20450 (9)	4.4 (1)
C(4)	0.8896 (4)	0.1232 (3)	0.17614 (8)	4.6 (1)
C(5)	0.8433 (4)	0.0101 (2)	0.19223 (8)	4.4 (1)
C(6)	0.8344 (3)	−0.0078 (2)	0.23664 (8)	3.8 (1)
C(7)	0.8567 (3)	0.0617 (2)	0.31396 (7)	3.2 (1)
C(8)	0.8924 (3)	0.1640 (2)	0.34577 (8)	3.5 (1)
C(9)	0.8781 (4)	0.1184 (2)	0.39237 (8)	3.9 (1)
C(10)	0.7764 (4)	0.3123 (3)	0.42521 (9)	5.4 (2)
C(11)	0.9280 (5)	0.1601 (3)	0.47044 (9)	6.0 (2)
H(OW)1	0.975 (7)	0.021 (5)	0.0185 (12)	14.3
H(OW)2	0.843 (7)	0.034 (4)	0.0510 (13)	14.3
H(N)	1.027 (4)	0.251 (2)	0.4206 (7)	4.8
H(C2)	0.942 (3)	0.262 (2)	0.2682 (7)	4.7
H(C3)	0.959 (4)	0.285 (2)	0.1925 (8)	5.3
H(C4)	0.890 (4)	0.133 (2)	0.1465 (9)	5.6
H(C5)	0.818 (4)	−0.052 (2)	0.1737 (7)	5.4
H(C6)	0.808 (3)	−0.082 (2)	0.2504 (8)	4.9
H1(C8)	0.802 (3)	0.228 (2)	0.3400 (7)	4.6
H2(C8)	1.007 (3)	0.188 (2)	0.3403 (7)	4.6
H1(C9)	0.974 (4)	0.057 (2)	0.3988 (8)	5.0
H2(C9)	0.750 (3)	0.090 (2)	0.3994 (8)	5.0
H1(C10)	0.663 (4)	0.282 (3)	0.4277 (7)	6.4
H2(C10)	0.771 (4)	0.350 (3)	0.3973 (9)	6.4
H3(C10)	0.813 (4)	0.375 (3)	0.4476 (9)	6.4
H1(C11)	0.954 (4)	0.219 (3)	0.4906 (9)	6.9
H2(C11)	1.028 (4)	0.104 (3)	0.4653 (8)	6.9
H3(C11)	0.804 (4)	0.126 (3)	0.4776 (8)	6.9

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$$* B_{eq} = \tfrac{4}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$