1,8-Dimethyl-2-naphthyl Acetate

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Abstract. $C_{14}H_{14}O_2$, monoclinic, $P2_1/c$, $Z = 4$, $M_r = 214$, $a = 9.54$, $b = 6.63$, $c = 19.87$ Å, $\beta = 110.2°$, $U = 1180$ Å^3, $D_x = 1.18$, $D_m = 1.21$ g cm^{-3}, $\lambda = 0.7107$ Å, μ(Mo $K\alpha$) = 0.86 cm^{-1}, $F(000) = 456$, $R = 6.1\%$. The $C(1)-C(9)-C(8)$ angle is $125.9°$.

Introduction. The systematic absences are $0k0$ when $k = 2n + 1$ and $h0l$ when $l = 2n + 1$, and the

Table 1. *Experimental conditions*

Diffractometer: Hilger & Watts Y290
Source: graphite-monochromated Mo $K\alpha$, $\lambda = 0.71069$ Å
Scan: ω–2θ; peak, 40 steps of $0.02°$, 2 s/step; background, two
   measurements of 20 s each
Reflexions measured: 1877, $I \geq 2\sigma(I)$, $2\theta \leq 52°$
Reflexions used in refinement: 1824, $|F_o| \geq 4\sigma(|F_o|)$
Crystal size: $1.5 \times 1 \times 0.5$ mm

Table 2. *Fractional atomic coordinates* ($\times 10^4$) *with e.s.d.'s in parentheses*

	x	y	z
C(1)	4869 (2)	4257 (3)	5901 (1)
C(2)	3468 (2)	4879 (3)	5488 (1)
C(3)	2780 (2)	6633 (4)	5598 (1)
C(4)	3526 (2)	7806 (3)	6164 (1)
C(5)	5694 (3)	8567 (4)	7212 (1)
C(6)	7061 (3)	8124 (4)	7677 (1)
C(7)	7803 (3)	6433 (4)	7553 (1)
C(8)	7188 (2)	5132 (3)	6985 (1)
C(9)	5702 (2)	5517 (3)	6496 (1)
C(10)	4980 (2)	7293 (3)	6621 (1)
C(11)	5436 (4)	2276 (4)	5714 (2)
C(12)	1539 (2)	2591 (4)	4875 (1)
C(13)	837 (4)	1561 (6)	4171 (2)
O(14)	2690 (2)	3763 (3)	4864 (1)
O(15)	1156 (2)	2453 (3)	5380 (1)
C(16)	8176 (3)	3424 (6)	6914 (2)
H(3)	1778 (29)	7058 (38)	5248 (12)
H(4)	3102 (25)	9003 (40)	6303 (12)
H(5)	5133 (27)	9772 (40)	7276 (12)
H(6)	7520 (30)	9084 (43)	8121 (14)
H(7)	8824 (30)	6083 (41)	7868 (13)
H(111)	6375 (40)	2350 (51)	5573 (18)
H(112)	5791 (32)	1401 (51)	6109 (16)
H(113)	4708 (41)	1904 (52)	5289 (18)
H(131)	84 (54)	2646 (68)	3881 (23)
H(132)	55 (37)	517 (51)	4169 (16)
H(133)	1493 (42)	1438 (56)	3950 (19)
H(161)	7716 (55)	2000 (77)	6947 (25)
H(162)	9223 (47)	3535 (62)	7268 (20)
H(163)	8288 (37)	3483 (53)	6427 (19)

experimental conditions for data collection are shown in Table 1.

The structure was solved with *MULTAN*. Least-squares optimization of the positional (C,O,H), anisotropic thermal (C,O) and isotropic thermal (H) parameters converged at $R = 6.1\%$.* The weighting scheme was $w = 1/(A + B|F_o| + C|F_o|^2)$ with $A = 0.1508$, $B = -0.0051$ and $C = 0.0038$. Fractional atomic coordinates are given in Table 2.

Discussion. The molecular geometry (Fig. 1) is not significantly different from that of the parent hydrocarbon (Bright, Maxwell & de Boer, 1973) and manifestations of *peri* strain are obvious.

Four modes of molecular deformation which alleviate *peri* strain have been discussed (Robert, Sherfinski, Marsh & Roberts, 1974). These are: (i) out-of-plane bending of the substituents at $C(1)$, δ_1, and $C(8)$, δ_8, in opposite directions, (ii) in-plane splaying such that the $C(9)-C(8)-C(16)$ and $C(9)-C(1)-C(11)$ angles are increased from their equilibrium values, (iii) rotation around $C(8)-C(16)$ and/or $C(1)-C(11)$ and (iv) a lengthening of $C(1)-C(9)$ and $C(8)-C(9)$. All these are observed to a greater or lesser extent in *peri*-substituted naphthalenes, but a consideration of elementary geometry indicates that this is not the whole story. If we temporarily neglect chemical energetics then the most effective method of separating $C(11)$ and $C(16)$ is an opposed linear motion along the $C(11)\cdots C(16)$ vector; this is clearly unreasonable and in reality we are forced to consider the next best alternative. Deformations (i)–(iv) certainly have the effect of separating $C(11)$ and $C(16)$ but they are not the most efficient practical way of doing so. $C(16)-C(8)-C(9)-C(1)-C(11)$ forms a pincer-shaped assembly whose apex is $C(9)$; a small angular deformation at $C(9)$ becomes a large linear motion of $C(11)$ and $C(16)$ by the time that the movement has been transmitted by the arms of the pincers. Table 3 shows the value of $\theta_{1.9.8}$ for a series of increasingly crowded $C(1)$ and/or $C(8)$ substituted

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* Lists of structure factors, anisotropic thermal parameters and details of the complete molecular geometry have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32767 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
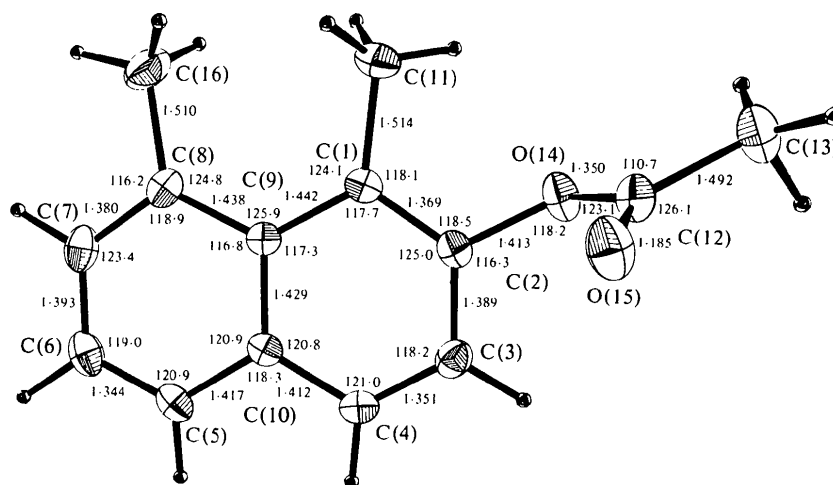
Fig. 1. A view of the molecule showing bond lengths (Å) and angles (°).

naphthalenes together with values for deformations (i) and (iv). The out-of-plane bending appears to be almost random and although the general trend of bond lengthening is upwards it is irregular, as is the accompanying reduction in the C(4)—C(10) and C(5)—C(10) lengths. In contrast, $\theta_{1\text{-}9\text{-}8}$ increases smoothly with increasing crowding of the substituents. It would, therefore, appear that, whilst deformations (i) to (iv) are utilized or not, depending on circumstances, $\theta_{1\text{-}9\text{-}8}$ is the only consistent indicator of steric crowding for *peri*-substituted naphthalenes.

The structures of 1-methyl-, 1-isopropyl- and 1,8-dimethyl-2-naphthyl acetates support the hypothesis that the rate of autoxidation of the corresponding naphthols is dependent on the steric strain present (Brady & Carnduff, 1974). There is, however, another possibility, namely that, although the reaction is driven by relief of strain when the intermediate is formed, the

Table 3. *Some geometrical parameters thought to be indicative of peri strain in* 1,8-*disubstituted naphthalenes*

Compound	$\theta_{1\text{-}9\text{-}8}$	$l_{1\text{-}9} + l_{8\text{-}9}$	$l_{4\text{-}10} + l_{5\text{-}10}$	$\lvert\delta_1\rvert + \lvert\delta_8\rvert$
(1)	120·2°	2·846 Å	2·846 Å	0·00 Å
(2)	122·3	2·845	2·838	0·07
(3)	123·2	2·859	2·832	0·05
(4)	125·8	2·878	2·828	0·81
(5)	125·9	2·880	2·829	0·23
(6)	127·0	2·870	2·840	0·42
(7)	127·5	2·922	2·836	0·79

(1) H/H (Pawley & Yeats, 1969). (2) H/Me (see first paper in this series). (3) H/iPr (see previous paper). (4) Me₂N/Me₂N (Einsphar *et al.*, 1973). (5) Me/Me (this work). (6) CH₂Br/CH₂Br (Robert *et al.*, 1974). (7) NO₂/NO₂ (Akopyan, Kitaigorodsky & Struchkov, 1965).

accessibility of the reaction site is important. Admittedly it is unlikely that the reaction site becomes more accessible as the alkyl group increases in size, but it is possible that strain and accessibility oppose each other to some extent. We therefore used the Wipke & Gund (1976) steric congestion algorithm to check this latter point and found no significant increase in congestion in progressing from the 1-methyl- to the 1,8-dimethyl-2-naphthyl acetate. To gain some idea of the relative energies of the alkyl-2-naphthyl acetates we computed the steric energies of the 1-methyl and 1,8-dimethyl compounds by molecular-mechanics methods with an *ad hoc* force field and a previously described minimization procedure (White, 1977), and found a difference of 4·5 kcal mol⁻¹.

Finally, we find no evidence that *peri* strain between C(1) and C(8) substituents is transmitted to H(4) and H(5) by a buttressing mechanism involving H(2), H(3), H(6) and H(7) (Bright, Maxwell & de Boer, 1973). Were this the case, then one would expect to find systematic distortions of the bond angles involving these latter four atoms. Although the H atoms are relatively poorly defined by X-ray analysis, the fact that no such distortions are found in the three alkyl-2-naphthyl acetates, 1,8-dimethylnaphthalene and 1,8-di(bromomethyl)naphthalene makes this argument reasonably conclusive. In any case it is extremely unlikely that this hypothetical strain-transmission system would concentrate its effect at H(4) and H(5), but would distribute it, insofar as was possible, amongst all the naphthalenic H atoms. The key to the non-parallel C(4)—H(4) and C(5)—H(5) vectors is contained in the lengthening of C(1)—C(9) and C(8)—C(9) with a corresponding shortening of C(4)—C(10) and C(5)—C(10): this pushes C(11) and C(16) apart and H(4) and H(5) together without affecting H(2), H(3), H(6) or H(7). Furthermore, H(5), C(5), C(8) and C(16), for instance,

still lie on a straight line and this would not be the case if a buttressing mechanism were operative.

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Book Review

Works intended for notice in this column should be sent direct to the Book-Review Editor (J. H. Robertson, School of Chemistry, University of Leeds, Leeds LS2 9JT, England). As far as practicable books will be reviewed in a country different from that of publication.

Kristallographie: Eine Einführung für Naturwissenschaftler. Von W. BORCHARDT-OTT. S. ix + 188, Fig. 140, Tabellen 1. Heidelberger Taschenbücher, Bd 180. Berlin, Heidelberg, New York: Springer, 1976. Price DM 19,80, US $8,20.

Eine kurze und klare Einführung, besonders für Chemiker, fehlte. Das Buch entspricht einem Vorlesungsmanuskript und ist als Lerntext ausgezeichnet. Wer hingegen ohne Vorlesung ersten Kontakt mit Kristallographie sucht, wird Verständnis-Schwierigkeiten haben. Denn abstrakte Formulierungen komplizieren oft einen einfachen Sachverhalt, wenn man sich scheut, zu 'erzählen', worum es sich handelt. Der Inhalt wechselt daraufhin mehrfach zwischen Elementarem und sehr Konzentriertem.

Das Buch beginnt konsequent mit dem Gitter; Morphologie und Symmetrie werden erläutert, es folgen Klassen (als Punktgruppen) und Raumgruppen. Abgeschlossen wird mit Grundbegriffen der Kristallchemie und Röntgenmethoden. Alles ist modern und instruktiv illustriert. Aufgaben zu den Kapiteln werden formuliert.

Referent findet, dass Kristallographie weniger abstrakt sein kann als es nach dem Buche scheint. Doch sind chemisch/physikalisch orientierte Leser auf eine ganz bestimmte Art der Entgegennahme von Wissen eingestellt, der das Buch weitgehend entspricht.

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