The Structure of (R)-2,2-Dimethyl-3-(2-naphthyl)butane, $C_{16}H_{20}$

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Abstract. $M_r = 212 \cdot 3$, monoclinic, $P2_1$, $a = 13 \cdot 703$ (8), $b = 6 \cdot 068$ (4), $c = 7 \cdot 872$ (6) Å, $\beta = 90 \cdot 87$ (8)°, $V = 654 \cdot 5$ (8) Å^3, $D_x = 1 \cdot 078$ g cm^{-3}, $F(000) = 232$, $Z = 2$, $\lambda(MoK\alpha) = 0 \cdot 7107$ Å, $\mu(Mo\ K\alpha) = 0 \cdot 65$ cm^{-1}, room temperature; refinement with 859 diffractometer data converged to $R = 0 \cdot 041$. The X-ray analysis has shown that in the solid state the hydrogen atom of the chiral centre is adjacent to H(1).

Introduction. Recently (R)-2,2-dimethyl-3-(1-naphthyl)butane (I) and (R)-2,2-dimethyl-3-(2-naphthyl)butane (II) were prepared (Piccolo, Menicagli & Lardicci, 1979) as suitable systems to investigate the chirooptical properties of isolated naphthalene chromophores, and their CD spectra in hydrocarbon solution, at room temperature, were reported (Salvadori, Piccolo, Bertucci, Menicagli & Lardicci, 1980). The limiting preferred conformations in hydrocarbon solution and in the crystalline state for (I) and (II) have been determined by using IR and NMR techniques as well as by recording the CD spectra at different temperatures (Piccolo, 1979). The presence in solution of a strongly prevailing conformation for (I) and of two almost equiprobable conformations for (II) (Fig. 1) and the existence in the crystalline state of a single conformation for both (I) and (II) have been established (Salvadori, Piccolo, Bertucci, Menicagli & Lardicci, 1980). Many efforts to obtain single crystals of (I) have so far been unsuccessful, probably because it has a low melting point (310–323 K) and it is difficult to avoid recrystallization phenomena during the preparation of samples for X-ray analysis. This paper reports the X-ray analysis carried out on single crystals of (II).

Experimental. (II) $\{[\alpha]_{589}^{25°C} = -33 \cdot 61°$ ($c = 20 \cdot 32$ g dm^{-3}, CCl$_4$) (o.p. 88·2%) (Piccolo, Menicagli & Lardicci, 1979)$\}$ crystallizes as colourless, elongated platelets; because of the low melting point (326–335 K) and high vapour pressure of the crystals they were sealed in Lindemann capillaries. Weissenberg photographs showed monoclinic symmetry, possible space groups $P2_1$ or $P2_1/m$; the chirality of the compound precluded the latter.

Cell parameters by least-squares procedure from 2θ values measured for 20 strong reflections on Philips PW1100 four-circle diffractometer with Zr-filtered Mo $K\alpha$; θ–2θ scan $0 \cdot 05°$ s^{-1}, 10 s stationary background counts, crystal $1 \cdot 0 \times 0 \cdot 45 \times 0 \cdot 2$ mm with the longest side parallel to the capillary axis; two reference reflections monitored every 50 reflections showed no significant decay in intensity; 921 unique reflections, $2\theta \leq 44 \cdot 4°$, 859 with $|F_o| \geq 4\sigma|F_o|$ used in the subsequent calculations, Lorentz–polarization corrections but not absorption (low μ), scattering factors for C and for H from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965) respectively; direct methods [*MULTAN* (Germain, Main & Woolfson, 1971)]; E map calculated with 100 terms for which $|E| > 1 \cdot 54$ had ten maxima corresponding to the aromatic moiety of the molecule; C(1) y coordinate kept fixed and aliphatic C atoms located on two successive Fourier maps; refinement with isotropic temperature factors [minimizing $\sum w(\Delta F)^2$] yielded
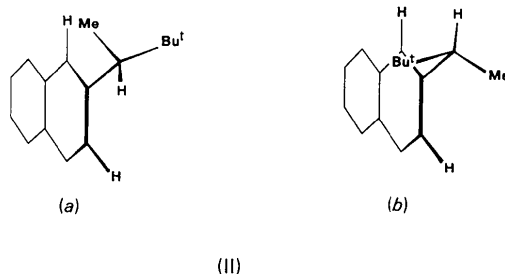

Fig. 1. The preferred conformations in hydrocarbon solution for (R)-2,2-dimethyl-3-(2-naphthyl)butane.

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$R = 0.11$; H atoms from ΔF synthesis included with $B_{iso} = B_{iso}(C)$; Cruickshank's (1965) weighting scheme: $w = (1 + F_o + 0.09\,F_o^2)^{-1}$; anisotropic refinement on C atoms, keeping H atoms fixed, reduced R to 0.041; final least-squares cycle refining the H positions gave $R = 0.041$ and $R_w = 0.050$; 204 parameters refined in last cycle, $(\Delta/\sigma)_{max} = 0.3$ (for C), final $\Delta\rho$ excursions $\leq |0.13|$ e Å^{-3}; calculations performed with XRAY76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).

Discussion. Final atomic coordinates for C atoms are listed in Table 1; Table 2 gives the main bond distances and angles. A perspective view of the molecule with the numbering is shown in Fig. 2.* The X-ray analysis has established that conformer (*b*) (Fig. 1) exists in the solid state.

The molecular structure consists of an aromatic moiety, which is almost planar, with C(2) connected to a substituted butyl chain. The least-squares plane of the side chain, which runs through C(2), C(11), C(13), C(15), makes an angle of 83.0 (3)° with the plane of the naphthalene moiety. The aromatic C—C bond lengths are similar to those observed in naphthalene and compare well with those found in other 2-substituted naphthalene derivatives (Stora & Rérat, 1974; Gadret, Goursolle, Léger & Colleter, 1975; Carpy, Léger & Nuhrich, 1978; Csöregh & Eckstein, 1979).

The aliphatic moiety, which in solution can rotate around C(2)—C(11), in the solid state arranges itself with the two more hindering substituents at C(11) as far as possible from H(1) and H(3); the torsional angle C(1)—C(2)—C(11)—H(11) is −17 (2)°, whereas C(3)—C(2)—C(11)—C(12) and C(3)—C(2)—C(11)—C(13) are 44.6 (5) and −84.3 (4)° respectively, in accordance with the relative steric hindrance of methyl and *tert*-butyl groups.

The molecular structure can be usefully compared with that of 2,2-dimethyl-3-(6-methoxy-2-naphthyl)-butanoic acid (Stora & Rérat, 1974). It should be noted that the long side chain is nearly perpendicular to the mean naphthalene plane in both compounds [dihedral angles 83.0 (3) and 89.5° respectively], although in the latter the benzyl H atom [H(11) following our numbering] is directed toward H(3) rather than in the H(1) direction. In that compound the naphthalene ring is not planar, unlike the present derivative: the planes defined by C(1),C(2)C(3) and C(5),C(6),C(7) are bent by 6.7° as a consequence of the interaction between the methoxy and carboxylic groups.

* Lists of structure factors, thermal parameters and atomic coordinates for H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38754 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final atomic parameters* ($\times 10^4$) *of the* C *atoms (e.s.d.'s in parentheses)*

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta).$$

	x	y	z	$U_{eq}(\text{Å}^2)$
C(1)	3607 (2)	4143	2577 (3)	44
C(2)	2985 (2)	2722 (7)	3380 (3)	46
C(3)	3367 (2)	685 (8)	3947 (4)	54
C(4)	4312 (2)	115 (7)	3694 (4)	54
C(5)	5958 (2)	1042 (9)	2616 (4)	60
C(6)	6548 (2)	2493 (9)	1817 (4)	69
C(7)	6185 (2)	4521 (9)	1222 (4)	65
C(8)	5237 (2)	5078 (8)	1460 (4)	52
C(9)	4597 (2)	3624 (7)	2293 (3)	42
C(10)	4959 (2)	1563 (7)	2871 (3)	44
C(11)	1930 (2)	3374 (8)	3692 (4)	56
C(12)	1653 (3)	2834 (12)	5542 (5)	86
C(13)	1199 (2)	2441 (8)	2333 (4)	58
C(14)	1450 (3)	3363 (11)	590 (5)	77
C(15)	163 (3)	3227 (11)	2719 (7)	84
C(16)	1208 (3)	−78 (9)	2262 (7)	83

Table 2. *Main bond lengths (Å) and angles (°) with e.s.d.'s in parentheses*

C(1)—C(2)	1.373 (4)	C(2)—C(3)	1.412 (6)	C(3)—C(4)	1.358 (4)
C(4)—C(10)	1.413 (5)	C(10)—C(5)	1.422 (4)	C(10)—C(9)	1.418 (6)
C(5)—C(6)	1.356 (6)	C(6)—C(7)	1.405 (7)	C(7)—C(8)	1.358 (4)
C(8)—C(9)	1.412 (5)	C(9)—C(1)	1.414 (4)	C(2)—C(11)	1.522 (4)
C(11)—C(12)	1.546 (5)	C(11)—H(11)	1.08 (5)	C(11)—C(13)	1.561 (5)
C(13)—C(14)	1.526 (6)	C(13)—C(15)	1.532 (6)	C(13)—C(16)	1.530 (7)

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C(1)—C(2)—C(3)	117.7 (3)	C(2)—C(3)—C(4)	121.8 (4)
C(3)—C(4)—C(10)	121.0 (4)	C(4)—C(10)—C(9)	118.5 (3)
C(9)·C(10)—C(5)	118.9 (3)	C(10)—C(5)—C(6)	120.2 (4)
C(5)—C(6)—C(7)	120.8 (3)	C(6)—C(7)—C(8)	120.4 (4)
C(7)—C(8)—C(9)	120.7 (4)	C(8)—C(9)—C(10)	118.9 (3)
C(10)—C(9)—C(1)	118.5 (3)	C(9)—C(1)—C(2)	122.5 (2)
C(1)—C(9)—C(8)	122.6 (3)	C(4)—C(10)—C(5)	122.6 (4)
C(1)—C(2)—C(11)	120.6 (3)	C(3)—C(2)—C(11)	121.7 (3)
C(2)—C(11)—C(12)	110.1 (3)	C(2)—C(11)—H(11)	106 (2)
C(2)—C(11)—C(13)	113.4 (3)	C(12)—C(11)—H(11)	107 (2)
C(12)·C(11)—C(13)	113.9 (3)	C(13)·C(11)—H(11)	105 (2)
C(11)—C(13)—C(14)	109.4 (3)	C(11)—C(13)—C(15)	109.8 (3)
C(11)—C(13)—C(16)	112.5 (3)	C(14)—C(13)·C(15)	106.6 (3)
C(14)—C(13)—C(16)	109.4 (4)	C(15)—C(13)—C(16)	109.0 (4)
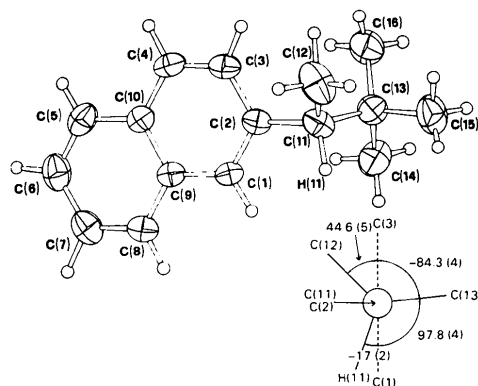
Fig. 2. An *ORTEP* (Johnson, 1965) projection of the molecule with C-atom numbering. Thermal ellipsoids are at the 40% probability level with H atoms drawn as spheres of arbitrary size. For clarity H(11) has also been indicated. Below is the Newman projection along C(11)—C(2).
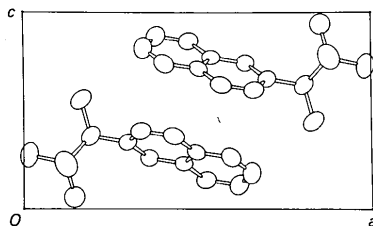
Fig. 3. Packing of the molecules projected along **b**.

A projection of crystal packing in the **c** direction is shown in Fig. 3. In the unit cell two molecules are arranged with the aromatic units facing each other and the aliphatic groups directed alternately up and down. The longer dimension of the molecule is parallel to the a axis. In the crystal, along the **a** direction, aromatic and aliphatic layers arrange themselves in a wafer-like structure. The forces responsible for the crystal packing are essentially of van der Waals type, the shortest intermolecular C$\cdots$H distances being 2·79 (3) Å between C(10) and H(4') and 2·96 (4) Å between C(8) and H(8'') [symmetry operations: (') $1 - x$, $0.5 + y$, $1 - z$; ('')$1 - x$, $y - 0.5$, $-z$].

References

CARPY, A., LÉGER, J. M. & NUHRICH, A. (1978). *Cryst. Struct. Commun.* **7**, 191–194.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

CRUICKSHANK, D. W. J. (1965). *Computing Methods in Crystallography*, p. 114 *ff.* Oxford: Pergamon Press.

CSÖREGH, I. & ECKSTEIN, M. (1979). *Acta Cryst.* B**35**, 852–856.

GADRET, M., GOURSOLLE, M., LÉGER, J. M. & COLLETER, J. C. (1975). *Acta Cryst.* B**31**, 1522–1526.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

PICCOLO, O. (1979). Tesi di Perfezionamento. Scuola Normale Superiore di Pisa, Pisa.

PICCOLO, O., MENICAGLI, R. & LARDICCI, L. (1979). *Tetrahedron*, **35**, 1751–1758.

SALVADORI, C., PICCOLO, O., BERTUCCI, C., MENICAGLI, R. & LARDICCI, L. (1980). *J. Am. Chem. Soc.* **102**, 6859–6860.

STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. L., HECK, H. & FLACK, H. (1976). The XRAY system. Tech. Rep. TR-446. Computer Science Centre, Univ. of Maryland, College Park, Maryland, USA.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

STORA, C. & RÉRAT, B. (1974). *Acta Cryst.* B**30**, 868–872.