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trans-6,10-Dimethylbicyclo[4.4.0]dec-1-ene-3 α -carbonitrile and the Conformation of its Ring System

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Abstract. C₁₃H₁₉N, $M_r = 189.30$, monoclinic, $P2_1/c$, $a = 9.000$ (2), $b = 10.477$ (2), $c = 14.067$ (3) Å, $\beta = 122.50$ (2)°, $V = 1118.7$ Å³, $Z = 4$, $D_c = 1.12$ Mg m⁻³, $F(000) = 416$, Mo $K\alpha$ radiation, $\mu = 0.07$ mm⁻¹, $\lambda = 0.71069$ Å, $R = 0.090$ for 406 reflexions with $\theta < 20.5^\circ$. The ring system has a relatively unstrained chair-half-chair conformation, common to several related molecules.

Introduction. In the course of synthetic approaches to sesquiterpene structures related to rosfoliol (1) (Southwell, 1978) a new strategy was adopted starting from the enone (2). Introduction of the 2-hydroxy-2-propyl substituent was envisaged as being developed from the corresponding nitrile (3a) which, in turn, would be produced by the action of *p*-tosylmethyl isocyanide (Oldenzel, van Leusen & van Leusen, 1977) on the conjugated enone (2). This investigation (Morton, 1980) led to the synthesis of a mixture of both epimeric nitriles (3a and 3b), one of which could be isolated in a crystalline form. Since the stereochemical assignment of the intermediate nitrile is of crucial importance to the development of a synthesis of biogenetically significant sesquiterpenes related to

rosfiliol (1) (MacSweeny, Ramage & Sattar, 1970) it was central to the synthetic work that the stereochemical assignment of the nitriles was made unambiguously. Accordingly, an X-ray study has been undertaken.

Approximate cell parameters were obtained from Nonius Weissenberg photographs (Cu $K\alpha$ radiation) and the space group $P2_1/c$ was indicated by the absences $h0l$ with l odd and $0k0$ with k odd. Preliminary attempts to collect intensity data using an Enraf-Nonius CAD-4 diffractometer (Mo $K\alpha$ radiation) revealed an unacceptably rapid reduction in the intensities of standard reflexions due to volatilization of the material. The CAD-4 data upon which the structure determination was based were collected using a clear crystal (<0.3 mm maximum dimension) sealed in a Lindemann capillary. The cell parameters were measured diffractometrically. Intensity measurements yielded 406 above-zero reflexions with $\theta < 20.5^\circ$, beyond which very few above-zero reflexions were observed. These 406 data included a large proportion of weak reflexions. Lorentz and polarization corrections were applied, but no absorption correction was made. The phase problem was solved with *MULTAN 78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), all the non-hydrogen atoms being revealed on a Fourier map.

Full-matrix least-squares refinement using *SHELX* (Sheldrick, 1976) produced a final R factor of 0.090, with isotropic vibrational parameters and the H atoms placed and constrained in chemically reasonable bonding positions. Fluctuations in the final difference map were $\leq \pm \frac{1}{4}$ e Å⁻³. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Unit weights were used throughout, and all

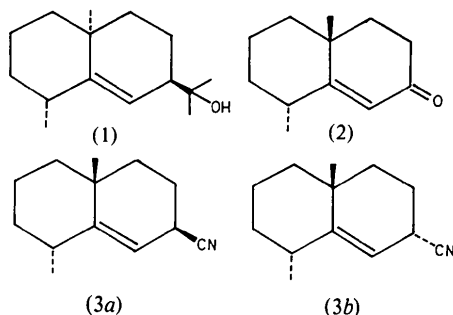


Table 1. Fractional atomic coordinates and isotropic thermal parameters for the non-hydrogen atoms

E.s.d.'s are in parentheses.

	x	y	z	U (Å ²)
C(1)	1.0166 (20)	0.1068 (15)	0.7235 (12)	0.034 (4)
C(2)	1.1130 (20)	0.1130 (16)	0.6777 (14)	0.035 (4)
C(3)	1.3119 (20)	0.1366 (17)	0.7421 (13)	0.044 (4)
C(4)	1.3954 (21)	0.1036 (18)	0.8684 (13)	0.047 (5)
C(5)	1.2919 (19)	0.1770 (15)	0.9099 (13)	0.043 (5)
C(6)	1.1000 (19)	0.1248 (15)	0.8502 (12)	0.035 (4)
C(7)	0.9933 (18)	0.2218 (17)	0.8703 (13)	0.043 (5)
C(8)	0.7942 (21)	0.1936 (18)	0.8069 (13)	0.053 (5)
C(9)	0.7215 (21)	0.1779 (17)	0.6815 (13)	0.052 (5)
C(10)	0.8205 (20)	0.0818 (16)	0.6553 (13)	0.043 (5)
C(11)	1.0983 (21)	-0.0050 (16)	0.9031 (14)	0.043 (5)
C(12)	0.7437 (25)	0.0694 (18)	0.5286 (14)	0.061 (6)
C(13)	1.3529 (21)	0.2651 (16)	0.7239 (14)	0.040 (4)
N(1)	1.3826 (20)	0.3683 (17)	0.7135 (13)	0.068 (5)

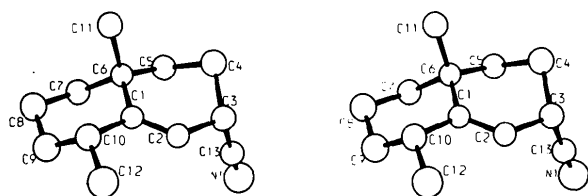


Fig. 1. Stereoscopic view showing the atom-numbering scheme. (Ellipsoids correspond to the 50% probability level.)

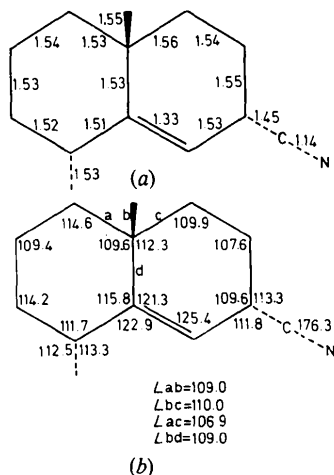


Fig. 2. (a) Bond lengths (Å) (average e.s.d. 0.02 Å). (b) Bond angles (°) (average e.s.d. 1.4°).

computations were carried out on the joint CDC 7600/ICL 1906A system of the University of Manchester Regional Computer Centre.

Final atomic parameters are given in Table 1.* Fig. 1 is a stereoscopic view of the heavy-atom skeleton

* Lists of structure factors, H-atom coordinates and torsion-angle data for related compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36588 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

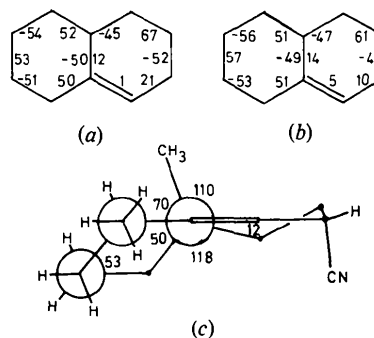


Fig. 3. (a) Ring torsion angles (°) (average e.s.d. 2°). (b) Mean ring torsion angles (°) for all the reported structures with the common ring conformations. (c) Composite Newman projection down the central bridging bond, showing values of appropriate dihedral angles (average e.s.d. 2°).

showing the atom numbering. Fig. 2 gives the bond lengths and angles, and Fig. 3(a) the ring torsion angles for the enantiomer whose coordinates appear in Table 1. In space group $P2_1/c$, enantiomeric pairs of molecules occur. The second enantiomer has a conformation which is the mirror image of that shown in Fig. 1 and torsion angles as in Fig. 3(a) but with all the signs reversed. [The sign convention is that of Klyne & Prelog (1960).]

Discussion. This structure determination establishes that the $-CN$ substituent in the crystalline isomer has the configuration required for further elaboration to rosifoliol-type sesquiterpenes. Preliminary work on the mixture of epimers has shown that the change in functionality [$-CN \rightarrow -CONH_2 \rightarrow -COOMe \rightarrow -CMe_2OH$] can be accomplished efficiently and without double-bond migration.

The second feature of conformational interest is the general conformation of the cyclohexane-cyclohexene fused-ring system: chair-half-chair. The computerized Crystal Structure Search Retrieval (1980) (CSSR) system, accessing the Cambridge Crystallographic Database (CCD), reveals at the present time six different molecules possessing this ring system with the double bond situated as in the title molecule, but not all the retrieved structures have the same ring conformations.*

Of eight structures, comprising the six retrieved structures, the title molecule and rosifoliol (Beagley, Pritchard, Ramage & Southwell, 1982), all but three have the relatively unstrained chair-half-chair ring conformations of Fig. 3 (or the enantiomeric structure). Fig. 3(b) gives the mean ring torsion angles

* The searches were run interactively on the DEC-10 computer at Edinburgh University, by means of the link from UMIST. We ignored structures eliminated by the NOSTR command. Torsion angles were calculated using the VIEW facilities.

for the five examples with the common structure* (Jones, Kearns & Wing, 1973; Enwall & van der Helm, 1974; the title molecule; Neuenschwander, Neuenschwander, Steinegger & Engel, 1979; Beagley *et al.*, 1982). In the cyclohexane ring of the average structure, the absolute torsion angles nearer to the bridge bond tend to be a little less than, and those remote from the bridge bond a little greater than, the $|\pm 55^\circ|$ calculated by molecular mechanics for cyclohexane itself (Beagley, 1978); the calculated torsion angles for free cyclohexene (0, 15, -45 , 60, -45 , 15°) are also similar to those in the fused structure (5, 10, -41 , 61, -47 , 14°). Thus, neither of the six-membered rings of this common structure is much strained by fusion. Of the three molecules with ring conformations* which differ from that of the common structure, capsidiol (Birnbaum, Stoessl, Grover & Stothers, 1974) still has a chair-half-chair conformation, but one of its rings is folded in the opposite sense to that in Fig. 3, perhaps under the influence of an isopropenyl side chain. The fluorinated structure of Hamor & Hamor (1976) has a much flatter cyclohexane ring, perhaps because of the possible conjugation involving its =O substituent. The structure of House, Phillips & Van Derveer (1979) has a twist-boat cyclohexane ring with a *tert*-butyl side chain.

Fig. 3(c) is a composite Newman projection of the title molecule which shows the rather exposed position of the bridgehead methyl group, projecting away from the folds of the two rings, on the rather convex side of the ring system. All five molecules with the common structure have a sterically similar bridgehead methyl group.

* Details of the individual molecules and their ring torsion angles are included with the deposited material (see deposition footnote).

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Hexamethylenefurazan *N*-Oxide

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Abstract. C₈H₁₂N₂O₂, monoclinic, $P2_1/n$, $a = 11.50$ (2), $b = 10.50$ (2), $c = 7.07$ (1) Å, $\beta = 101.0$ (3) $^\circ$, $Z = 4$, $D_c = 1.33$ g cm⁻³. Final $R = 0.056$

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for 523 observed reflections. The furazan *N*-oxide ring geometry is compared with that of the tetra- and trimethylene analogues whose structures have recently been determined [Barrow (1982). *Acta Cryst.* B38, 308–310; Barnes, Barrow, Harding, Paton, Ashcroft,