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(-) CAMPHENE-8-CARBOXYLIC ACID: DISTORTION INVOLVING THE GEM. DIMETHYL GROUP OBSERVED BY X-RAY DIFFRACTION

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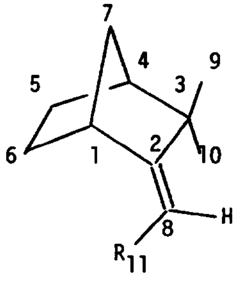
We wish to report an analysis of x-ray diffraction data tending to support an argument advanced by one of us[1] on chemical grounds that almost exclusive _exo_-methyl migration in the Nametkin portion of camphene (1) racemization (via the camphenehydro ion) may be attributable to a strain-induced (C-10 - C-5-_endo_-H) distortion of the dihedral (torsion) angles α and β (Fig. 1). The diffraction data are reported for (-) camphene-8-carboxylic acid (2)[2] with the absolute configuration illustrated[3]. The angles α and β are found to differ significantly from the 60° suggested by Dreiding models.



Camphene (1) R = H; (-) camphene-8-carboxylic acid (2) R = CO_2H

X-ray diffraction data for 2 were collected on a capillary-enclosed single crystal of 2 at 5°C on a Picker Corporation FACS-I four-circle diffractometer using CuKα radiation. Carbon and oxygen atoms were located by direct phasing methods[4] and the structure refined anisotropically using the 1382 reflections with $F \geq 4\sigma(F)$. Hydrogen atom positions were determined from difference Fourier maps; the final residual[5] was 4.8 per cent.

Crystal Data: $C_{11}H_{16}O_2$; MW = 180.2; F(000) = 196; triclinic; $\underline{a}$ = 7.429 ± 0.002 Å, $\underline{b}$ = 12.020 ± 0.003 Å, $\underline{c}$ = 6.081 ± 0.002 Å, α = 98.06 ± 0.02°, β = 104.86 ± 0.03°, γ = 88.63 ± 0.02°; Volume = 519.6 Å^3, $\underline{d}_c$ = 1.15 g cm^{-3} for Z = 2; $\underline{d}_m$ = 1.13 g cm^{-3} by flotation. No extinctions. Space group: P1(No. 1, C_1^1).

The structure contains two molecules in the asymmetric unit which form a hydrogen-bonded dimer through their carboxyl groups (Fig. 2). The camphene skeleton (atoms C(1) - C(10)) is very similar in the two independent molecules; a least-squares superposition of the two molecules leads to a root-mean-square deviation of only 0.05 Å in the position of chemically equivalent atoms, with the largest difference between two corresponding atoms being 0.07 Å. Molecule A is shown in Figure 1. Torsion angles[6] about the C(2) - C(3) bond are given in

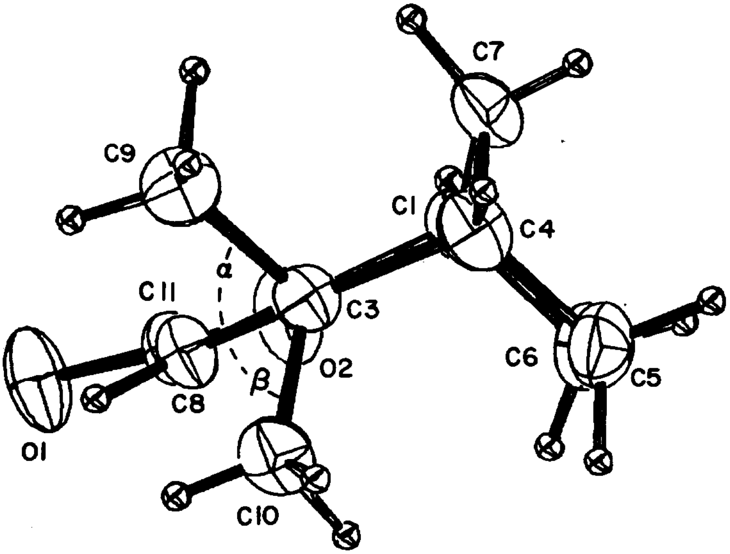


Fig. 1 Molecule A of compound $\underline{2}$ projected along C(3)-C(2) bond.

Table 1. The first two torsion angles in the Table (α and β, Fig. 1) deviate from 60° by more than seven times their calculated error (0.5°). Further confidence in the reality of this deviation comes from the fact that for each dihedral angle (α or β), the direction of the twist is the same in both of the crystallographically independent molecules.

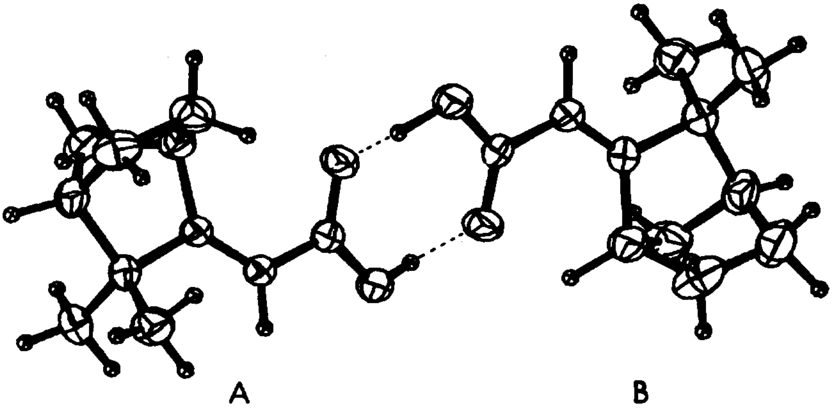


Fig. 2. The two independent molecules in the crystallographic cell projected along c.

Table 1. Torsion angles (deg.) about the C(2)-C(3) bond

	Molecule A	Molecule B
C(8)C(2) - C(3)C(9)	-66.7	-63.5
C(8)C(2) - C(3)C(10)	55.0	56.4
C(1)C(2) - C(3)C(9)	111.4	114.3
C(1)C(2) - C(3)C(10)	-126.9	-125.9
C(1)C(2) - C(3)C(4)	-4.0	-1.6
C(8)C(2) - C(3)C(4)	177.9	179.3

These crystallographic results reveal a significant distortion in the direction proposed[1] and clearly imply an appreciable energetic favoring of exo-methyl migration. This distortion brings C-10 closer to its ultimate position after complete rearrangement and aligns the σorbital of C-9/C-3 more nearly parallel with the p-orbital of the trigonal carbon (C-2). Presumably the camphenehydro ion approximates the ground state for both *exo*- and *endo*-methyl migration; but the orbital alignments may be irrelevant to the energies of the two transition states except insofar as the reason for these alignments gives clues to factors (eg. C-10/C-5 repulsion and probable increase therein during C-10 migration) which may be more important to transition state than to ground state geometry.

REFERENCES AND NOTES

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2. W. R. Vaughan, J. Wolinsky, R. R. Dueltgen, S. Grey and F. S. Seichter, *J. Org. Chem.*, **35**, 400 (1970).
3. The use of *2* instead of *1* in this preliminary study was dictated by the volatility and x-ray sensitivity of *1* and is justified by the general character of the Nametkin-type rearrangement in all camphene derivatives as well as simpler norbornane derivatives. See J. A. Berson, J. H. Hammons, A. W. McRowe, R. G. Bergman, A. Remanic and D. Houston, *J. Amer. Chem. Soc.*, **89**, 2590 (1967) and references cited therein. We are now engaged in examining (*1*) itself.
4. Program MULTAN. G. Germain, P. Main and M. M. Woolfson, *Acta Crystallogr.*, **A27**, 368 (1971).
5. Residual = $\Sigma \big| |F_O| - |F_C| \big| / \Sigma |F_O|$, where F_o and F_c are the observed and calculated structure factors amplitudes.
6. Zero angle is defined with front and rear bond superposed in projection down middle bond. Angle is positive if right hand rotation at either bond is required for their superposition.