D—H···*A*	H···*A*	*D*···*A*	*D*—H···*A*
C(24)—H(C24)···O(1)	2.63	3.55 (1)	146
C(34)—H(C34)···O(2)	2.26	3.22 (1)	152
C(44)—H(C44)···O(1)	2.63	3.56 (1)	146
O(1)—H(O1)···O(*W*2)	2.13	3.04 (1)	153
O(2)—H(O2)···Cl(1)	2.09	3.165 (9)	177

The crystal for data collection was sealed in a glass capillary with a small quantity of mother liquor. The structure was solved by direct methods and refined by block-diagonal least squares. The H atoms were located on a difference map except for eight of those attached to water molecules. All non-H atoms were refined anisotropically and the H atoms were fixed with isotropic displacement parameters (U = 0.06 Å^2) in the final cycles of refinements. All calculations were performed using the *SHELXTL* crystallographic software package (Sheldrick, 1983).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: AS1097). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Camphene-1-carboxylic Acid: Stereochemistry of the Nametkin Shift

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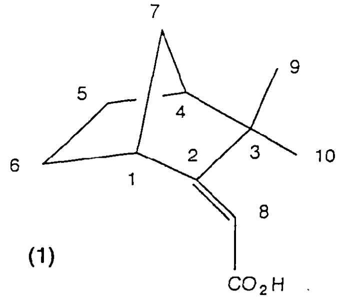
Abstract

The title compound, 2,2-dimethyl-3-methylenebicyclo[2.2.1]heptane-1-carboxylic acid, is a hydrogen-bonded dimer, $(C_{11}H_{16}O_2)_2$. This structure determination provides some evidence for the idea that, in the Nametkin Shift, migration of the *exo* methyl group may be marginally preferred.

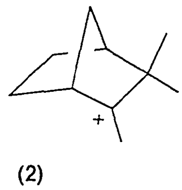
Comment

The Nametkin rearrangement refers to 3,2-methyl shifts in norbornyl cations (Nametkin & Brussoff, 1927). Both the methyl and the 3,2-hydride shifts have been well documented, and a general preference for an *exo* shift is observed (Berson, Hammons, McRowe, Bergman, Remanik & Houston, 1967; David, Everling, Kilian, Stothers & Vaughan, 1973), although authentic examples of *endo* shifts exist (Bushell & Wilder, 1967; Dadson, Hutchinson & Money, 1990). Attention has centred on the reasons for the preferred *exo* shifts and, in particular, on the nature of the transition state for migration.

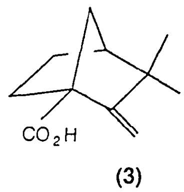
A crystal structure determination of camphene-8-carboxylic acid, (1), revealed that the methyl groups were unsymmetrically disposed with respect to the double bond (Moews, Knox & Vaughan, 1978). Thus, the dihedral angle C8—C2—C3—C9 was 65.1°, compared with a value of 55.9° for C8—C2—C3—C10. From this, the authors concluded that the observed conformations of the *gem*-dimethyl groups could result, in the corresponding cation (2) of the Nametkin rearrangement (shown as the classical ion for convenience), in a preferred *exo,exo* 3,2-methyl migration, since the *p* orbital at C2 and the C3—C9 [*i.e.* the C3—C(Me)$_{exo}$] bond are closer to being parallel. Camphene-8-carboxylic acid exists, as is normal, as a hydrogen-bonded dimer in the solid state. However, this structure carries a carboxylic acid group on the double bond, which is the part of the molecule under closest scrutiny. Accordingly, we have undertaken an X-ray structure determination of camphene-1-carboxylic acid (3) in which the carboxylic acid group is located at the bridgehead position.



(1)



(2)



(3)

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As in (1), the title compound (3) forms a hydrogen-bonded dimer of two unique molecules. However, both these molecules are very similar, with the exception of the orientations of the carboxyl groups, and, in most instances, the average values of their dimensions will be used in this discussion. The enantiomers chosen were those which corresponded to the structure of (1); attempts to establish the absolute configuration were not successful. Absolute values are quoted in the text for most torsion angles in order to correspond with those given in the discussion of (1) (Moews, Knox & Vaughan, 1978). In (3), the two dihedral angles which indicate the disposition of the methyl groups with respect to the double bond are C8—C2—C3—C9 [62.3 (5)°] and C8—C2—C3—C10 [58.3 (6)°]. The values of these are comparable with the aforementioned corresponding values in (1) (65.1 and 55.9°). Other relevant dihedral angles in (3) are those of the appropriate methyl and methylene groups around the C3—C4 bond; C9—C3—C4—C7 is 81.6 (4)°, compared to values of 79.1 and 158.2° for (1). The ring dihedral angles around the two carbon bridges in (3), C1—C2—C3—C4 −0.7 (4)° and C4—C5—C6—C1 4.6 (4)°, may be compared with values of 2.8 and 2.9°, respectively, in (1). Similarly, the angles C1—C2—C8 of 128.4 (4), C3—C2—C8 of 125.3 (4) and C1—C2—C3 of 106.3 (4)° around the 'essentially planar' ring atom C2 can be compared with 130.2 (3), 123.72 and 106.1 (3)°, respectively, in (1).

The data for (1) led Moews, Knox & Vaughan (1978) to suggest that the asymmetric angular distortion at C2 results from a contact between the H atom at C1 and an O atom of the carbonyl group. In (3), the bridgehead angle C2—C1—C11 is widened to 118.4 (4)° and is similar to C7—C1—C11 of 116.4 (4)°; the other valence angle at this bridgehead, C6—C1—C11, is significantly smaller, at 110.9 (4)°. The orientations of the carboxylic acid groups in the two molecules of (3) are significantly different and the torsion angles involving the ring atoms are C11—C1—C2—C8 15.5 (6)° (mean), C2—C1—C11—O2 −36.1 (8) and 128.4 (6)° and C2—C1—C11—O1 144.5 (5) and −53.4 (7)°. Our data for (3) do not indicate any significant interaction between the carboxyl groups and the double bonds, and thus the carboxyl group has no influence on the conformations of the double bonds with respect to the methyl group.

The present structure is consistent with the proposal of Moews, Knox & Vaughan (1978) on the significance of the *p*-orbital orientation at C2 (see above), although our torsion-angle values are slightly smaller. Here we have provided a second and, with the shifted carboxyl group, more appropriate example of the proposal. Thus, the conformation of the methyl groups with respect to the exocyclic double bond (which simulates the *p* orbital of a carbocation) is, together with the reaction pathway, relevant to the question of which methyl group migrates.

On the basis of the X-ray data for (3) and (1), the migration of the *exo*-methyl group is the preferred option. However, it is not the overwhelmingly preferred option, since there are a small number of cases where the *endo* 3,2-migration occurs and these cases need further structural investigation.

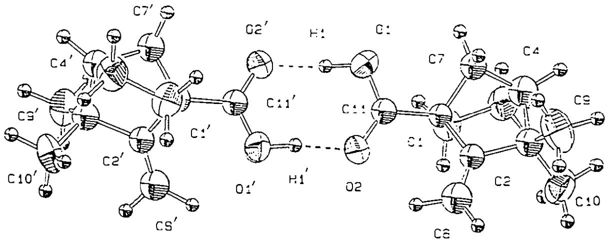

Fig. 1. A view of the molecules in the unit cell, projected onto the plane of the carboxyl group.

Experimental

Crystal data

$C_{11}H_{16}O_2$
$M_r = 180$
Monoclinic
$P2_1$
$a = 6.193\ (2)$ Å
$b = 10.609\ (2)$ Å
$c = 15.492\ (4)$ Å
$\beta = 86.42\ (2)°$
$V = 1015.9\ (1)$ Å^3
$Z = 4$
$D_x = 1.11$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 10–12°$
$\mu = 0.074$ mm^{-1}
$T = 291$ K
Tablet
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1604 measured reflections
1457 independent reflections
708 observed reflections $[I > \sigma(I)]$

$R_{\rm int} = 0.03$
$\theta_{\rm max} = 22.0°$
$h = 0 \rightarrow 6$
$k = 0 \rightarrow 11$
$l = -17 \rightarrow 17$
3 standard reflections monitored every 100 reflections intensity variation: none

Refinement

Refinement on F
$R = 0.0407$
$wR = 0.0429$
$S = 0.241$
708 reflections
166 parameters
H-atom parameters not refined
$w = 0.02/[\sigma^2(F_o) + 0.01995F_o^2]$

$(\Delta/\sigma)_{\rm max} = 0.147$ (U_{23} of C9)
$\Delta\rho_{\rm max} = 0.107$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.154$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{iso}/U_{eq}
C1	−0.0662 (10)	−0.1892 (6)	0.0522 (4)	0.0387 (14)†
C2	−0.1097 (10)	−0.2796 (6)	0.1249 (4)	0.0442 (15)†
C3	0.0076 (11)	−0.2289 (7)	0.2011 (4)	0.0520 (17)†
C4	0.1093 (12)	−0.1064 (8)	0.1619 (4)	0.0624 (19)†
C5	0.2971 (11)	−0.1377 (8)	0.0947 (5)	0.0658 (48)
C6	0.1783 (10)	−0.2033 (7)	0.0214 (4)	0.0571 (44)
C7	−0.0635 (12)	−0.0625 (6)	0.1000 (4)	0.0497 (17)†
C8	−0.2220 (13)	−0.3842 (8)	0.1263 (5)	0.0662 (21)†
C9	−0.1558 (16)	−0.1957 (11)	0.2767 (5)	0.0978 (69)
C10	0.1725 (14)	−0.3219 (8)	0.2342 (5)	0.0802 (57)
C11	−0.2018 (11)	−0.1963 (6)	−0.0228 (4)	0.0452 (16)†
O1	−0.2468 (10)	−0.0913 (5)	−0.0591 (3)	0.0770 (35)
O2	−0.2686 (10)	−0.2964 (5)	−0.0508 (3)	0.0799 (36)
C1′	−0.6555 (10)	−0.2302 (6)	−0.3046 (4)	0.0447 (16)†
C2′	−0.6046 (11)	−0.3361 (6)	−0.3690 (4)	0.0454 (17)†
C3′	−0.7052 (11)	−0.2970 (7)	−0.4527 (4)	0.0529 (17)†
C4′	−0.8135 (11)	−0.1717 (6)	−0.4258 (4)	0.0508 (18)†
C5′	−1.0062 (11)	−0.1940 (9)	−0.3620 (5)	0.0705 (51)
C6′	−0.9052 (11)	−0.2406 (8)	−0.2789 (5)	0.0641 (52)
C7′	−0.6487 (11)	−0.1155 (7)	−0.3640 (4)	0.0515 (17)†
C8′	−0.4879 (12)	−0.4380 (7)	−0.3576 (5)	0.0600 (19)†
C9′	−0.5248 (13)	−0.2782 (8)	−0.5255 (5)	0.0755 (54)
C10′	−0.08593 (14)	−0.3987 (9)	−0.4804 (5)	0.0788 (56)
C11′	−0.05254 (11)	−0.2212 (7)	−0.2271 (4)	0.0459 (16)†
O1′	−0.05154 (10)	−0.3215 (5)	−0.1806 (3)	0.0836 (40)
O2′	−0.04380 (9)	−0.1225 (5)	−0.2079 (3)	0.0643 (30)

† U_{iso}.

Table 2. *Selected geometric parameters* (Å, °)

C1—C2	1.491 (9)	C1′—C2′	1.521 (9)
C1—C6	1.566 (9)	C1′—C6′	1.577 (10)
C1—C7	1.536 (9)	C1′—C7′	1.524 (9)
C1—C11	1.477 (9)	C1′—C11′	1.490 (9)
C2—C3	1.522 (9)	C2′—C3′	1.532 (9)
C2—C8	1.310 (10)	C2′—C8′	1.318 (10)
C3—C4	1.552 (10)	C3′—C4′	1.535 (10)
C3—C9	1.540 (12)	C3′—C9′	1.549 (11)
C3—C10	1.532 (11)	C3′—C10′	1.521 (11)
C4—C5	1.547 (11)	C4′—C5′	1.519 (10)
C4—C7	1.552 (10)	C4′—C7′	1.560 (10)
C5—C6	1.556 (10)	C5′—C6′	1.547 (11)
C11—O1	1.287 (8)	C11′—O1′	1.289 (9)
C11—O2	1.229 (8)	C11′—O2′	1.223 (8)
C2—C1—C6	107.1 (5)	C2′—C1′—C6′	105.9 (5)
C2—C1—C7	101.8 (5)	C2′—C1′—C7′	101.4 (5)
C2—C1—C11	118.5 (5)	C2′—C1′—C11′	118.3 (5)
C6—C1—C7	101.0 (5)	C6′—C1′—C7′	101.4 (5)
C6—C1—C11	110.0 (5)	C6′—C1′—C11′	111.8 (5)
C7—C1—C11	116.6 (5)	C7′—C1′—C11′	116.1 (5)
C1—C2—C3	106.6 (5)	C1′—C2′—C3′	106.0 (5)
C1—C2—C8	129.0 (6)	C1′—C2′—C8′	127.7 (6)
C3—C2—C8	124.4 (6)	C3′—C2′—C8′	126.2 (6)
C2—C3—C4	101.2 (5)	C2′—C3′—C4′	101.4 (5)
C2—C3—C9	110.4 (6)	C2′—C3′—C9′	109.8 (6)
C2—C3—C10	113.1 (6)	C2′—C3′—C10′	110.0 (6)
C4—C3—C9	109.8 (6)	C4′—C3′—C9′	111.7 (6)
C4—C3—C10	114.1 (6)	C4′—C3′—C10′	114.8 (6)
C9—C3—C10	108.3 (6)	C9′—C3′—C10′	108.8 (6)
C3—C4—C5	110.7 (6)	C3′—C4′—C5′	110.8 (6)
C3—C4—C7	102.4 (6)	C3′—C4′—C7′	101.9 (5)
C5—C4—C7	99.7 (6)	C5′—C4′—C7′	100.3 (5)
C4—C5—C6	102.5 (6)	C4′—C5′—C6′	104.4 (6)
C1—C6—C5	103.1 (5)	C1′—C6′—C5′	102.0 (6)
C1—C7—C4	93.7 (5)	C1′—C7′—C4′	94.1 (5)
C1—C11—O1	116.7 (6)	C1′—C11′—O1′	116.4 (6)
C1—C11—O2	122.8 (6)	C1′—C11′—O2′	121.3 (6)
O1—C11—O2	120.5 (6)	O1′—C11′—O2′	122.2 (6)
C2—C1—C6—C5	−73.8 (6)	C2′—C1′—C6′—C5′	−72.2 (6)
C6—C1—C2—C3	70.0 (5)	C6′—C1′—C2′—C3′	71.9 (6)
C6—C1—C2—C8	−109.0 (8)	C6′—C1′—C2′—C8′	−111.5 (7)
C2—C1—C7—C4	54.0 (5)	C2′—C1′—C7′—C4′	53.5 (5)
C7—C1—C2—C3	−35.6 (6)	C7′—C1′—C2′—C3′	−33.6 (6)
C7—C1—C2—C8	145.4 (7)	C7′—C1′—C2′—C8′	143.1 (7)
C2—C1—C11—O1	144.5 (5)	C2′—C1′—C11′—O1′	−53.4 (7)
C2—C1—C11—O2	−36.1 (8)	C2′—C1′—C11′—O2′	128.4 (6)
C11—C1—C2—C3	−165.0 (4)	C11′—C1′—C2′—C3′	−161.7 (4)
C11—C1—C2—C8	16.0 (9)	C11′—C1′—C2′—C8′	14.9 (9)
C6—C1—C7—C4	−56.2 (5)	C6′—C1′—C7′—C4′	−55.4 (5)
C7—C1—C6—C5	32.3 (6)	C7′—C1′—C6′—C5′	33.3 (6)
C6—C1—C11—O1	−91.9 (6)	C6′—C1′—C11′—O1′	70.0 (7)
C6—C1—C11—O2	87.5 (7)	C6′—C1′—C11′—O2′	−108.1 (7)
C11—C1—C6—C5	156.2 (5)	C11′—C1′—C6′—C5′	157.6 (5)
C7—C1—C11—O1	22.3 (7)	C7′—C1′—C11′—O1′	−174.3 (5)
C7—C1—C11—O2	−158.3 (6)	C7′—C1′—C11′—O2′	7.5 (8)
C11—C1—C7—C4	−175.4 (4)	C11′—C1′—C7′—C4′	−176.8 (4)
C1—C2—C3—C4	0.8 (6)	C1′—C2′—C3′—C4′	−2.1 (6)
C1—C2—C3—C9	116.9 (6)	C1′—C2′—C3′—C9′	116.1 (5)
C1—C2—C3—C10	−121.6 (6)	C1′—C2′—C3′—C10′	−124.1 (6)
C8—C2—C3—C4	179.8 (5)	C8′—C2′—C3′—C4′	−178.8 (5)
C8—C2—C3—C9	−64.0 (8)	C8′—C2′—C3′—C9′	−60.6 (7)
C8—C2—C3—C10	57.4 (8)	C8′—C2′—C3′—C10′	59.2 (8)
C2—C3—C4—C5	−71.5 (6)	C2′—C3′—C4′—C5′	−69.7 (6)
C2—C3—C4—C7	34.0 (6)	C2′—C3′—C4′—C7′	36.3 (6)
C9—C3—C4—C5	171.9 (6)	C9′—C3′—C4′—C5′	173.5 (5)
C9—C3—C4—C7	−82.7 (6)	C9′—C3′—C4′—C7′	−80.6 (6)
C10—C3—C4—C5	50.2 (7)	C10′—C3′—C4′—C5′	48.9 (7)
C10—C3—C4—C7	155.7 (5)	C10′—C3′—C4′—C7′	154.9 (5)
C3—C4—C5—C6	66.5 (6)	C3′—C4′—C5′—C6′	68.5 (6)
C3—C4—C7—C1	−53.9 (5)	C3′—C4′—C7′—C1′	−56.0 (5)
C5—C4—C7—C1	60.0 (5)	C5′—C4′—C7′—C1′	58.0 (5)
C7—C4—C5—C6	−40.8 (6)	C7′—C4′—C5′—C6′	−38.5 (6)
C4—C5—C6—C1	5.4 (6)	C4′—C5′—C6′—C1′	3.7 (6)

The structure was solved using *SHELX*76 (Sheldrick, 1976). H atoms were located in the difference map and included in chemically sensible positions. Anisotropic refinement of all non-H atoms showed that the C atoms in the centre of the molecule had almost isotropic character and so refinement was repeated, with only those atoms on the periphery modelled anisotropically. This gave a better observation/parameter ratio.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: HU1124). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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