

GF thanks NSERC (Canada) for Grants in Aid of Research.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, and a molecular packing diagram, have been deposited with the IUCr (Reference: BK1128). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(–)-(1*S*,3*R*,4*R*,6*S*)-4,7,7-Trimethyl-5-oxobicyclo[4.1.0]heptane-3-carbonitrile

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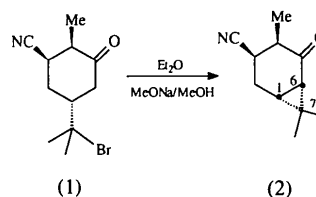
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Abstract

The crystal structure of the title compound, $C_{11}H_{15}NO$, consists of discrete molecules held together by van der Waals interactions. The molecule contains a three-membered cyclopropane ring fused with a six-membered cyclohexanone ring, with a fold angle along the common bond of $65.4(1)^\circ$. The relative stereochemistry of the molecule is established.

Comment

Cocker, Grayson & Shannon (1995) have recently described a series of fused isoxazolo–lactam compounds obtained from β -cyano- α -methylcycloalkanones by regio-specific nitrosation at the α -position by pentanenitrile in methanolic sodium hydroxide. The reaction pathway probably involves sequential cycloalkanone cleavage, isoxazole formation and lactamization. In the course of the study, (–)-(1*R*,2*R*,5*R*)-5-(1-bromo-1-methylethyl)-2-methyl-3-oxocyclohexanecarbonitrile, (1), was prepared, but its relative configuration could not be assigned on the basis of spectral results. We therefore undertook an X-ray structure determination of the derived cyanocarbanone, (2), in order to determine the relative stereochemistry of these compounds unambiguously.



The structure of (2) is shown in Fig. 1, which also indicates the atom-numbering scheme used. Although the absolute configuration could not be determined unambiguously from the refinement results, due to the absence of significant anomalous scattering, the relative stereochemistries at positions 1, 3, 4 and 6 are clearly revealed as *S*, *R*, *R* and *S*, respectively. The cyclopropane ring makes an angle of $65.4(1)^\circ$ with the mean plane formed by atoms C1, C2, C5 and C6 [maximum deviation $0.015(1)\text{Å}$]. The six-membered ring as a whole is non-planar and has a twisted chair conformation with torsion angles C6–C1–C2–C3 $-23.7(2)$, C1–C2–C3–C4 $53.5(2)$, C2–C3–C4–C5 $-61.1(2)$, C3–C4–C5–C6 $40.7(2)$, C4–C5–

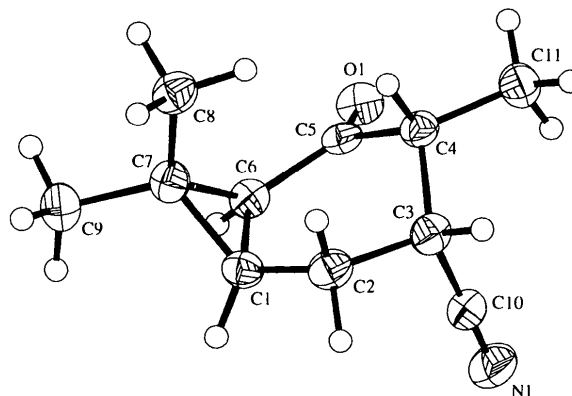


Fig. 1. The molecular structure of (2) showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by small circles.

C6—C1—12.7 (2) and C2—C1—C6—C5 3.2 (2)°. The sum of the interbond angles at atom C5 is 359.7°, suggesting planar geometry around C5. The C5—O1 bond distance is 1.228 (2) Å, consistent with the double-bond character of the carbonyl group. The C3—C10—N1 moiety is nearly linear, with an angle of 177.6° and an N—C distance of 1.147 (2) Å, confirming the bond order of 3 in the carbonitrile group. The C—C distances are as expected for this type of compound.

Experimental

Compound (2) was obtained on cyclization of (1), by treatment of its ethereal solution with a slight excess of sodium methoxide in methanol, and crystallized from ethyl acetate-hexane solution to give colourless prismatic crystals (Cocker, Grayson & Shannon, 1995) (m.p. 327–328 K). IR bands (Nujol): ν_{\max} (cm⁻¹) 3364, 2241 and 1687. ¹H NMR (300 MHz): δ (CDCl₃) 1.12 (3H, s, Me), 1.15 (3H, s, Me), 1.18 (3H, d, $J = 6.8$ Hz, 4-Me), 1.60 (1H, d, $J = 7.7$ Hz, 6-H), 1.68 (1H, m, 1-H), 1.80 (1H, m, 2 α -H or 2 β -H), 2.14 (1H, m, 4-H), 2.42 (1H, m, 2 β -H or 2 α -H) and 3.05 p.p.m. (1H, m, 3-H). ¹³C NMR: δ 13.46, 16.33, 22.97 (CH₂), 28.16 (overlapping signals, one quaternary), 28.73, 34.33, 36.9, 44.8, 119.9 (CN) and 205.87 p.p.m. (C=O).

Crystal data

C₁₁H₁₅NO
 $M_r = 177.24$
 Orthorhombic
 $P2_12_12_1$
 $a = 9.502$ (3) Å
 $b = 9.980$ (4) Å
 $c = 10.680$ (4) Å
 $V = 1012.8$ (6) Å³
 $Z = 4$
 $D_x = 1.162$ Mg m⁻³

Mo $K\alpha$ radiation
 $\lambda = 0.71069$ Å
 Cell parameters from 250 reflections
 $\theta = 2.79$ – 25.04°
 $\mu = 0.074$ mm⁻¹
 $T = 150$ (2) K
 Parallelepiped
 0.30 × 0.24 × 0.20 mm
 Colourless

Data collection

Delft instruments FAST area detector
 Intensity measurements as described by Darr, Drake, Hursthouse & Malik (1993)
 Absorption correction: none
 4347 measured reflections

1574 independent reflections
 1469 observed reflections
 $[I > 2\sigma(I)]$
 $R_{\text{int}} = 0.044$
 $\theta_{\text{max}} = 25.04^\circ$
 $h = -11 \rightarrow 11$
 $k = -8 \rightarrow 11$
 $l = -11 \rightarrow 11$

Refinement

Refinement on F^2
 $R(F) = 0.0365$
 $wR(F^2) = 0.0881$
 $S = 1.096$
 1574 reflections
 178 parameters
 H atoms refined isotropically
 $w = 1/[\sigma^2(F_o^2) + (0.0550P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$

$\Delta\rho_{\text{max}} = 0.193$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.137$ e Å⁻³
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
 Absolute configuration: Flack (1983) parameter = -0.7 (16)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*$$

	x	y	z	U_{eq}
N1	1.1066 (2)	0.8187 (2)	0.9862 (2)	0.0454 (5)
O1	0.92288 (14)	0.86209 (11)	0.65037 (11)	0.0337 (3)
C1	0.7602 (2)	1.0026 (2)	0.9366 (2)	0.0278 (4)
C2	0.8819 (2)	1.0922 (2)	0.9753 (2)	0.0314 (4)
C3	1.0207 (2)	1.0556 (2)	0.9114 (2)	0.0290 (4)
C4	1.0050 (2)	1.0506 (2)	0.7669 (2)	0.0271 (4)
C5	0.8975 (2)	0.9435 (2)	0.73354 (14)	0.0249 (4)
C6	0.7694 (2)	0.9301 (2)	0.80996 (15)	0.0263 (4)
C7	0.6600 (2)	1.0415 (2)	0.8357 (2)	0.0286 (4)
C8	0.6666 (2)	1.1766 (2)	0.7728 (2)	0.0345 (4)
C9	0.5101 (2)	0.9911 (2)	0.8488 (2)	0.0354 (5)
C10	1.0706 (2)	0.9233 (2)	0.9554 (2)	0.0322 (4)
C11	1.1439 (2)	1.0343 (2)	0.6995 (2)	0.0368 (5)

Table 2. Selected geometric parameters (Å, °)

N1—C10	1.147 (2)	C3—C4	1.551 (2)
O1—C5	1.228 (2)	C4—C11	1.512 (3)
C1—C7	1.490 (2)	C4—C5	1.520 (2)
C1—C2	1.519 (3)	C5—C6	1.471 (2)
C1—C6	1.537 (2)	C6—C7	1.547 (2)
C2—C3	1.529 (2)	C7—C8	1.508 (3)
C3—C10	1.480 (3)	C7—C9	1.517 (2)
C7—C1—C2	122.0 (2)	C6—C5—C4	119.32 (14)
C7—C1—C6	61.46 (11)	C5—C6—C1	119.49 (15)
C2—C1—C6	118.26 (15)	C5—C6—C7	126.1 (2)
C1—C2—C3	113.22 (15)	C1—C6—C7	57.80 (11)
C10—C3—C2	110.36 (15)	C1—C7—C8	121.9 (2)
C10—C3—C4	108.55 (15)	C1—C7—C9	116.5 (2)
C2—C3—C4	111.63 (14)	C8—C7—C9	112.2 (2)
C11—C4—C5	113.54 (15)	C1—C7—C6	60.74 (11)
C11—C4—C3	113.15 (15)	C8—C7—C6	122.38 (15)
C5—C4—C3	108.70 (13)	C9—C7—C6	114.18 (14)
O1—C5—C6	120.2(2)	N1—C10—C3	177.6 (2)
O1—C5—C4	120.19 (15)		

H atoms were located from the difference map and refined isotropically. The calculations were carried out on a P5-90 Pentium personal computer.

Data collection: *MADNES* (Pflugrath & Messerschmidt, 1989). Data reduction: *ABSMAD* (Karaulov, 1992). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SNOOPI* (Davies, 1983). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1286). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2,6-Dimethylphenylammonium Chloride at 173 and 293 K

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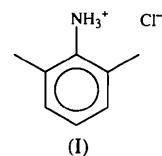
Abstract

The X-ray structure of 2,6-dimethylphenylammonium chloride, $C_8H_{12}N^+Cl^-$, has been determined at 173 and 293 K. The slight distortion of the phenyl ring of the cation can be attributed to the additive effects of the ring substituents. Hydrogen bonds link the ions into infinite sandwich-type layers where the anions act as the sandwich filling.

Comment

The structure of 2,6-dimethylphenylammonium chloride (I) has been investigated in order to compare its $N-H \cdots Cl$ hydrogen-bonding interactions with those of other methyl- or methoxy-substituted phenylammonium chloride derivatives. Such compounds have shown reasonably strong correlations between various parameters; *viz.* $N-H$ bond force constant K versus pK_a (or base strength), ΔK versus pK_a , atomic core level binding energy E_b versus pK_a , ΔK versus ΔE_b and $E_b(Cl\ 2p)$ versus $E_b(N\ 1s)$. These results indicate that the degree of hydrogen bonding in the solids depends

on the type and position of substituents on the aromatic ring of the base (Jiang, James, Liesegang & Day, 1994). The general purpose NDDO molecular orbital method AM1 (Austin Model 1), which is incorporated in the *MOPAC* (version 7.00) package (Stewart & Coolidge, 1993), may be used to calculate net atomic charges based on known crystal structures. Until recently, only two simple methyl- or methoxy-substituted phenylammonium chloride structures were known: for the 4-methyl derivative (Colapietro, Domenicano & Portalone, 1982) and a lower quality data set for the 2-methyl compound (Cameron, Duffin & Singh, 1976), both obtained from room-temperature measurements. Thus, high quality data have been sought for other similarly substituted phenylammonium chlorides and to this end the structure determination of the 2-methoxy derivative as well as a more accurate redetermination of the 2-methyl derivative have already been undertaken (Jiang, Liesegang, James, Skelton & White, 1995). The structure of (I), reported here, expands this series further.



Since the atomic coordinates are most precisely obtained from low-temperature measurements, the determination was originally carried out at 173 K. However, particularly marked changes were observed in the calculated charge on N with a modelled variation of the H-atom position in the $N-H \cdots Cl$ system (Jiang, James, Liesegang & Day, 1994). Therefore, for comparison purposes, the room-temperature atomic coordinates were also required, because the other substituted derivatives had also been measured at this temperature.

Views of (I) at 173 and 293 K, showing the displacement ellipsoids and the atomic numbering, are given in Fig. 1. With the exception of minor changes in the positions of the ammonium H atoms, the structure of (I) at 173 K is the same as that at 293 K. At the higher temperature, the estimated standard deviations of the atomic parameters are larger, which is to be expected as a result of increased thermal vibration. A TLS thermal motion correction (Schomaker & Trueblood, 1968) applied to the atoms of the cation suggested that the bond lengths given in the tables are too short by 0.003–0.005 Å at 173 K and 0.007–0.011 Å at 293 K. This correction reduces the mean differences in the bond lengths at the two temperatures from 0.007 to 0.004 Å, or to 0.003 Å if the anomalously short C(4)—C(5) bond in the structure at 293 K is discounted. The corrections to the bond angles are less than one standard deviation at both temperatures. The slightly high values of the goodness-of-fit parameter (S) for each refinement