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(+)-(1*S*,3*S*)-1-Bromo-3-(bromomethyl)-1,2,2-trimethylcyclohexane. X-ray Structure at 123 K, NMR Spectrum and Molecular Mechanics Calculations

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Abstract. The structure of the title compound has been redetermined from low temperature X-ray data. C₁₀H₁₈Br₂, *M_r* = 298.07, orthorhombic, *P*2₁2₁2₁, *a* = 8.435 (1), *b* = 10.345 (2), *c* = 12.944 (3) Å, *V* = 1129.5 Å³, *Z* = 4, *D_x* = 1.75 g cm⁻³, λ(Mo Kα) = 0.71073 Å, μ = 70.6 cm⁻¹, *F*(000) = 592, *T* = 123 K, *R* = 0.024, *wR* = 0.033, *S* = 1.24 for 1380 unique observed reflections. Comparison of observed ¹H NMR parameters with those calculated from the Karplus equation based on the observed structure confirm that the solid and solution phase structures are identical. This indicates that the solution species is restricted in conformational freedom. Theoretical calculations (MMX) indicate that the observed conformation is the most favorable. Δ*H_f* is almost the same for the *cis* and *trans* isomers confirming the previously postulated mechanism for product formation.

Introduction. We have recently reported the synthesis and characterization of (+)-(1*S*,3*S*)-1-bromo-3-(bromomethyl)-1,2,2-trimethylcyclohexane (Longton, Bagrodia, Lutz, Pinkerton & Fry, 1987). A full characterization of this compound is important to us in

the design of strategies for asymmetric synthesis. In our original report we described an approximate structure for this compound based on room temperature X-ray data. The structure was however poorly defined due to the high volatility of this material (small data set due to sublimation of the crystal, high thermal parameters and no observed hydrogen positions).

The result of this study showed that only the *trans* isomer (axial 1-bromo, equatorial 3-bromomethyl) was formed in the synthesis. Using calculated hydrogen positions based on the approximate carbon skeleton coupled with ¹H NMR data, it appeared that the conformation of the bromomethyl group was the same in solution as in the solid state. This implies conformational rigidity with restricted rotation of this substituent in solution.

We have since obtained much better X-ray data measured at 123 K and re-refined the structure. We have also carried out molecular mechanics calculations (Serena Software, 1986) on the different possible rotamers of the bromomethyl group to confirm that the observed structure has the lowest energy. In addition we have carried out the same calculations for the *cis*

Table 1. Positional parameters and their estimated standard deviations

	x	y	z	B (Å ²)
Br1	0.21021 (5)	0.93023 (5)	0.92729 (4)	2.142 (8)
Br2	-0.31682 (5)	1.07403 (5)	0.67035 (4)	1.825 (8)
C1	-0.3005 (5)	0.8781 (4)	0.6733 (3)	1.32 (8)
C2	-0.2336 (5)	0.8364 (5)	0.7802 (3)	1.29 (8)
C3	-0.0607 (5)	0.8869 (5)	0.7928 (3)	1.25 (8)
C4	0.0447 (5)	0.8477 (5)	0.7011 (4)	1.76 (9)
C5	-0.0220 (6)	0.8903 (5)	0.5978 (4)	1.70 (9)
C6	-0.1909 (6)	0.8426 (5)	0.5838 (4)	1.66 (8)
C7	-0.3375 (6)	0.8878 (5)	0.8692 (4)	2.04 (9)
C8	-0.2385 (6)	0.6875 (5)	0.7856 (4)	2.05 (9)
C9	-0.4704 (6)	0.8330 (5)	0.6504 (4)	2.0 (1)
C10	0.0115 (5)	0.8403 (5)	0.8942 (4)	1.70 (9)
H1	-0.063 (7)	0.987 (6)	0.801 (5)	1.6*
H2	0.068 (8)	0.762 (6)	0.693 (5)	2.3*
H3	0.147 (7)	0.877 (6)	0.712 (5)	2.3*
H4	0.044 (7)	0.857 (7)	0.549 (4)	2.2*
H5	-0.035 (8)	0.983 (7)	0.593 (5)	2.2*
H6	-0.235 (7)	0.863 (6)	0.518 (5)	2.1*
H7	-0.185 (8)	0.753 (6)	0.577 (5)	2.1*
H8	-0.066 (8)	0.864 (7)	0.950 (5)	2.2*
H9	0.043 (8)	0.751 (6)	0.890 (5)	2.2*
H10	-0.445 (9)	0.847 (7)	0.860 (5)	2.7*
H11	-0.309 (8)	0.848 (7)	0.934 (5)	2.7*
H12	-0.352 (8)	0.980 (7)	0.878 (5)	2.7*
H13	-0.356 (7)	0.655 (7)	0.773 (5)	2.6*
H14	-0.168 (7)	0.656 (7)	0.742 (5)	2.6*
H15	-0.195 (8)	0.670 (7)	0.851 (5)	2.6*
H16	-0.552 (8)	0.862 (7)	0.705 (5)	2.6*
H17	-0.504 (8)	0.865 (7)	0.590 (5)	2.6*
H18	-0.470 (8)	0.742 (7)	0.639 (5)	2.6*

* Atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $\frac{1}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

isomer (equatorial 1-bromo, equatorial 3-bromo-methyl) in order to gain insight into the mechanism responsible for the stereoselectivity of the reaction.

Experimental.

X-ray

The title compound was obtained as colorless plates by sublimation in vacuo. The crystal used for data collection (0.35 × 0.28 × 0.08 mm) was mounted on a glass fiber and immediately cooled to 123 K on the diffractometer. Preliminary examination and data collection (ω - 2θ scans to $2\theta = 60.0^\circ$) were carried out with Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) on an Enraf-Nonius CAD-4 diffractometer. Lattice parameters from 25 reflections, θ range 13–15°. hkl range $-1, -1, -1$ to 10, 12, 16. 13 standard reflections, 4.8% intensity variation. The measured intensities (1785 total, 1631 unique, $R_{\text{int}} = 1.8\%$) were corrected for absorption ($\mu = 70.6 \text{ cm}^{-1}$, transmission factors 0.79–0.92) and decay. Starting coordinates were taken from the room temperature structure and refined on F by full-matrix least squares. In the final cycles all the non-hydrogen atoms were refined anisotropically and hydrogen atoms assigned isotropic temperature factors equal to 1.3 times the U_{eq} of the atom to which they are bonded. The refinement converged with $R = 0.024$,

Table 2. Bond distances (Å) and angles (°)

Br1—C10	1.965 (5)	C5—H4	0.92 (6)
Br2—C1	2.032 (4)	C5—H5	0.96 (7)
C1—C2	1.555 (6)	C6—H6	0.95 (6)
C1—C6	1.528 (6)	C6—H7	0.93 (6)
C1—C9	1.536 (6)	C7—H10	1.01 (7)
C2—C3	1.558 (6)	C7—H11	0.97 (7)
C2—C7	1.542 (7)	C7—H12	0.97 (7)
C2—C8	1.542 (7)	C8—H13	1.06 (6)
C3—C4	1.537 (6)	C8—H14	0.88 (6)
C3—C10	1.526 (6)	C8—H15	0.95 (6)
C3—H1	1.04 (7)	C9—H16	1.03 (6)
C4—C5	1.517 (7)	C9—H17	0.90 (7)
C4—H2	0.91 (7)	C9—H18	0.95 (7)
C4—H3	0.92 (6)	C10—H8	1.01 (6)
C5—C6	1.519 (7)	C10—H9	0.97 (6)
Br2—C1—C2	108.6 (3)	C1—C6—C5	113.5 (4)
Br2—C1—C6	105.5 (3)	C1—C6—H6	113 (4)
Br2—C1—C9	103.7 (3)	C1—C6—H7	110 (4)
C2—C1—C6	112.9 (3)	C5—C6—H6	114 (4)
C2—C1—C9	115.2 (4)	C5—C6—H7	107 (4)
C6—C1—C9	110.2 (4)	H6—C6—H7	99 (6)
C1—C2—C3	109.8 (4)	C2—C7—H10	107 (4)
C1—C2—C7	111.3 (4)	C2—C7—H11	111 (4)
C1—C2—C8	107.9 (3)	C2—C7—H12	120 (4)
C3—C2—C7	109.8 (3)	H10—C7—H11	99 (5)
C3—C2—C8	110.8 (3)	H10—C7—H12	108 (6)
C7—C2—C8	107.2 (3)	H11—C7—H12	111 (6)
C2—C3—C4	111.9 (3)	C2—C8—H13	109 (4)
C2—C3—C10	110.9 (3)	C2—C8—H14	109 (5)
C2—C3—H1	109 (3)	C2—C8—H15	103 (4)
C4—C3—C10	110.4 (4)	H13—C8—H14	114 (5)
C4—C3—H1	111 (3)	H13—C8—H15	116 (5)
C10—C3—H1	104 (3)	H14—C8—H15	104 (6)
C3—C4—C5	112.9 (4)	C1—C9—H16	114 (4)
C3—C4—H2	118 (4)	C1—C9—H17	110 (4)
C3—C4—H3	109 (4)	C1—C9—H18	109 (4)
C5—C4—H2	105 (4)	H16—C9—H17	106 (6)
C5—C4—H3	113 (4)	H16—C9—H18	113 (6)
H2—C4—H3	98 (6)	H17—C9—H18	104 (6)
C4—C5—C6	111.1 (4)	Br1—C10—C3	112.2 (4)
C4—C5—H4	106 (4)	Br1—C10—H8	106 (4)
C4—C5—H5	113 (4)	Br1—C10—H9	103 (4)
C6—C5—H4	111 (4)	C3—C10—H8	107 (4)
C6—C5—H5	102 (4)	C3—C10—H9	111 (4)
H4—C5—H5	114 (6)	H8—C10—H9	117 (5)

Numbers in parentheses are estimated standard deviations in the least significant digits.

$wR = 0.033$ and $S = 1.24$ for 163 variables and 1380 reflections with $F_o^2 > 3.0\sigma(F_o^2)$. Weighting scheme $w = 4F_o^2/\sigma^2(F_o^2)$. $(\Delta/\sigma)_{\text{max}} = 0.16$. $\Delta\rho$ max. and min. = 0.49 (11) and -0.45 (11) $e \text{ \AA}^{-3}$. The scattering factors for the neutral atoms and anomalous scattering coefficients were taken from *International Tables for X-ray Crystallography* (1974). All calculations were carried out on a VAX 11/750 computer using *SDP/VAX* (Frenz, 1978). Final atomic coordinates are given in Table 1, derived bond lengths and angles in Table 2. A perspective drawing of the molecule along with the atom numbering is shown in Fig. 1.*

* Lists of calculated and observed structure factors, anisotropic thermal parameters and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51430 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Theoretical calculations

All molecular mechanics calculations were carried out with the program *MMX86* (Serena Software, 1986) using a Heath-Zenith Z-248 computer. Geometries were optimized for all possible rotamers of the bromomethyl group for the *cis* and *trans* compounds and their heats of formation calculated. The torsion angles from the optimized geometries and those observed in the crystal structure were used to calculate the vicinal proton *J* couplings for the bromomethyl group (Haasnoot, De Leeuw & Altona, 1980).

Discussion. The crystal structure obtained from the low temperature X-ray data confirms the overall structure previously reported, albeit with better accuracy. Of the two possible isomers, the bromine and the bromomethyl group are *trans* to each other. By using low temperature data we are now able to report refined hydrogen positions, even in the presence of the heavy bromine atoms.

Using the modified Karplus equation (Haasnoot, De Leeuw & Altona, 1980) we have calculated the expected vicinal *J* coupling constants for both the crystallographic torsion angles and those obtained for

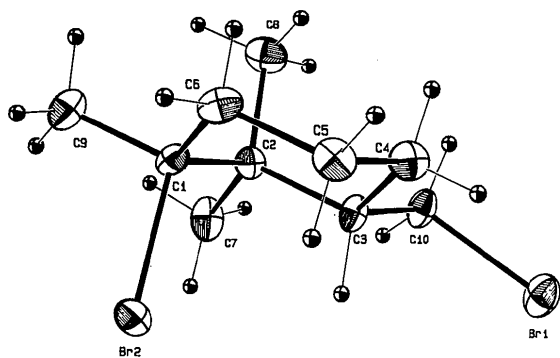
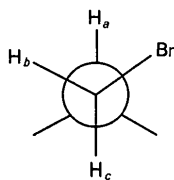


Fig. 1. (+)-(1*S*,3*S*)-1-bromo-3-(bromomethyl)-1,2,2-trimethylcyclohexane structure at 123 K.



Torsion angle	X-ray(³ J)	MM(³ J)	³ J _{obs}
H _a -C-C-H _b	65.2 (1.9)	68.5 (2.4)	2.64
H _a -C-C-H _c	-166.1 (11.6)	-167.8 (11.3)	10.32

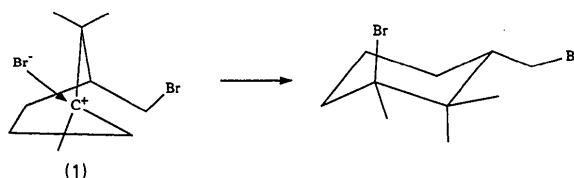
Fig. 2. Observed and calculated torsion angles (°) and observed and calculated ³J_{HH} (Hz) for the bromomethyl group.

the preferred conformation using molecular mechanics calculations. The calculated values are close to those observed in the ¹H solution NMR spectrum (Fig. 2). This indicates that the rotation of the bromomethyl group is restricted in solution and that the conformation is the same, both in the solid and in solution.

We have calculated the heats of formation, ΔH_f, for the three possible staggered rotamers of the bromomethyl group for the *trans* compound having first optimized the geometry of the whole molecule. We find that the conformer found in the crystal structure is 8.8 and 10.5 kJ mol⁻¹ more stable than the other two. This result is thus in accord with the conformational rigidity observed in the NMR spectrum.

In order to gain some insight into the mechanism of the formation of the title compound, we have also calculated ΔH_f for the *cis* isomer. We find that the lowest energy form has the same conformation of the bromomethyl group and that this isomer should only be 2.5 kJ mol⁻¹ less stable than the equivalent *trans* isomer. As the *trans* isomer is the only one observed in the reaction products, we can thus be confident that the reaction is not controlled by the thermodynamics of the products.

This is in agreement with our postulate that the product is the result of stereospecific bromide attack on the tertiary carbocation (1). The attack from the sterically least-hindered side gives rise to the observed product.



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