Crystal Structure of 2-Iodoadamantane—an Axial Iodide

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Summary A single crystal X-ray diffraction study of 2-iodotricyclo[3,3,1,1^{3,7}]decane (2-iodoadamantane) reveals no significant distortion as a result of the axial iodine substituent.

There has been considerable interest of late in the use of 2-substituted adamantane derivatives as models for axially substituted cyclohexanes.[1–5] It has been stated that 2-substituents should suffer from enhanced *axial* non-bonded repulsions.[2] Axial Cl, Br, and I in chiral derivatives of adamantanone exhibit effects contrary to predictions of the octant rule. We thus felt it of interest to examine the structure of a few such compounds. Since 2-iodoadamantane is readily available[6] and contains a large, "heavy" atom it was the first compound of choice.

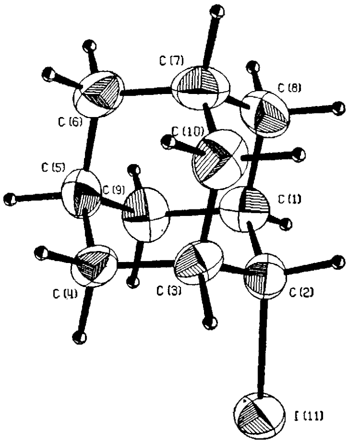

Figure. Structure of 2-iodoadamantane.

Crystals suitable for an X-ray analysis were grown by slow sublimation at room temperature and atmospheric pressure. Their volatility precluded simple mounting of a single crystal. Thus a crystal (0·1 × 0·2 × 0·1 mm) was mounted in a 0·3 mm glass capillary using epoxy cement and the tube was sealed. One Angstrom (maximum sin $\theta/\lambda = 0{\cdot}5$) intensity data was collected on a Syntex $P1$ diffractometer using Mo-K_α radiation ($\lambda = 0{\cdot}71069$ Å). Monochromatic radiation was obtained by the application of a graphite incident beam monochromator.

Table. Bond angles and distances

Atom–Atom	Distance(Å)	Atom–Atom–Atom	Angle(°)
C(1)–C(2)	1·531(15)	8–1–2	106·7(8)
C(1)–C(8)	1·521(14)	8–1–9	109·1(8)
C(1)–C(9)	1·544(15)	2–1–9	110·5(8)
C(2)–C(3)	1·504(13)	1–2–3	111·5(8)
C(2)–I(11)	2·199(9)	1–2–11	111·2)6)
C(3)–C(4)	1·526(13)	3–2–11	111·4(6)
C(3)–C(10)	1·523(13)	2–3–4	111·7(7)
C(4)–C(5)	1·530(14)	2–3–10	106·0(8)
C(5)–C(6)	1·524(15)	4–3–10	108·8(8)
C(5)–C(9)	1·517(15)	3–4–5	109·7(8)
C(6)–C(7)	1·507(15)	4–5–6	109·8(8)
C(7)–C(8)	1·524(16)	4–5–9	109·6(8)
C(7)–C(10)	1·540(16)	6–5–9	110·0(9)
		5–6–7	108·7(9)
		6-7–8	110·9(9)
		6–7–10	109·9(9)
		8–7–10	108·8(9)
		7–8–1	109·3(9)
		7–10–3	109·8(8)
		1–9–5	109·8(8)

Crystal data: $C_{10}H_{15}I$; monoclinic $P2_1/c$; $a = 6{\cdot}75(1)$, $b = 21{\cdot}88(2)$, $c = 6{\cdot}67(1)$ Å, $\beta = 103{\cdot}61(9)°$; $U = 958(1)$ Å^3; $D_m = 1{\cdot}78$ g/cm^3; $D_c = 1{\cdot}83$ g/cm^3 for $Z = 4$. Non-zero reflections = 888; Total unique reflections = 1035; Scan mode: $\theta/2\theta$; Scan rate: 2°/minute in 2θ.

The structure was solved using conventional Patterson and Fourier techniques. No correction for absorption was made ($\mu = 33{\cdot}2$ cm^{-1}). The first electron density map revealed the entire structure which refined smoothly to a final R index of 0·047. The final cycles of full matrix least squares refinement contained the carbon and iodine positions, their anisotropic temperature factors, and the scale factor in one matrix. While the hydrogen positions were calculated and added to the final structure factor calculations, their positions were not refined. A final difference Fourier revealed no missing or misplaced atoms in the refined model. An ORTEP drawing of the final structure is shown in the Figure. Bond distances and angles along with their estimated standard deviations are shown in the Table. The relatively large standard deviations are a consequence of the glass capillary technique as well as the presence of the large iodine atom.

Although the I–C(4) or (9) distance is only 3·5 Å, considerably less than the sum of Pauling van der Waals radii (4·15 Å)[7] there is only a deviation of about 2° of the C–C–I angles from the "normal" tetrahedral value. More recent estimates of van der Waals radii[8] are more in line with the minimal distortion found here. No other significant systematic distortions as compared with the parent hydrocarbon[9] are found. Any "major" distortion would be apparent even with the standard deviations obtained in this work. Thus, any explanation of the anomalies noted earlier[2] must be based on factors other than skeletal distortion.

Tables of atomic parameters as well as calculated and observed structure factors may be obtained from the authors.

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