'Paddle-Wheel' Hydrocarbons. Intracyclic C—C Bond Length Shortening in Rotanes. X-Ray Crystal Structures of [3]- and [4]-Rotane

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Summary Single crystal X-ray determinations of the structures of [3]- and [4]-rotane reveal that bond-length shortening occurs in the inner central cyclopropane or cyclobutane ring; this may be attributed to a π bond order enhancement resulting from the disposition of the adjacent (paddle-like) peripheral cyclopropane rings.

Recent[1] photoelectron spectroscopic investigations[1] of rotanes[2] (polycyclopropylidenes) indicated large resonance integrals between linked $2p$ atomic orbitals of the adjacent cyclopropane rings. This would result from particular geometrical parameters in these unusual hydrocarbons, which we have now investigated by single crystal X-ray diffraction.

[3]Rotane (1), m.p. 30—32 °C, and [4]rotane (2), m.p. 118 °C, were purified by g.l.c. Highly volatile single crystals were grown by slow sublimation in Lindemann capillaries, maintained at −10 °C, and mounted on a Phillips PW-1100 automatic four-circle diffractometer; Cu-K_α radiation ($\lambda = 1.5418$ Å) was used for (2) and Mo-K_α radiation ($\lambda = 0.717$ Å) for (1). The temperature was kept at +17 and −45 °C, respectively.†

163 reflections with $I > 2\sigma(I)$ were used. The molecule is centred around a three-fold axis in the mirror plane; [4]rotane (2), $C_{12}H_{16}$, monoclinic; space group $P2_1/n$ (alternative setting of $P2_1/c$) with $a = 7.613(4)$, $b = 7.126(4)$, $c = 9.738(3)$ Å, $\beta = 112°1'(1)$, $Z = 2$. The molecule is located on a centre of symmetry. 478 reflections were used.

The structures were solved by direct methods and refined‡ with anisotropic thermal parameters for heavy atoms, and isotropic thermal parameters for hydrogens. The final conventional R factors were 5.4% for (1) and 4.7% for (2). The bond distances and angles in (2) were corrected for the rigid body motion approximation by the method of Schomaker and Trueblood[3] with the aid of a local version of JMTFAC.[4] This was not done for (1), however (one and half independent atoms and thermal parameter restrictions).
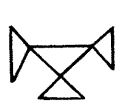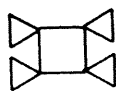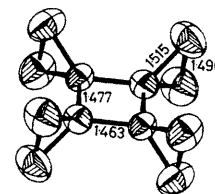

(1)   (2)
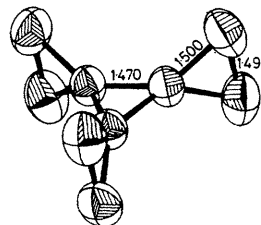
(1)   (2)

Figure. ORTEP drawings (heavy atom ellipsoids at 50% electronic density) for [3]rotane (1) (bond length e.s.d.s ±0.004 Å) and [4]rotane (2) (e.s.d.s ±0.005 Å). Hydrogen atoms are omitted for clarity.

Crystal data: [3]rotane (1), C_9H_{12}, hexagonal; space group $P6_3/m$; $a = b = 6.826(4)$, $c = 9.738(5)$ Å, $Z = 2$.

Literature data[5] for cyclopropane compounds show that average C–C bond lengths usually fall in the 1·49—1·55 Å range. The central [3]rotane C–C bond length [1·470(4) Å] is just less than the lower limit of this range, strongly suggesting a π bonding contribution, evidence for which was also indicated by the photoelectron spectroscopy investigations.[1]

For (2) the cyclobutane ring, because of the symmetry elements of the cell, is planar, a situation only observed in highly symmetrical cyclobutane species, i.e., 1,2,3,4-tetraphenylcyclobutane.[6] The X-ray determination gives two values for the inner C–C bond length in the cyclobutane ring: 1·463(5) for C(1)–C(2) and 1·477(4) Å for C(1)–C(1'). The mean value, 1·470 Å, the same as in (1), also lies below the lower limit of the range of previously observed four-membered ring bond distances (1·54—1·55 Å).[7]

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