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THE OCTANT RULE VI.[1] CIRCULAR DICHROISM OF (1*S*)-4^{e}-DEUTERIOADAMANTAN-2-ONE.

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Application of the Octant Rule[1,3] to interpret n-π* Cotton effects (CE's) of chiral ketones with deuterium perturbers[4] has received very little experimental investigation aside from the recent work of Djerassi *et al.*[4] on chiral (3*R*)-deuteriocyclopentanone. The latter, despite its conformational mobility, exhibited negative circular dichroism (CD) CE's ($\Delta\varepsilon_{304}$ = -0.019 at 25°C and $\Delta\varepsilon_{302}$ = -0.021 at -196°C). The observed CE's are doubtless weighted averages over the contributions of all conformations of the 3-deuteriocyclopentanone and can reflect both deuterium as well as ring atom contributions.[5] In order to establish the Octant Rule contribution due only to a deuterium perturber, we chose to prepare a stereochemically rigid, chiral molecule, (1*S*)-4^{e}-deuterioadamantan-2-one (1).

Deuterium was introduced stereospecifically by reaction of the ethylene ketal of the known (1*S*)-4^{e}-bromoadmantan-2-one (2)[6] with Masamune's reagent.[7] Hydrolysis of the deuterioketal afforded 1 after purification by thin layer chromatography and sublimation [mass spec. at 20 eV: *m/e* 151 (100%) 150 (16%), m.p. 256-7°, no depression upon admixture with adamantan-2-one, and IR, ν: 2155 and 2170 cm^{-1} (C-D)]. From the mass spectrum, the sample was judged to contain 86% of 1 and 14% of admantan-2-one. Since the optical purity of starting 2 was known to be 99% from earlier work,[8] we conclude that 1 is similarly optically pure. Its epimeric homogeniety was established as > 95% equatorial deuterium by PMR analysis of the nicely separated sets of axial and equatorial hydrogens following Eu(fod)$_3$ addition. This technique cleanly separates the sets of four identical axial and four identical equatorial hydrogens at C-4, 8, 9 and 10 of adamantan-2-one.[9]

The CD spectrum of 1 in isopentane at 23°C is shown in the Figure, where 1 exhibits a surprisingly strong $\Delta\varepsilon_{max}$ = +0.08 at 295 nm, corrected for 14% of adamantan-2-one in the sample. An octant projection diagram[3] of 1 places the D-perturber in a (-) back octant[1]; whereas, the observed CE is positive. Since 3^{e}-perturbers (except fluorine) on cyclohexanones are known to obey the Octant Rule[1,10] and do not lie close to octant boundaries[1], and since (1*S*)-4^{e}-methyladamantan-2-one derived from the precursor of 2 exhibits the expected (-) CE ($\Delta\varepsilon_{294}$ = -0.51 isooctane)[6], we conclude that deuterium, like fluorine[3,6] makes a sign-reversed octant contribution. The reasons for this are not immediately clear. The facts that D, like F, has an atomic refractivity less than H[4] and the C-D bond length is shorter than C-H might offer explanations.

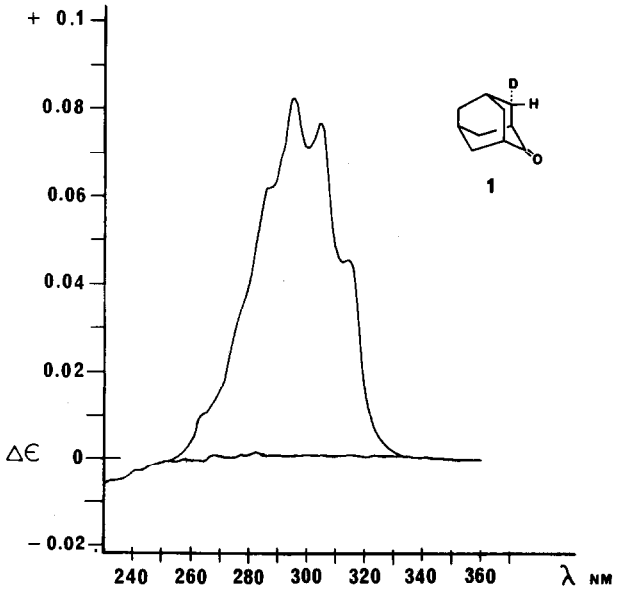

FIGURE. The circular dichroism spectrum of (1*S*)-4^{e}-deuterio-adamantan-2-one measured in isopentane at 23°C on a circular dichroism instrument built by Dr. J. Horwitz[2] and using a CAT (32 scans). A base-line is provided at or near $\Delta\varepsilon = 0$. The pertinent CD data are: $\Delta\varepsilon_{295} = +0.082$, $\Delta\varepsilon_{305} = +0.076$, $\Delta\varepsilon_{320} = +0.045$. Corrections are made to 100% optical purity and 100% d_1.

Further studies on deuterioadamantanones and 2-deuteriobicyclo[2.2.1]heptan-7-ones are in progress. This work and a theoretical treatment (T. D. Bouman) will be reported on in detail.

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