1.901 (7) and 1.906 (6) Å in $(CH_3)_3PBH_3$[12] and (CH_3)-PH_2BH_3.[12] For the B_5H_9 moiety, distances generally compare well with boron hydrides.[1] The largest non-bonded distance of adjacent borons B(2)–B(3) averages 2.95 Å compared to 2.97 Å in B_5H_{11}.[13]

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A. V. Fratini, G. W. Sullivan

Department of Chemistry, University of Dayton
Dayton, Ohio 45469

M. L. Denniston, R. K. Hertz, S. G. Shore*

Department of Chemistry, Ohio State University
Columbus, Ohio 43210

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The Octant Rule. III.[1] An Experimental Proof for Front Octants[2]

Sir:

Although the octant rule[3,4] associated with the n–π* transition of saturated alkyl ketones was formulated over 15 years ago,[5] only the back octants have been verified experimentally. For this reason, among others, the octant rule has been challenged, and arguments supporting a "quadrant rule" have been offered.[6,7] In a "quadrant rule," as in the octant rule, all space is divided into quadrants determined by the orthogonal symmetry planes (local symmetry) of the carbonyl chromophore. In the octant rule, however, all space is further divided into octants by a third nonsymmetry derived surface approximated by a plane which is orthogonal to the two quadrant forming planes and bisects the carbon–oxygen double bond.[8] In the octant rule, the signed contribution to the Cotton effect (CE) of each dissymmetric perturber of carbonyl chromophore is determined by the octant in which it is located.[3,4] The octants reverse sign with each reflection across the octant-producing surfaces.[9] Therefore, if

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(8) The shape of this third surface is not well understood (ref 3). Its precise contour and location should be defined for each different type of perturber.
(9) The (+) back octants or quadrants are upper left and lower right; the (−) are upper right and lower left. The sign convention is reversed for front octants, all viewed from oxygen toward carbon.

the octant rule is obeyed, perturbers located in front octants would give signed contributions *opposite* to those expected if a "quadrant rule" obtains.

Although there is good theoretical evidence supporting the octant rule[10,11] the experimental evidence on which it rests is drawn from numerous examples wherein the inherently symmetric[4] carbonyl chromophore is perturbed in a nonsymmetric way by atoms located *behind* the carbon of the carbonyl group (*back octants*), e.g., 3(e)-methylcyclohexanone.[12] There are extremely few examples in which dissymmetric perturbers are located in front of the carbonyl carbon or oxygen, and even these examples also have back octant perturbers. Such cases where front octant perturbers were recognized include 1-oxo, 7-oxo and 11-oxo steroids as well as 1-decalones.[13,14] Even more recent examples of front octant compounds[14–16] have back as well as front octant perturbers, although in one case[16] an effort was made to subtract the contribution of the back octant perturbers. In the present work we offer conclusive evidence for front octants from an analysis of the CD behavior of *syn*-(1'S)-spiro[cyclobutan-2-one-1,4'-(2'(a)-methyladamantane)] (1) in the region of its long wavelength n–π* transition. The lone dissymmetric perturber in 1 is a methyl group located in a front octant.

The synthesis of 1 was accomplished from optically active (1S)-2(a)-methyladamantan-4-one of known absolute configuration[17] using the Trost spiro-annelation procedures.[18] Steric control by its axial methyl group, coupled with two different spiro-annelation sequences, allowed us to prepare either 1 or its *anti* isomer, 2. Thus, the stereospecific reaction of (1S)-2(a)-methyladamantan-4-one with diphenylcyclopropylsulfonium fluoroborate and potassium hydroxide in dimethyl sulfoxide followed by workup with fluoroboric acid gave 99% pure 1 in 29% yield and recovery of 55% of starting ketone. The isomeric spiro ketone 2 was isolated from a mixture of 1 and mainly 2 produced by reaction of the cyclopropylidene derivative of (1S)-2(a)-methyladamantan-4-one with m-chloroperbenzoic acid. The configurations (*syn* or *anti*) of 1 and 2 were determined by the selection of the synthetic procedure and could be distinguished further by nmr spectroscopy in which the deshielded axial methyl group of 1 (d, centered at δ 1.11 ppm) is found farther downfield than that of 2 (d, centered at δ 1.07 ppm) and exhibits a greater downfield shift with added $Eu(dpm)_3$.

An octant projection diagram of 1 places the lone dissymmetric perturber (CH_3) in a lower right or upper left (−) *front* octant, and, indeed, 1 exhibits a strong (−) CE. Even the slight distortion from planarity in

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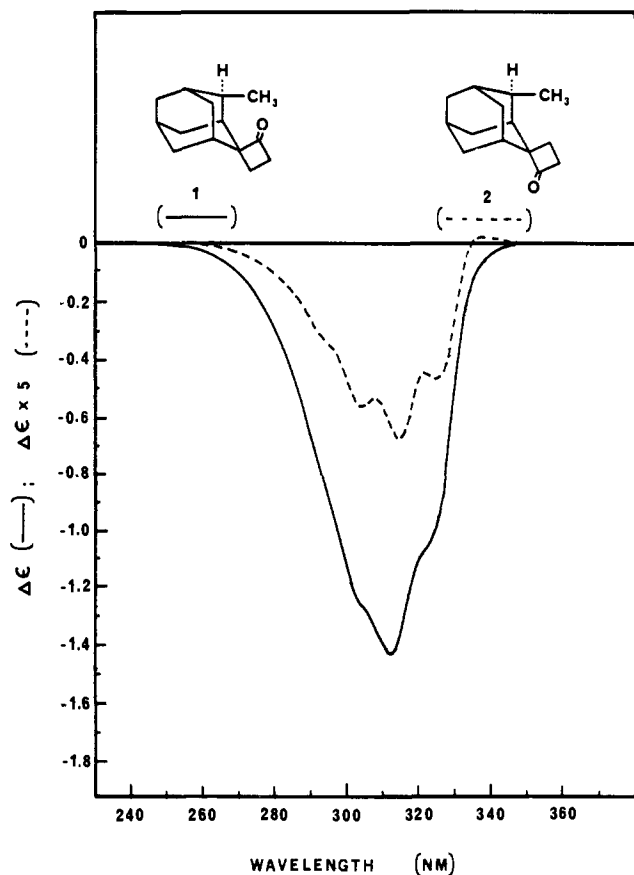(18) B. M. Trost and M. J. Bogdanowicz, *J. Amer. Chem. Soc.*, 95, 5321 (1973).

Figure 1. Circular dichroism spectra of syn-(1'S)-spiro[cyclo-butan-2-one-1,4'-(2'(a)-adamantane)] (1) (—) and anti-(1'S)-spiro[cyclobutan-2-one-1,4'-(2'(a)-adamantane (2) (------) in isopentane at 20° as determined on a JASCO Model J-20 ORD-CD spectrophotometer with photoelastic modulator. Corrections are made to 100% optical purity.

the cyclobutanone ring introduced by puckering does not place the methyl perturber in a back octant, and all possible back octant contributions located in such conformations are essentially canceling. Thus, we cite 1 with its strongly negative n–π^* CE as compelling evidence for the existence of front octants and the validity of the octant rule. A "quadrant rule," wherein the predicted CE sign is (+) for 1 cannot be operating. The nature of the contour and location of the third octant surface remains to be discerned;[1,19] however, it seems likely at present that the so-named "anti-octant" effect found in a few saturated alkyl ketones is probably due to front octant contributions.

The isomeric anti-spiro ketone (2) exhibits the expected weak (—) CE due to the location of the lone dissymmetric methyl perturber in a lower left or upper right back octant. In fact, the location of the methyl group of 2 is almost identical with that in (1 S)-endo-2-methylbicyclo[2.2.1]heptan-7-one,[1] and their CE magnitudes are comparable.

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D. A. Lightner,* T. C. Chang[20]

Department of Chemistry, Texas Tech University
Lubbock, Texas 79409

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Photorearrangements and Photosolvolyses of syn- and anti-7-Chloro- and -7-Bromobenzonorbornadienes[1]

Sir:

As photosolvolyses involving carbocationic intermediates are rare,[2] we were surprised to observe that direct or sensitized photoexcitation in methanol of either anti-7-(1-Br) or syn-7-bromobenzonorbornadiene (2-Br) gave the same solvolysis product, syn-7-methoxy-benzonorbornadiene (2-OCH₃). Furthermore, in acetone or hexane, 1-Br was quantitatively converted into 2-Br. Similar irradiation of 2-Br in acetone or hexane was without apparent effect. The naphthonorborna-dienes, 3-Br and 4-Br, gave analogous results.
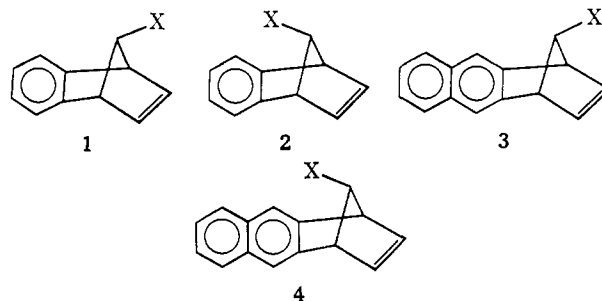
These results were interesting for several reasons. First, we knew that ground-state solvolyses of 1-Cl lead[3] cleanly to 1 species, that 2-Cl gives 2 species,[3] and that the bromides react analogously.[4] The inversion of configuration in the "photosolvolysis" experiment, compared with retention in ground-state solvolyses, was intriguing, as was the corresponding photoepimerization, assuming that carbocationic intermediates intervened. Further, our experience on irradiation of unsaturated and phenyl-substituted aliphatic halides[1,2f–h,5] suggested that photosolvolysis involving carbocationic intermediates occurs only in benzyl systems, even though rearrangements which can be ascribed to carbenium ion intermediates do occur in allylic and other systems. Additionally, all the literature reports on photosolvolyses are with benzyl systems.[2]

While our results could be accommodated to the idea that the photochemical process leads to a vibrationally excited cation[1,5] having enough energy to traverse the high barrier which undoubtedly separates 5 and 6 ions and analogous species,[3,6] an alternative path also suggested itself for consideration. Edman[7] has shown that benzonorbornadienes rearrange photochemically (by

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