Syn-(1′*R*)-spiro[cyclobutan-2-one-1,7′-(2′-*exo*-methylnorbornane)]: A Front Octant Compound

By David A. Lightner* and Dennis E. Jackman
(*Department of Chemistry, Texas Tech University, Lubbock, Texas* 79409)

Summary The positive Cotton effect (CE) for *syn*-(1′*R*)-spiro[cyclobutan-2-one-1,7′-(2′-*exo*-methylnorbornane)] is controlled by the lone dissymmetric perturber (methyl group) which projects into a front octant.

In the octant rule[1,2] for the n–π^* transition of saturated alkyl ketones all space is divided into octants, and the signed contribution which each dissymmetric perturber makes to the CE is determined by the octant in which the perturber lies. The octants are determined by the orthogonal carbonyl symmetry planes (quadrants) and a third non-symmetry derived surface (approximated by a plane) which is orthogonal to the other two and bisects the carbon–oxygen bond.[1,2] Thus, as viewed from oxygen toward carbon, perturbers in upper left or lower right back octants give (+) contributions to the CE while those in the upper right and lower left back octants give (−) contributions. The sign convention is reversed for front octants. The wealth of experimental evidence convincingly supports the octant rule for back octants; however, good experimental evidence for front octants has been difficultly accessible, and the octant rule has been challenged by "quadrant" and other rules.[3,4] The possibility of front-octant contributions was recognized[2] for 1-oxo, 7-oxo- and 11-oxo-steroids; however, such front-octant contributions were not the singular CE sign determining contributions for the entire molecule because back-octant contributions were also present.[5] In order to resolve the problem, Kirk *et al.*[6,7] prepared related D-homo- and D-nor-7-ketosteroids and, by subtracting the back-octant CE effect of the D-norsteroid from the front plus back octant-determined CE of the D-homosteroid, the authors concluded in favour of an octant rather than a quadrant rule. Because there have been no reported front-octant studies in which the ketone possesses dissymmetric perturbers in front octants only, we report on the preparation and circular dichroism (c.d.) of *syn*-(1′*R*)-spiro-[cyclobutan-2-one-1,7′-(2′-*exo*-methylnorbornane)] (**1**) which satisfies that criterion and is a true front-octant compound.

Compound (**1**) was prepared from 7,7-dimethoxybicyclo[2,2,1]heptene[8] by oxymercuration to give *exo*-7,7-dimethoxybicyclo[2,2,1]heptan-2-ol (90%)† which was resolved *via* the half-acid phthalate *l*-ephedrine salt. Chromic-acid oxidation of the (+)-alcohol gave the (−)-2-ketone which was converted into its (+)-*exo*methylene derivative by a Wittig reaction. Catalytic hydrogenation of the 2-*exo*-methylene-7,7-dimethoxybicyclo[2,2,1]heptane gave *exo*-2-methyl-bicyclo[2,2,1]heptan-7-one (80%) after deketalization. The *endo*-isomer was removed by column adsorption or g.l.c. and the pure *exo*-isomer was converted stereospecifically into (**1**) by the Trost spiroannelation procedure.[9] In the spiroannelation reaction, the bulky sulphonium ylid approaches the carbonyl group from the least hindered side; stereospecific rearrangement of the intermediate spiro-oxirane gives unreacted starting material and (**1**) (20%). The methyl doublet of (**1**) appears at $\delta = 1{\cdot}08$, J 6 Hz ($CDCl_3$), and is shifted downfield to $\delta = 1{\cdot}22$ in C_6D_6 in accord with the *syn* relationship of the methyl and carbonyl groups.[9,10] An upfield benzene solvent shift is expected for the *anti*-isomer. It is also noteworthy and in keeping with the stereochemical relationships in (**1**) that addition of a very small amount of Eu(DPM)$_3$ induces as large a downfield shift of the methyl group ($\Delta\delta$ = 65 Hz) as the methylene alpha to the carbon group ($\Delta\delta$ = 70 Hz). The absolute configuration of (**1**) was determined by conversion of (+)-*exo*-7,7-dimethoxy bicyclo[2,2,1]heptan-2-ol into the known[11] (1*S*)-norcamphor with a (−) CE.

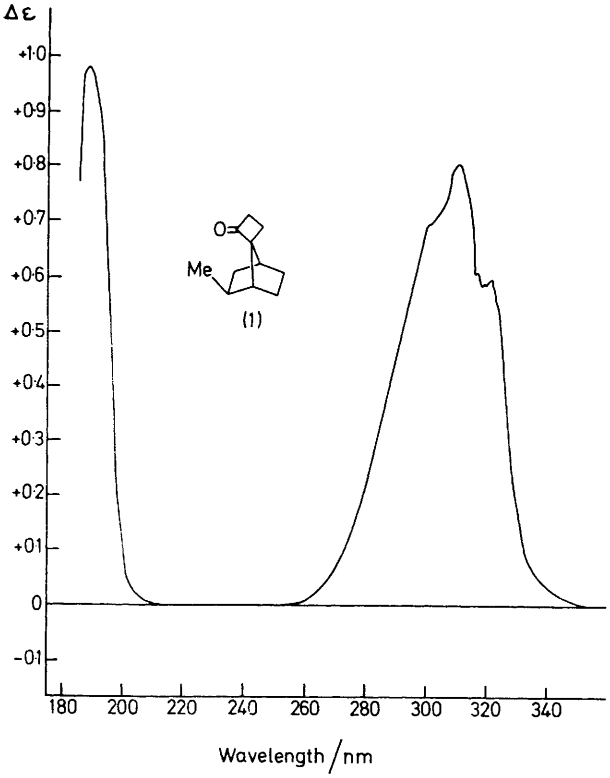

FIGURE. Circular dichroism spectra of *syn*-(1′*R*)-spiro[cyclobutan-2-one-1,7′-(2′*exo*-methylnorbornane)] (**1**) in isopentane at 20 °C, measured on a JASCO model J-20 ORD-CD spectrometer with photoelastic modulator. Corrections are made to 100% optical purity.

As may be noted from the Figure, (**1**) exhibits a strong (+) CE near 310 nm and a second strong (+) CE near 190 nm. The former transition, ϵ *ca.* 30, is doubtless associated with the carbonyl n–π^* transition. Indeed, an octant projection diagram of (**1**) places the lone dissymmetric methyl perturber in a (+) lower left or (+) upper right front octant. Even with a puckered cyclobutanone ring, all back-octant contributions are nearly cancelling, and the CE is dominated by the methyl group. Thus, with the moderately strong (+) CE of (**1**), we feel that the octant rule for front octants is proved, and a "quadrant rule" is not operative.

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† Satisfactory analyses and spectral data for all new compounds were obtained.

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