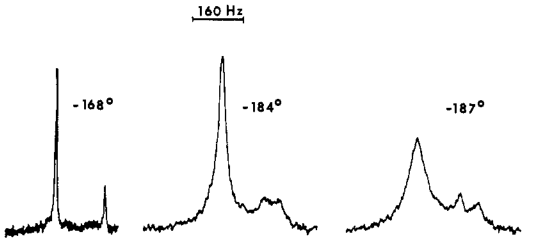
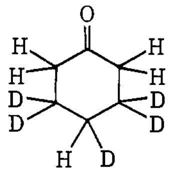


Figure 1. 251-MHz ^{1}H nmr spectra of cyclohexanone-*3,3,4,5,5-d*$_5$ in a 5:1 mixture of $CHClF_2$ and $CHCl_2F$ at various temperatures.

prepared and studied the nmr spectrum of cyclohexanone-*3,3,4,5,5-d*$_5$ (I). Exchange of 4-hydroxycyclohexanone with D_2O–Na_2CO_3 gave the 2,2,6,6-tetradeuterio derivative[8] which was converted into its *p*-toluenesulfonylhydrazone.[9] Treatment of the latter compound with $LiAlD_4$ in tetrahydrofuran followed by decomposition with water[9] gave cyclohexanol-*3,3,4,5,5-d*$_5$, which on chromic acid oxidation[10] gave I, isolated by vpc.



I

The 251-MHz proton nmr spectrum of I, obtained with the deuterons decoupled, is shown at several temperatures in Figure 1. From room temperature down to about −170° the spectrum consists of two lines (intensity ratio $\simeq$4:1) which can be assigned to the four α protons and the single γ proton, respectively. The line of the γ proton broadens greatly below −180° and splits into a doublet below −184°.[11] The α-proton line merely broadens continuously as the temperature is lowered below −180°, but does not separate into two lines down to −190°. The much greater broadening of the α-proton line as compared to the γ-proton lines at temperatures below −185° is ascribed to faster intramolecular dipole–dipole relaxation in the CH_2 group as compared to the CHD group.[12] Thus, the advantage of deuteration in the present situation is not merely a simplification of the spectrum because of the reduction of the number of chemical shifts and the removal of strong *J* coupling effects, but includes an important reduction in the inherent line widths. The chemical-shift difference between an axial and equatorial γ proton in I is 0.24 ppm, and is thus considerably smaller than the 0.47-ppm chemical-shift difference in cyclohexane.[13]

From the nmr data on I the rate constant for ring inversion at −183° is calculated to be 130 sec^{-1}. The boat or twist-boat being assumed as an intermediate, the $\Delta G^{\ddagger}$ at −183° for the chair–boat process is calculated to be 4.0 ± 0.1 kcal/mol ($\Delta G^{\ddagger}$ at −183° for the chair–chair process is 4.1 kcal/mol). These kinetic parameters are expected to be valid for cyclohexanone itself since isotope effects should be very small.[14]

Strain-energy calculations give a value of 3.9 kcal/mol for the barrier to ring inversion in cyclohexanone,[15] in excellent agreement with the present experimental results. The barrier in cyclohexanone is substantially lower than the barriers in cyclohexanone oxime methyl ether[2] ($\Delta G^{\ddagger}$ = 5.6 ± 0.5 kcal/mol), methylenecyclohexane[2,16] ($\Delta G^{\ddagger}$ = 8.4 ± 0.1 kcal/mol), and cyclohexane[13,14] ($\Delta G^{\ddagger}$ = 10.2 kcal/mol) mainly because of differences in the torsional barriers about sp^3–sp^3 and various kinds of sp^3–sp^2 C–C bonds.[2,15]

Acknowledgment. This work was supported by the National Science Foundation.

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(9) M. Fischer, Z. Pelah, D. H. Williams, and C. Djerassi, *Chem. Ber.*, **98**, 3236 (1965).

(10) H. C. Brown and C. P. Carg, *J. Amer. Chem. Soc.*, 83, 2952 (1961).

(11) For temperatures much below −170°, the cooling gas was cold helium obtained from a storage liquid helium dewar fitted with an electric heater and a helium transfer line.

(12) The intramolecular dipole–dipole relaxation rate is 16 times larger in a CH_2 group than in an otherwise similar CHD group. Intermolecular relaxation with solvent nuclei, however, probably becomes important in the case of CHD groups: J. H. Noggle and R. E. Schirmer, "The Nuclear Overhauser Effect," Academic Press, New York, N. Y., 1971, p 33.

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(14) Cyclohexane and cyclohexane-d_{11} undergo ring inversion at the same rate: A. Allerhand, F. Chen, and H. S. Gutowsky, *J. Chem. Phys.*, **42**, 3040 (1965).

(15) N. L. Allinger, M. Tribble, and M. A. Miller, *Tetrahedron*, **28**, 1173 (1972); see also R. Bucourt and D. Hainaut, *Bull. Soc. Chim. Fr.*, 4562 (1967); J. Fournier and B. Waegell, *Tetrahedron*, **26**, 3195 (1970).

(16) J. T. Gerig, *J. Amer. Chem. Soc.*, **92**, 1219 (1970).

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Detection of a Crown Family Conformation in Cyclooctane by Proton and Carbon-13 Nuclear Magnetic Resonance

Sir:

Cyclooctane and its simple derivatives appear to exist predominantly in boat–chair conformations, as shown by X-ray diffraction[1] and nmr[2] studies. The introduction of certain substituents or heteroatoms, however, can make a crown family[2f,3] conformation

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(1) M. Dobler, J. D. Dunitz, and A. Mugnoli, *Helv. Chim. Acta*, **49**, 2492 (1966); H. B. Burgi and J. D. Dunitz, *ibid.*, **51**, 1514 (1968); P. Groth, *Acta Chem. Scand.*, **19**, 1497 (1965); 21, 2695 (1967); T. Srikrishnan, R. Srinivasan, and R. Zand, *J. Cryst. Mol. Struct.*, **1**, 199 (1971).

(2) (a) F. A. L. Anet and J. S. Hartman, *J. Amer. Chem. Soc.*, **85**, 1204 (1963); (b) F. A. L. Anet and M. St. Jacques, *ibid.*, **88**, 2585, 2586 (1966); (c) J. E. Anderson, E. D. Glazer, D. L. Griffith, R. Knorr, and J. D. Roberts, *ibid.*, **91**, 1386 (1969); (d) F. A. L. Anet, M. St. Jacques, and P. M. Henrichs, *Intrasci. Chem. Rep.*, 4, 251 (1970); (e) F. A. L. Anet in "Conformational Analysis, Scope and Present Limitations," G. Chiurdoglu, Ed., Academic Press, New York, N. Y., 1971, p 15; (f) F. A. L. Anet and P. J. Degen, *J. Amer. Chem. Soc.*, **94**, 1390 (1972); (g) F. A. L. Anet, *Fortschr. Chem. Forsch.*, in press. (h) A very recent claim (H.-J. Schneider, T. Keller, and R. Price, *Org. Magn. Resonance*, **4**, 907 (1972)) that *monosubstituted* cyclooctanes exist to the extent of 25–50% in chair–chair conformations is based, in our view, on fallacious chemical-shift arguments, and furthermore is in disagreement with other nmr evidence.

(3) (a) J. M. Lehn and F. G. Riddell, *Chem. Commun.*, 803 (1966); (b) M. N. Ferguson, D. D. MacNicol, R. Oberhausli, R. A. Raphael, and R. Zabkiewicz, *ibid.*, 103 (1968); (c) J. Dale and J. Krane, *J. Amer. Chem. Soc.*, **94**, 1389 (1972); (d) L. Pauling and D. L. Carpenter, *ibid.*, **58**, 1274 (1936); (e) D. Grandjean and A. Leclaire, *C. R. Acad. Sci. Paris*, **265**, 795 (1967); (f) H. H. Cady, A. C. Larson, and D. T. Comer, *Acta Crystallogr.*, **16**, 617 (1963); (g) H. Schenck, *Acta Crystallogr., Sect. B*, **27**, 185 (1971); (h) R. Sass and J. Donohue, *Acta Crystallogr.*, 11, 497 (1958); (i) E. W. Lund and S. R. Svendsen, *Acta Chem. Scand.*, 11, 940 (1957); (j) S. C. Abrahams, *Acta Crystallogr.*, **8**, 661 (1955).

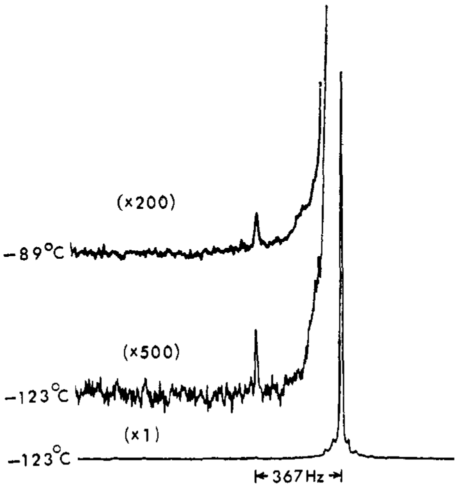


Figure 1. Proton-decoupled 63.1-MHz ^{13}C Fourier transform spectra of cyclooctane (25% in CS_2; 500 transients).

be of lower energy than the boat–chair. In particular, *trans-syn-trans*-1,2,5,6-tetrabromocyclooctane (I) has a twist-chair–chair conformation in the crystalline state.[3b] The 100-MHz ^1H nmr spectrum of I in solution is consistent with this result, and also indicates the presence of a minor amount of a second form, presumably a boat–chair.[3b,4] We now show that cyclooctane itself exists to a small extent (6% at room temperature) in a crown family conformation.

The 63.1-MHz ^{13}C nmr spectrum of cyclooctane (25% in carbon disulfide) is a single sharp line at room temperature. The resonance broadens below about −20°, reaching a maximum width at a half-height of 9 Hz at −45°. The peak narrows below −45° and becomes sharp again below −75°. Only a slight shift in the resonance position is observed during this process and no new peak is immediately evident at −75°. A careful examination, however, shows a second very weak and broad (*ca.* 50 Hz) band 367-Hz downfield from the main cyclooctane line. At still lower temperatures this minor band gradually sharpens as shown in Figure 1. At −123°, the new peak represents about 0.3% of the total ^{13}C resonance of cyclooctane. The spectral changes described above can be quantitatively reproduced[5] with the thermodynamic and kinetic parameters for an interconversion between two different conformational families as shown in Scheme I.

The major peak can be assigned to the boat–chair (BC) conformation, which is known[2] to pseudorotate rapidly down to at least −170°, and is therefore expected to give a single ^{13}C chemical shift in the temperature range under consideration. The minor conformation is consistent with a crown family conformation, which is also expected to give a single peak because of rapid pseudorotation (crown $\rightleftarrows$ CC $\rightleftarrows$ TCC).[6]

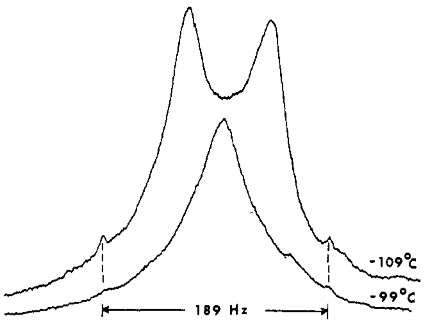
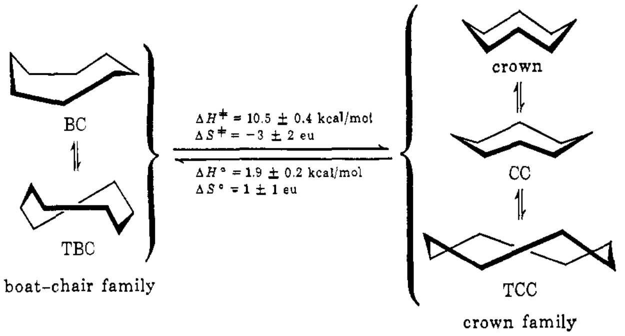


Figure 2. Deuteron-decoupled 251-MHz ^1H spectra of *cis*-1,2-h_2-cyclooctane-d_{14} (≃6% in vinyl chloride).

Scheme I



Additional information is provided by the deuteron-decoupled ^1H spectrum of *cis*-1,2-h_2-cyclooctane-d_{14}[7] (Figure 2). At −109°, the spectrum is very broad because ring inversion in the boat–chair is occurring at an intermediate rate. Two small peaks, however, are clearly visible and are assigned to crown forms which are *inverting slowly* on the nmr time scale; they cannot be isotopic impurities, ^{13}C satellites, nor spinning side bands of the boat–chair conformation, as all such bands must be very broad at this temperature. The small peaks are greatly broadened at −100°, as expected from the ^{13}C data. The relatively large chemical-shift difference (0.71 ppm) in the crown form is expected and consistent with previous data.[2f,3a–c]

Hendrickson's strain-energy calculations[6] on cyclooctane show that the boat–chair is of lowest energy, and that the strain energies in kilocalories/mole relative to this conformation are as follows: twist-boat (TB), 0.9; boat–boat (BB), 1.4; twist-chair–chair (TCC), 1.7; chair–chair (CC), 1.9; twist-boat–chair (TBC), 2.0; crown, 2.8. Although the relative energies of the conformations in the crown and boat–chair families agree well with our results, it is clear that the boat family conformations (BB and TB) must be more than 1 kcal/mol higher in energy than the values calculated, since such forms are not observed.[8]

The detection of a crown-family conformation in

(4) An examination of the 251-MHz ^1H spectrum of I has confirmed this interpretation: F. A. L. Anet and L. Kozerski, unpublished results.

(5) The line shape was calculated according to the expression for two unequally populated sites given by H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956). For very unequally populated sites, the *maximum* broadening of the coalesced peak depends on the chemical-shift difference (a constant) and the population ratio of the two forms. In the present instance, the maximum broadening of 9 Hz at −45° corresponds to 2% of the minor form.

(6) For strain-energy calculations on cyclooctane see: (a) J. B. Hendrickson, *J. Amer. Chem. Soc.*, **89**, 7036, 7043, 7047 (1967); (b) K. B. Wiberg, *ibid.*, **87**, 1070 (1965); (c) M. Bixon and S. Lifson, *Tetrahedron*, **23**, 769 (1967); (d) N. L. Allinger, J. A. Hirsch, M. Miller, J. J. Tyminski, and F. A. Van Catledge, *J. Amer. Chem. Soc.*, **90**, 1199 (1968).

(7) This compound was previously investigated at 60 MHz,[2b] but the signal-to-noise ratio was insufficient to detect very weak peaks.

(8) The BB and TB cannot be the observed minor forms of cyclooctane because rapid pseudorotation (BB $\rightleftarrows$ TB) should occur at −100 to −120°, leading to three ^1H chemical shifts in the ratio of 2:1:1 and to two ^{13}C chemical shifts, in disagreement with experiment. If additional pseudorotation occurs *via* the high-energy boat as an intermediate, the ^1H spectrum then becomes a single line, again in disagreement with experiment. The nmr results also exclude the possibility that the BB or TB are averaging rapidly with either the BC or crown at −120°.

cyclooctane provides a satisfactory quantitative explanation for previously puzzling proton spin–echo measurements on this compound.[9] It also supports a new rationalization[2g] of the low-temperature ^{19}F nmr spectrum of 1,1,2,2-tetrafluorocyclooctane,[2c,10] based on a 1:1 mixture of boat-chair and twist-chair–chair conformations. The fact that I exists predominantly in the twist-chair–chair with one vicinal pair of bromines diequatorial and the other diaxial is probably a result of repulsions in the boat–chair, where all the bromines are equatorial,[11,12] although other effects[13] may also be important.

Acknowledgment. This work was supported by the National Science Foundation.

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[9] S. Meiboom, paper presented at the Symposium on High Resolution Nuclear Magnetic Resonance at Boulder, Colo., July 1962. The existence in cyclooctane of two distinct T_2 effects in the range of −50 to −100° was established and thought to be due to a partial averaging of chemical shifts in a single conformation. This interpretation is in conflict with other nmr evidence,[2] however, and we have recently suggested that the spin–echo results could be explained if a small amount of a crown family conformation coexisted with the boat–chair.[2g]

[10] The original explanation[2c] was based on a 1:1 mixture of two different twist-boats.

[11] *trans*-1,2-Dibromocyclohexane exists preferentially in the diaxial conformation.[12]

[12] F. R. Jensen and C. H. Bushweller, *Advan. Alicycl. Chem.*, 3, 139 (1971).

[13] *trans*-1,4-Dibromo- (or dichloro-) cyclohexane exists to a much greater extent in the diaxial form than expected from a simple additivity of *A* value;[12] see also R. J. Abraham and Z. L. Rossetti, *Tetrahedron Lett.*, 4965 (1972).

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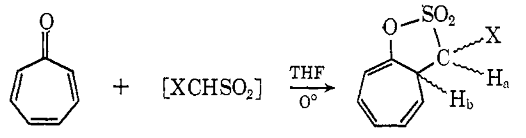
Stereoselective Sulfene–Tropone Cycloadditions and Stereospecific Thermolysis of Resulting Adducts

Sir:

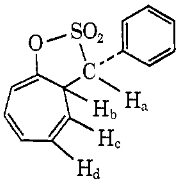
Several sulfenes have been found to cycloadd to tropone in a highly stereoselective fashion to form the corresponding γ-sultones[1] (eq 1 and Table I). A



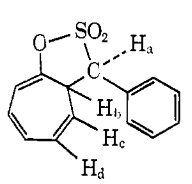
(1)

solution of freshly distilled triethylamine (0.005 mol) in anhydrous tetrahydrofuran was added dropwise (over a 2–3 hr period) to a stirred solution of tropone (0.005 mol) and α-toluenesulfonyl chloride (0.005 mol) in anhydrous tetrahydrofuran at 0° under nitrogen. Filtration of triethylamine hydrochloride and removal of tetrahydrofuran *in vacuo* gave a brown oily residue, which solidified in absolute ethanol at ice bath temperature. Recrystallization from absolute ethanol gave a white crystalline solid in good yield, mp 139–140°. *Anal.* Calcd for $C_{14}H_{12}SO_3$: C, 64.61; H, 4.62; S, 12.31; mol wt, 260. Found: C, 64.34; H, 4.79; S, 12.58; mol wt (osmometer), 262.7. Mass spectra data: *m/e* 260, 196, 181, 178, 177, 176, 167, 165. Ir (Nujol, μ): 6.05, 7.31, 8.28, 8.7, 9.08, 12.0, 12.85, 13.45, 13.98. Nmr (60 Mc, $CDCl_3$–TMS, δ): 3.5–3.8 (1 H, complex multiplet), 4.7–4.95 (2 H, doublet overlapping double doublet), 5.9–6.3 (2 H, complex multiplet), 6.3–6.5 (2 H, complex multiplet), 7.40 (5 H, s).

All of the above data are clearly consistent with a one to one sulfene–tropone adduct, either IIa or IIb.



IIa cis



IIb trans

Investigation of the nmr spectrum using double resonance further supports structure II. Irradiation at δ 3.67 (H_b) collapses the doublet at δ 4.9 (H_a) to a singlet and the double doublet at δ 4.8 (H_c) to a doublet (J_{ab} = 9 cps, J_{bc} = 4 cps, J_{cd} = 9 cps).

Treatment of the initial adduct with base yielded a new compound, mp 126–127°, believed to be the geometric isomer of the initial adduct. *Anal.* Calcd for $C_{14}H_{12}SO_3$: C, 64.61; H, 4.62; S, 12.31; mol wt, 260. Found: C, 64.75; H, 4.86; S, 12.14; mol wt (osmometer), 260.2. Ir (Nujol, μ): C, 6.02, 7.31, 8.28, 8.90, 11.90, 12.30, 12.8, 14.1, 14.4. Nmr (60 Mc, $CDCl_3$–TMS, δ): 3.4–3.55 (1 H, complex multiplet), 4.72 (1 H, doublet), 5.0–5.3 (1 H double doublet), 6.0–6.6 (4 H, complex multiplet), 7.42 (5 H, s) (J_{ab} = 9 cps, J_{bc} = 4 cps, J_{cd} = 9 cps). Mass spectral data: *m/e* 260, 196, 181, 178, 177, 176, 167, 165.

Different chemical shifts in the nmr (but with identical splitting patterns), similar ir data, nearly identical mass spectra, and satisfactory elemental analysis data establish that the second compound is the stereoisomer of the initial adduct, *i.e.*, IIa and IIb are cis–trans isomers. Furthermore, thermolysis of the adducts (eq 2 and 3 and Table I) and other analogous reactions show that the initial adduct is the cis isomer.

It is striking that we were unable to detect the trans adduct in any of the unpurified reaction mixtures. All initial adducts appear in the nmr to be the cis isomer. The fact that "X" is in every case capable of bearing substantial negative charge might indicate that Coulombic attractions between the tropylium cation and the negatively charged "X" group leads to preferential collapse of a zwitterionic intermediate[1] to cis product without competition between bond rotations and ring closure. A thermally allowed $[{}_{\pi}8_s + {}_{\pi}2_s]$ cycloaddition would just as well explain the great stereoselectivity.

When these sulfene–tropone adducts (γ-sultones) are heated, they undergo a novel thermodecomposition with loss of sulfur dioxide to yield stilbene or styrene derivatives in a highly stereospecific manner (eq 2 and 3). The cis sulfene–tropone adduct (IIa, X = C_6H_5, mp 139–140°) was dissolved in dioxane (or DMSO, dioxane–water, THF) and heated to about

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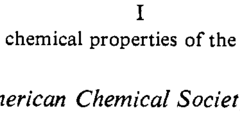
[1] J. Ciabattoni and M. Cabell, *Tetrahedron Lett.*, 2693 (1968), reported a two to one adduct of sulfene and tropone, which was interpreted to arise *via* a dipolar intermediate, I. Neither the stereochemistry of the reaction nor the chemical properties of the product were discussed.



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