3.64 (2) A. The Mo–Mo distance of 2.82 (1) Å, although longer than the value found for the analogous oxo-bridged dimer Mo_2O_4(histidine)$_2$, indicates considerable Mo–Mo interaction, which accounts for the diamagnetism of the complex. The Mo_2S_2 bridge is not planar, with a dihedral angle between the planes $Mo_1S_1S_2$ and $Mo_2S_1S_2$ of 160.9 (9°). Although it is difficult to forward an explanation for the nonplanarity of the Mo_2S_2 unit at this time, close examination of molecular models suggest that this is not a result of packing in the crystal. It is interesting to note that in the complex $[C_5H_5MoO]_2S_2$[12] where the Mo_2S_2 unit is strictly planar, the Mo–Mo distance of 2.89 (5) Å is considerably longer. Since in both structures the Mo–S distances and the S–Mo–S and the Mo–S–Mo bond angles are very similar, the nonplanarity of the Mo_2S_2 unit is probably dictated by the shorter Mo–Mo distance.

These results are of particular interest in view of the model proposed by Hardy, Burns, and Parshall for the configuration of molybdenum and iron in the active site of nitrogenase.[13] In this model, the two metal ions are held by a bridging atom in a manner which allows the nitrogen molecule to bind simultaneously to both metal ions. This model requires a relatively short Mo–Fe distance and an acute Mo–X–Fe angle (X = bridging atom). The Mo–Mo distance observed in this structure and, more important, the small Mo–S–Mo angle clearly suggest that one cannot rule out sulfur as the bridging atom (by sulfur we mean sulfide ion or a mercaptide).

A complete description of this structure and analysis of the hydrogen bonds will be presented in a subsequent publication.

Table I. Bond Angles Around the Coordination Sphere of the Molybdenums

Atoms	Angle	Atoms	Angle
Mo_1–S_1–Mo_2	74.8 (5)	Mo_1–S_2–Mo_2	75.0 (5)
S_1–Mo_1–S_2	103.5 (5)	S_1–Mo_2–S_2	104.1 (5)
S_1–Mo_1–O	96.3 (6)	S_1–Mo_2–O	106.1 (7)
S_1–Mo_1–O_1	84.2 (6)	S_1–Mo_2–O_1'	94.0 (6)
S_1–Mo_1–N_1	86.6 (7)	S_1–Mo_2–N_1'	161.2 (7)
S_1–Mo_1–N_2	162.0 (7)	S_1–Mo_2–N_2'	84.7 (8)
S_2–Mo_1–O	102.5 (7)	S_2–Mo_2–O	103.5 (6)
S_2–Mo_1–O_1	91.2 (6)	S_2–Mo_2–O_1'	90.8 (6)
S_2–Mo_1–N_1	158.1 (8)	S_2–Mo_2–N_1'	87.7 (7)
S_2–Mo_1–N_2	86.0 (7)	S_2–Mo_2–N_2'	164.8 (6)
O–Mo_1–O_1	165.7 (7)	O–Mo_2–O_1'	151.3 (7)
O–Mo_1–N_1	95.4 (8)	O–Mo_2–N_1'	84.8 (7)
O–Mo_1–N_2	96.4 (8)	O–Mo_2–M_2'	85.6 (8)
O_1–Mo_1–N_1	70.3 (7)	O_1–Mo_2–N_1'	70.9 (7)
O_1–Mo_1–N_2	80.4 (8)	O_1–Mo_2–N_2'	76.0 (8)
N_1–Mo_1–N_2	79.6 (8)	N_1'–Mo_2–N_2'	80.9 (8)

(12) D. L. Stevenson and L. F Dahl, *J. Amer. Chem. Soc.*, **89**, 3721 (1967).

(13) R. W. F. Hardy, R. C. Burns, and G. W. Parshall, *Advan. Chem. Ser.*, No. **100**, 219 (1971).

* Address correspondence to this author at the Department of Chemistry, Technion-Israel Institute of Technology, Technion City, Haifa, Israel.

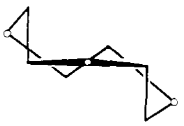
Bruce Spivack, Arthur P. Gaughan, Zvi Dori*
Department of Chemistry, Temple University
Philadelphia, Pennsylvania 19122

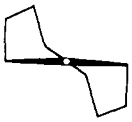
Received May 4, 1971

The Conformation of Cyclononane. Evidence from 251-MHz ^1H Nuclear Magnetic Resonance and 63-MHz ^{13}C Fourier Transform Nuclear Magnetic Resonance

Sir:

Hitherto, knowledge about the conformation of cyclononane has come largely from X-ray diffraction studies on derivatives of cyclononane and from semiempirical strain-energy calculations on cyclononane itself. Thus, X-ray work has shown that the nine-membered skeletons of cyclononylamine hydrobromide[1] and cyclononanone–mercuric chloride[2] have approximately C_2 symmetry and are essentially twist chair–boats (TCB). In contrast, trimeric acetone peroxide[3] exists in the twist boat–chair (TBC) of D_3 symmetry; the presence of three *gem*-dimethyl moieties in this compound, however, introduces large steric strains in other possible conformations, such as the TCB. The TBC form has also been assigned to 1,1,4,4-tetramethylcyclononane and related derivatives on the basis of low-temperature nmr measurements and steric strain considerations.[4] The strain-energy calculations of Hendrickson[5] show that the TBC is 2.2 kcal/mol more stable than the TCB. Bixon and Lifson[6] come to similar conclusions and also suggest that the occurrence of the TCB in cyclononylamine hydrobromide may reflect lattice forces rather than any inherent conformational stability of this form over the TBC. However, Allinger, *et al.*, in a very recent paper give results of calculations showing that the TCB is of lower energy than the TBC form[7] (in the structures circles represent carbon atoms lying on C_2 axes).


TBC
(D_3)


TCB
(C_2)

We now report that cyclononane shows both ^1H and ^{13}C temperature-dependent spectra,[8] and that an analysis of these spectra, together with nmr measure-

(1) R. F. Bryan and J. D. Dunitz, *Helv. Chim. Acta*, **43**, 3 (1960).

(2) S. G. Dahl and P. Groth, *Acta Chem. Scand.*, **25**, 1114 (1971).

(3) P. Groth, *ibid.*, **23**, 1311 (1969).

(4) G. Borgen and J. Dale, *Chem. Commun.*, 1105 (1970).

(5) J. B. Hendrickson, *J. Amer. Chem. Soc.*, **86**, 4854 (1964); **89**, 7036, 7043, 7047 (1967).

(6) M. Bixon and S. Lifson, *Tetrahedron*, **23**, 769 (1967). Conformations I, II, and III of this reference correspond to Hendrickson's TBC, TCC (twist chair–chair), and TCB, respectively. Bixon and Lifson find that the TCC is lower in energy than the TCB, although higher than the TBC form, in qualitative agreement with Hendrickson's 1964 paper.[5] Hendrickson's 1967 papers[5] give new calculations on the TBC and TCB, but omit any mention of the TCC.

(7) N. L. Allinger, M. T. Tribble, M. A. Miller, and D. H. Wertz, *J. Amer. Chem. Soc.*, **93**, 1637 (1971). Professor Allinger has informed us that in view of the strong evidence for the TBC given in the present paper, he and his coworkers have reexamined the calculations reported in the above reference, and they have found that by error no calculation had been carried out for the TBC conformation. They have now made such a calculation and find that the TBC (D_3) form has a calculated heat of formation of −32.20 kcal/mol, as compared with −30.08 kcal/mol for the TCB (C_2) and −31.8 kcal/mol determined experimentally for cyclononane. Thus, these calculations are now in agreement with previous ones[5,6] in showing that the TBC is more stable than the TCB.

(8) At 60 MHz, the single line given by cyclononane in its proton spectrum has been reported to remain unsplit at low temperatures (J. D. Roberts, Abstracts, Nineteenth National Organic Chemistry Symposium of the American Chemical Society, Tempe, Ariz., June 1965). Even at 100 MHz, only broadening of the cyclononane line was observed by us down to −165°.

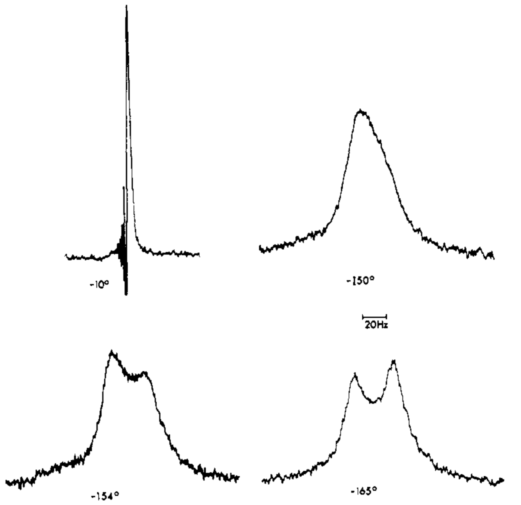


Figure 1. The 251-MHz ^1H spectra of a 1.5% solution of cyclononane in a 2:1 mixture of $CHFCl_2$ and CHF_2Cl at various temperatures.

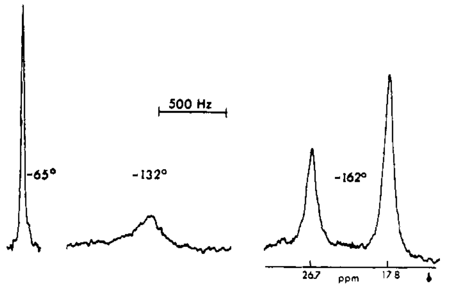


Figure 2. The 63.1-MHz ^{13}C Fourier transform nmr spectra (^{13}C in natural abundance, protons noise decoupled at 251 MHz) of a 4% solution of cyclononane in a 3:1 mixture of $CHFCl_2$ and $CH_2{=}CHCl$ at various temperatures. Each spectrum is the Fourier transform of the sum of 512 free induction spectra and required a total time of 5 min. The chemical shifts are given in parts per million downfield from internal tetramethylsilane.

ments on 1,1-dimethylcyclononane, lends support to the TBC conformation for cyclononane, and provides information on conformational processes in nine-membered rings.

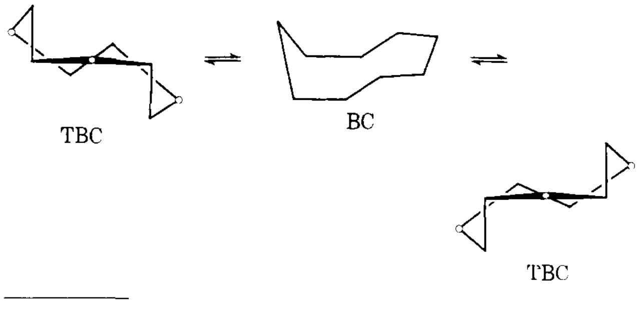
The 251-MHz proton spectrum[9] of cyclononane at various temperatures is shown in Figure 1. The spectrum changes from a single line at room temperature to two broad overlapped bands below about −150°. Thus, some conformational process with a free-energy barrier of about 6 kcal/mol has become slow on the nmr time scale at this latter temperature. However, because of the complexity of the spectrum as a result of spin–spin coupling, as well as the broadening induced by comparatively slow molecular tumbling at low temperatures, no detailed analysis of the spectrum is possible.

In contrast to the proton spectrum, the 63.1-MHz ^{13}C Fourier transform nmr spectrum[10] of cyclononane changes in a simple fashion as the temperature is lowered, as shown in Figure 2. At −162°, there are two well-resolved resonances with a chemical-shift difference of 570 Hz (9 ppm) and an intensity ratio of about 2:1. The conformational process observed here has a free-energy barrier of about 6 kcal/mol, the same as found from the proton spectrum.

The ^{13}C results are consistent with a conformation of D_3 symmetry such as the twist boat–chair, TBC. In order to exclude conformations of lower symmetry, *e.g.*, the twist chair–boat, TCB, the possibility of coincidences of chemical shifts or a fast-averaging process at −162° must be considered. The TCB should show five different ^{13}C chemical shifts and, in view of the dispersion expected of ^{13}C chemical shifts,[11] it is highly unlikely that coincidences would reduce the five resonances to just two in the ratio of 2:1. The possibility that the TCB is undergoing a fast degenerate conformational isomerization at −162°, so that the time-average symmetry becomes D_3, is more difficult to exclude. The free-energy barrier for such a process would have to be not more than about 4 kcal/mol, and examination of molecular models and possible conformational processes indicates that such a low barrier is unlikely.[12] We thus conclude that our nmr results strongly support the TBC, but do not completely exclude the TCB, as the favored conformation of cyclononane.

A *gem*-dimethyl group can be introduced into the TBC form only on a carbon atom lying on one of the three C_2 axes of that form. Therefore, 1,1-dimethylcyclononane should have C_2 symmetry and its ^1H nmr spectrum should show a dynamic nmr effect only for the ring protons and not for the methyl protons. Further, the ^{13}C spectrum should show no dynamic nmr effect at all. Experimentally, this is exactly, what we observe. The change in the methylene proton band takes place at about −85° and corresponds to a process with a free-energy barrier of about 9 kcal/mol, considerably greater than the 6 kcal/mol found in cyclononane itself, but much less than the 20 kcal/mol barrier in 1,1,4,4-tetramethylcyclononane.[4]

The conformational process observed by nmr in cyclononane probably involves conversion of the TBC into the boat–chair (BC) and back into a different (and enantiomeric) TBC form.



---

[9] The spectra were obtained on a superconducting solenoid nmr spectrometer: F. A. L. Anet, G. W. Buchanan, and C. H. Bradley, paper presented at the 11th Experimental Nuclear Magnetic Resonance Conference, Pittsburgh, Pa., April 1970.

[10] Acquisition and Fourier transform of free induction spectra were carried out with a Data General Nova computer having 12K 16-bit words: F. A. L. Anet, V. J. Basus, C. H. Bradley, and A. Cheng, paper presented at the 12th Experimental Nuclear Magnetic Resonance Conference, Gainesville, Fla., Feb 1971. For references to Fourier transform nmr see: R. R. Ernst and W. A. Anderson, *Rev. Sci. Instrum.*, **37**, 93 (1966); A. Allerhand, D. W. Cochran, and D. Doddrell, *Proc. Nat. Acad. Sci. U. S.*, **67**, 1093 (1970); W. Voelter, E. Breitmaier, G. Jung, T. Keller, and D. Hiss, *Angew. Chem.*, **82**, 812 (1970); *Angew Chem., Int. Ed. Engl.*, **9**, 803 (1970); W. Horsley, H. Sternlicht, and J. S. Cohen, *J. Amer. Chem. Soc.*, **92**, 680 (1970).

[11] D. K. Dalling and D. M. Grant, *ibid.*, **89**, 6612 (1967); D. Doddrell, C. Charrier, B. L. Hawkins, W. D. Crain, L. Harris, and J. D. Roberts, *Proc. Nat. Acad. Sci. U. S.*, **67**, 1588 (1970).

[12] It is assumed that the resonances which are averaged have a frequency separation of the order of 1 kHz. Although Hendrickson[5] has discussed the problem of interconversions between cyclononane conformations, no actual calculations of energy barriers have been published. The TCC[6] is also made very unlikely by the arguments given against the TCB.

Five cycles of TBC–BC–TBC interconversions are required to average the three different proton chemical shifts of the TBC form to one chemical shift, whereas only two cycles are required to average the two ^{13}C chemical shifts.

In 1,1-dimethyl- and 1,1,4,4-tetramethylcyclononane the changes observed are racemization of chiral conformations. Here, three cycles of TBC–BC–TBC interconversions are required and the itinerary goes through BC's and TBC's with sterically hindered methyl groups. Very large transannular methyl–methyl repulsions are found in these intermediate forms for the tetramethyl compound in agreement with a barrier which is 14 kcal/mol greater than that of cyclononane. The smaller transannular methyl–hydrogen repulsions for the dimethyl case lead to an increase in barrier of only 3 kcal/mol. Thus, the pathway described above rationalizes the conformational barriers in a satisfactory way.

Acknowledgments. This work was supported by the National Science Foundation and the United States Public Health Service. J. J. W. is indebted to the Centre National de la Recherche Scientifique (France) and NATO for fellowship support.

F. A. L. Anet,* J. J. Wagner
Contribution No. 2858
Department of Chemistry, University of California
Los Angeles, California 90024

Received July 2, 1971

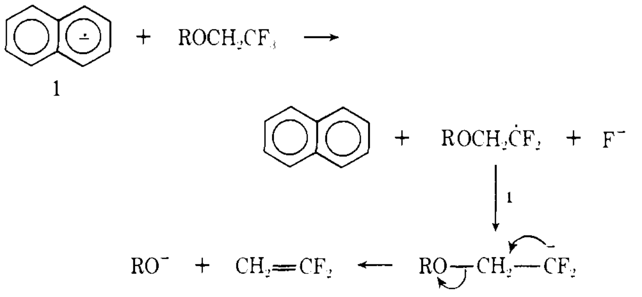
The Sodium Naphthalene Promoted Cleavage of Trifluoroethyl Ethers

Sir:

Several recent investigations have established that solvolysis of simple secondary derivatives, even in acetic and formic acids, is strongly assisted by nucleophilic solvent participation.[1] These investigations serve to reinforce an awareness that solvolysis of primary systems must also be so assisted.[2] This awareness has important consequences for the investigation of neighboring group participation, since strong solvent assistance to solvolysis may well mask the potential intervention of less potent internal nucleophiles. Anchimeric assistance by such neighboring groups can be made manifest by employing solvents of low intrinsic nucleophilicity. Considerable success in this direction has been achieved utilizing trifluoroacetic acid as a solvolysis medium,[3] but this approach is limited by the high relative acidity of trifluoroacetic acid and the consequent instability of many substrates and products in this solvent. 2,2,2-Trifluoroethanol (TFE) appears to be a solvent which combines the advantages of acceptably low acidity ($pK_a = 12.37$)[4] and low intrinsic nucleophilicity.[5] Given these features it is at first glance surprising how little attention this solvent has received as a solvolysis medium. A principal reason for this disinterest may well be the difficulty encountered to date in identifying and assaying the products of solvolysis in trifluoroethanol. Few authentic trifluoroethyl ethers are known, and synthesis of compounds of this type is not trivial in many cases.

Prompted by the requirement for a solvolysis medium of low intrinsic nucleophilicity and minimal acidity in which quantitative correlation of rates and products of reaction could be achieved, we have sought to develop an efficient stereospecific method for converting trifluoroethyl ethers to the corresponding alcohols. We are now pleased to describe such a technique and to exemplify its application.

All alkyl halides react with 1,2-dimethoxyethane (DME) solutions of sodium naphthalene by initial dissociative electron transfer to yield alkyl radicals and halide ion.[6] The radicals thus produced can undergo a variety of reactions, one of which is rapid reduction by a second molecule of radical anion to the alkyl anion.[7,8] Alkyl fluorides represent no exception to this generalization, although the rate of the initial dissociative electron transfer is much slower than for other halides.[8] These considerations suggest the following scheme for cleaving 2,2,2-trifluoroethyl ethers.



Since the initially formed radical is kinetically much more susceptible to further reduction than is a second fluoro substituent, and since β-alkoxide should prove a superior leaving group to α-fluoride in the subsequently formed anion, the possibility of carbene formation resulting from the second reduction step—a reaction which does, indeed, occur with alkyl *gem*-dichlorides and the polychloromethanes[9]—appears unlikely.

Hexyl 2,2,2-trifluoroethyl ether was synthesized by

---

[1] J. M. Harris, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 5729 (1970); H. C. Brown, C. J. Kim, C. J. Lancelot, and P. v. R. Schleyer, *ibid.*, **92**, 5244 (1970); J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *ibid.*, **92**, 2538 (1970); J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *ibid.*, **92**, 2540 (1970); P. v. R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *ibid.*, **92**, 2542 (1970); A. F. Diaz and S. Winstein, *ibid.*, **91**, 4300 (1969); C. J. Lancelot and P. v. R. Schleyer, *ibid.*, **91**, 4291, 4296, 4297 (1969); C. J. Lancelot, J. J. Harper, and P. v. R. Schleyer, *ibid.*, **91**, 4294 (1969); C. J. Kim and H. C. Brown, *ibid.*, **91**, 4287, 4289 (1969); J. A. Thompson and D. J. Cram, *ibid.*, **91**, 1778 (1969); J. E. Nordlander and W. J. Kelley, *ibid.*, **91**, 996 (1969); J. E. Nordlander and W. G. Deadman, *ibid.*, **90**, 1590 (1968).

[2] M. D. Bentley and M. J. S. Dewar, *ibid.*, **92**, 3996 (1970); J. M. Harris, F. L. Schadt, P. v. R. Schleyer, and C. J. Lancelot, *ibid.*, **91**, 7508 (1969); R. J. Jablonski and E. I. Snyder, *ibid.*, **91**, 4445 (1969); M. G. Jones and J. L. Coke, *ibid.*, **91**, 4284 (1969); J. L. Coke, F. E. McFarlane, M. C. Mourning, and M. G. Jones, *ibid.*, **91**, 1154 (1969); A. Diaz, I. Lazdins, and S. Winstein, *ibid.*, **90**, 6546 (1968); J. E. Nordlander and W. G. Deadman, *ibid.*, **90**, 1590 (1968).

[3] I. L. Reich, A. Diaz, and S. Winstein, *ibid.*, **91**, 5635 (1969), and references cited therein; A. Streitwieser, Jr., and G. A. Dofian, *Tetrahedron Lett.*, 1263 (1969); P. E. Peterson, R. E. Kelley, Jr., R. Belloli, and K. A. Sipp, *J. Amer. Chem. Soc.*, **87**, 5169 (1965).

[4] P. Ballinger and F. A. Long, Jr., *ibid.*, **81**, 1050 (1959).

[5] M. D. Bentley and J. A. Lacadie, *Tetrahedron Lett.*, 741 (1971); V. J. Shiner, Jr., W. Dowd, R. D. Fisher, S. R. Hartshorn, M. A. Kessick, L. Milakofsky, and M. W. Rapp, *J. Amer. Chem. Soc.*, **91**, 4838 (1969); W. S. Trahanovsky and M. P. Doyle, *Tetrahedron Lett.*, 2155 (1968).

[6] J. F. Garst, J. T. Barbas, and F. E. Barton, II, *J. Amer. Chem. Soc.*, **90**, 7159 (1968); G. D. Sargent and G. A. Lux, *ibid.*, **90**, 7160 (1968), and references therein cited.

[7] J. F. Garst, P. W. Ayers, and R. C. Lamb, *ibid.*, **88**, 4260 (1966).

[8] J. F. Garst and F. E. Barton, II, *Tetrahedron Lett.*, 587 (1969).

[9] C. M. Tatum, Jr., and G. D. Sargent, unpublished.