begun an investigation of the mass spectra of various pairs of cis–trans isomeric model compounds.

Mandelbaum and coworkers[4] have very recently shown that certain unsaturated cyclic diketones, *e.g.*, **1**, decompose in the mass spectrometer by a RDA reaction if cis at the central ring junction, but not if trans. They point out that this is the behavior expected if the mass spectral RDA reaction is concerted and follows symmetry rules analogous to those established for thermal reactions.[5]

We wish here to give a preliminary account of our results, since our data with regard to the mass spectral retro-Diels–Alder reaction in simple bicyclic Δ^2 olefins (compounds **2**, **3**, and **4**) show that the occurrence of abundant ions formed by this reaction is not generally dependent upon the stereochemistry at the central bond.

The relative abundance at 70 eV of the molecular ions and the ions associated with the RDA process in the mass spectra of the isomers of **2**, **3**, and **4** is given in Table I.[6]

Table I. Relative Abundance of RDA Ions[a]

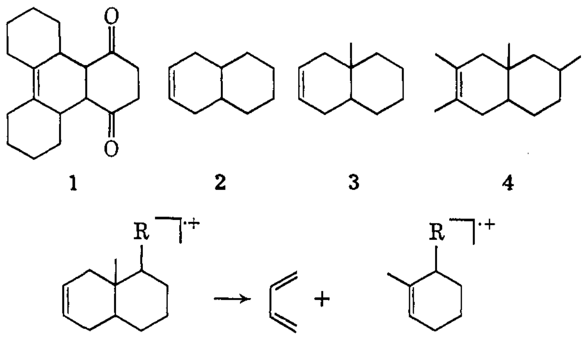
Compd	M	[M − C_4H_6]$\cdot^+$	[M − C_4H_6 − CH_3]$^+$
2, cis	15.1[b]	5.3	12.1
2, trans	17.8[b]	2.1	9.8
3, cis	10.4	20.4[b]	11.0
3, trans	11.0	29.9[b]	11.7
4a	7.6	11.3	14.8[b]
4b	8.2	8.2	12.0[b]
4c	10.1	7.8	12.1[b]

[a] Measured at 70 eV on an AEl MS-9 mass spectrometer by Mr. R. G. Ross and expressed in per cent of Σ_{40}. [b] Base peak.

In **3**, the RDA reaction gives rise to the base peak in the cis as well as in the trans isomers, and only a slight difference appears between the propensity of the cis and trans isomers of **2**, **3**, and **4** to decompose *via* this process. Spectra obtained at low ionizing voltage show the same pattern, even though the relative abundance of the RDA product ions at 12 eV is increased slightly in the cis compounds relative to the trans. To further study the behavior at low energies we have examined the relative intensities of the [M − C_4H_6]$\cdot^+$ peaks in a mixture of *cis*-9-methyl-2-octalin and labeled *trans*-9-methyl-2-octalin (see Scheme I) while decreasing the ionizing voltage to less than the appearance potential of these ions. Within the limits of detectability the abundance of both ions decreased to below measurable values simultaneously, showing that even at onset no significant difference exists in this respect between the cis and trans compounds.[7]

Comparison of the RDA decomposition of cis and trans isomers in the field-free regions is not possible, since neither of the spectra exhibit measurable metastable peaks corresponding to the RDA process.[8] Rather than taking this to imply that the reaction occurs from an excited state[5] we believe that the absence of metastable peaks in both field-free regions shows that nearly all the reactive molecular ions either fragment or undergo double bond migration in the ion source. The latter process is likely on the basis of the recently described[9] results in cyclohexene in which such double bond migration was shown to be operative before the molecules reach the field-free regions of the mass spectrometer.

Scheme I



m/*e* 96 for R = H
m/*e* 97 for R = D

These results thus show that the mass spectral retro-Diels–Alder reaction of the simplest polycyclic olefins is not dependent in any marked fashion on the stereochemistry at the ring junction and therefore lend support to the earlier suggestion[3b] that this process is stepwise rather than concerted.

Acknowledgments. We are indebted to the National Institutes of Health (Grants AM 04257 and GM 06840) and to Statens Naturvidenskabelige Forskningsraad, Copenhagen (Grant 511-1224 to S. H.), for financial support.

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(4) A. Karpati, A. Rave, J. Deutsch, and A. Mandelbaum, *J. Amer. Chem. Soc.*, **95**, 4244 (1973); we thank Dr. Mandelbaum (Technion, Haifa, Israel) for making his manuscript available to us prior to publication.

(5) R. C. Dougherty, *J. Amer. Chem. Soc.*, 90, 5780, 5788 (1968).

(6) Only three of the possible four isomers of 4 have been examined; the stereochemical identity of each of these has not yet been unambiguously determined, but at least one must be cis and at least one trans at the ring junction; they are given in Table I in the order they were collected by preparative glc (10% SE-30 on Chromosorb W at 175°).

(7) This procedure allows us to assess the difference in appearance potentials while avoiding the pitfalls of attempting to measure the exact numerical values.

(8) Confirmed by metastable defocusing experiments on the [M − C_4H_6]$\cdot^+$ ions of *cis*- and *trans*-3.

(9) P. J. Derrick, A. M. Falick, and A. L. Burlingame, *J. Amer. Chem. Soc.*, **94**, 6794 (1972).

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On Homoaromatic Stability

Sir:

The concept of homoaromaticity, proposed over a decade ago by Winstein and his collaborators,[1] provided a plausible explanation for the unusually high stability of a large class of cyclic molecules and ions. In the original formulation of the theory a homoaromatic molecule was pictured as being a cyclic ($4n + 2$) "aromatic" polyene in which the ring conjugation had been interrupted in one or more places by aliphatic chains of varying lengths. In certain instances the π-electron structure of the original polyene was envisioned to be only slightly perturbed and to maintain a signifi-

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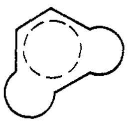
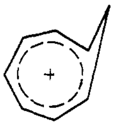
(1) For reviews see: (a) S. Winstein, *Quart. Rev., Chem. Soc.*, **23**, 141 (1969); (b) P. R. Story and B. C. Clark, Jr., in "Carbonium Ions," G. A. Olah and P. v. R. Schleyer, Ed., Vol. III, Wiley-Interscience, New York, N. Y., 1972, p 1007.

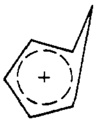


cant part of its original aromatic stability. Thus, bicyclo[5.1.0]octadienyl cation "homotropylium" (I)



I

might be thought of as a fractured tropylium ion and be expected (as is experimentally observed[1,2] and theoretically predicted[3]) to exhibit some of the high stability of this 6π electron aromatic. Correspondingly, the bicyclo[3.1.0]hexenyl cation "homocyclopentadienyl" (II),



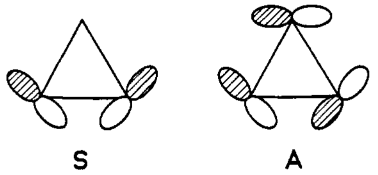
II

based on the severed antiaromatic (4π electron) skeleton of cyclopentadienyl, should show partial destabilization. Recent experimental[2j,4] and theoretical[3] work provides strong evidence for this.

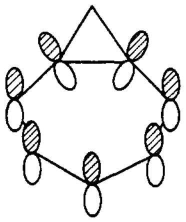
In this communication we propose an alternative, molecular orbital based model to account for the unusual stability (or instability) of homoaromatic and antihomoaromatic molecules. Our ideas are meant to complement Winstein's original formulaton rather than to replace it; taken together they provide grounds for the description of an entire range of homoaromatic systems.

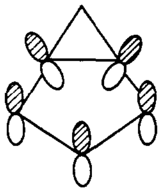
For the present we shall limit our discussion to molecules in which but a single interruption of the cyclic polyene is considered. Furthermore, we restrict the aliphatic chain to a single methylene group such as, for example, is found in the homotropylium and bicyclo[3.1.0]hexenyl carbocations. Extensions to include systems with multiple interruptions, as well as a discussion of the consequences of greater aliphatic chain lengths, will be dealt with in a forthcoming full report.

Instead of considering the external methylene as an isolated entity we shall treat it together with its two CH neighbors as part of a cyclopropane ring.[5] The degenerate pair of valence orbitals (highest occupied molecular orbitals) of cyclopropane are well known[6] and the striking resemblence of the symmetric component (S) to the π orbitals of a double bond is reflected in the



markedly similiar behavior of unsaturated and small ring molecules.[7] As visualized by Winstein the two electrons occupying this orbital should be able to delocalize over the ring (but certainly less effectively than an ethylenic π bond), the resulting (homoaromatic) polyene being of the same structure and containing the same number of electrons in cyclic conjugation as its (aromatic) parent. This we would expect to be a satisfactory description in those cases where the cyclopropane is fully closed; that is, for example, in the hypothetical classical structures for the homotropylium and bicyclo[3.1.0]hexenyl cations, the orbital basis descriptions for which would incorporate the symmetric cyclopropane Walsh component.





Alternatively we might visualize a relatively open cyclopropane moiety, thus effectively ruling out transmission of conjugation along the ring-fused bond and necessitating the involvement of the basis orbitals of the external methylene. In this instance *two factors distinguish the homoaromatic from its parents.* The number of electrons in the cycle has *increased by two.* Homotropylium now has eight electrons in conjugation. At the same time, however, electron delocalization through the valence orbitals of cyclopropane has *increased by one* the number of nodes present in the atomic orbital basis of the cyclic polyene. That is to say, the increase in the number of electrons in cyclic conjugation (for example, from $4n + 2$ in tropylium to $4n'$ in homotropylium) has been paralleled by a change from a Hückel to a Möbius ring structure. Thus, both homotropylium and bicyclo[3.1.0]hexenyl may be thought of as Möbius molecules,[8] with an odd number of nodes in their atomic orbital representation. Below we show the sequence of *atomic orbitals* which form the Möbius array. The enhanced stability of this homoaromatic arrangement follows directly from the theories of Heilbronner, [10]Dewar,[11] and Zimmerman.[9] Homotropylium with eight π electrons in cyclic conjugation is a

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[2] For recent work on monohomotropylium ions not summarized in ref 1 see: (a) G. D. Mateescu, C. D. Nenitzescu, and G. A. Olah, *J. Amer. Chem. Soc.*, **90**, 6235 (1968); (b) O. L. Chapman and R. A. Fugiel, *ibid.*, **91**, 215 (1969); (c) L. Paquette, J. Malapass, and T. Barton, *ibid.*, **91**, 4714 (1969); (d) Y. Sugimura and N. Soma, *Tetrahedron Lett.*, 1721 (1970); (e) P. Warner, D. L. Harris, C. H. Bradley, and S. Winstein, *ibid.*, 4013 (1970); (f) Y. Sugimura, N. Soma, and Y. Kishida, *ibid.*, 91 (1971); (g) R. F. Childs, M. A. Brown, F. A. L. Anet, and S. Winstein, *J. Amer. Chem. Soc.*, **94**, 2175 (1972); (h) R. Huisgen and J. Gasteiger, *Tetrahedron Lett.*, 3661 (1971); J. Gasteiger and R. Huisgen, *ibid.*, 3665 (1972); (i) M. S. Brookhart and M. A. M. Atwater, *ibid.*, 4399 (1972); (j) J. A. Berson and J. A. Jenkins, *J. Amer. Chem. Soc.*, **94**, 8907 (1972).

[3] W. J. Hehre, *ibid.*, **94**, 8908 (1972).

[4] P. Vogel, M. Saunders, N. M. Hasty, Jr., and J. A. Berson, *ibid.*, **93**, 1551 (1971), and references therein.

[5] Such an approach has been taken by Hoffmann and by Günther in explaining substituent effects on the cyclohepatatriene–norcaradiene equilibrium: R. Hoffmann, *Tetrahedron Lett.*, 2907 (1970); H. Günther, *ibid.*, 5173 (1970).

[6] For a discussion see: R. Hoffmann and R. B. Davidson, *J. Amer. Chem. Soc.*, **93**, 5699 (1971).

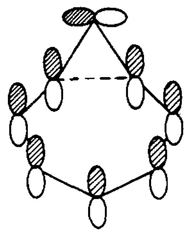
[7] For a recent and readable account see: F. J. McQuillin, "Alicyclic Chemistry," Cambridge University Press, New York, N. Y., 1972.

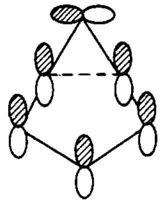
[8] Other representatives include cyclopropane itself trimethylenemethane, barrelene, and the cumulenes with an odd number of carbons; see ref 9.

[9] H. E. Zimmermann, *Accounts Chem. Res.*, **4**, 272 (1971).

[10] E. Heilbronner, *Tetrahedron Lett.*, 1923 (1964).

[11] M. J. S. Dewar, *Tetrahedron, Suppl.*, **8**, 75 (1966); see also M. J. S. Dewar, *Angew. Chem., Int. Ed. Engl.*, **10**, 761 (1971).





Möbius aromatic while the 6π bicyclo[3.1.0]hexenyl cation might equally well be termed Möbius antiaromatic.

It should be noted that the two alternative descriptions lead to the same conclusion. Thus, homotropylium is stabilized through aromatic conjugation, either *via* six π electrons in a Hückel ring or eight in a Möbius arrangement. Correspondingly, applying either model, bicyclo[3.1.0]hexenyl is seen to suffer in stability from its antiaromatic character. The description of choice would seem to depend heavily upon geometrical arguments: that is, a fully formed cyclopropane ring favoring a Hückel polyene and a more open structure, the Möbius arrangement. In actual practice both mechanisms for electron delocalization are no doubt operative.

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Electronic Structure and Reactivity of Small Ring Compounds. VI. Carbon–Carbon Coupling Constants in 1-Cyanobicyclo[1.1.0]butane[1]

Sir:

The considerable strain in the bicyclo[1.1.0]butane ring system[2,3] has prompted numerous calculations of the electronic structure at all levels of sophistication.[4-10] By employing the Muller–Pritchard relationship between hybridization and ^{13}C–H coupling constant,[11,12] these calculations are, at least for hybridization, subject to experimental verification. The observed coupling constants in bicyclobutane[13] therefore suggest the C_1–H orbital is $sp^{1.44}$, the C_2–H_{exo} orbital is $sp^{2.27}$, and the C_2–H_{endo} orbital is $sp^{1.96}$. Analogous results have been obtained for 1-cyanobicyclo[1.1.0]butane.[14]

A similar type of linear correlation between hybridization and ^{13}C–^{13}C coupling constants was suggested by Frei and Bernstein.[15] The relationship was justified theoretically by Pople and Santry[16] and used by Roberts[17] in the form

$$J_{^{13}C-^{13}C} = 550(S_{1(2)})(S_{2(1)}) \qquad (1)$$

where $S_{1(2)}$ and $S_{2(1)}$ are the s characters of the hybrid orbitals comprising the C_1–C_2 bond on carbons 1 and 2, respectively. Thus, for example, the ^{13}C–^{13}C coupling constant of 34.6 Hz in ethane[18] corresponds to s characters of 0.25 or sp^3 hybridization. Recently an alternative equation has been suggested, but it requires the bond overlap, S, calculated using the maximum overlap approximation.[12] It has also been used with maximum overlap derived hybridizations to predict coupling constants. It is important to point out that these coupling constant–hybridization relationships probably do not apply to highly strained small ring systems. Roberts,[17b] and more recently Schulman and Newton,[19] have suggested that the problem is due to contributions from terms other than the contact term.

In this communication we wish to report the ^{13}C–^{13}C coupling constants in 1-cyanobicyclobutane and compare these values to those predicted by the calculations. In addition the possibility of inserting these values into the coupling constant–hybridization equations and comparing the hybridizations to those calculated is discussed.

The nmr spectra were obtained on a Varian XL-100 FT spectrometer operating at 25.2 MHz with complete proton decoupling. The sample of 1-cyanobicyclobutane and about 30% of acetonitrile-d_3 were codistilled into a 12-mm nmr tube at 10^{-5} Torr, degassed and sealed. The peak corresponding to carbons 2 and 4 showed a single coupling constant to carbons 1 and 3 of 22 ± 0.5 Hz. This is in excellent agreement with the value of 21 Hz reported recently by Grant and Allred and coworkers for bicyclobutane itself.[20] Because of the symmetry of the system these authors were unable to obtain a value for the C_1–C_3 coupling constant. The value for the C_1–C_3 coupling constant, obtained from the side bands of both the C_1 and C_3 resonances of cyanobicyclobutane was 16 ± 0.5 Hz. In addition C_1 and C_3 were coupled by 22 Hz to C_2 and C_4.

If one assumes that the C_1–C_3 bond is symmetrical, that is the CN group exerts only a minimal perturbation, then eq 1 suggests the hybridization is $sp^{4.85}$–$sp^{4.85}$ (*i.e.*, 17.1% s character in each orbital.)

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(9) K. B. Wiberg, *Tetrahedron*, 24, 1083 (1968).

(10) T. Yonezawa, K. Simizu, and H. Kato, *Bull. Chem. Soc. Jap.*, **41**, 2336 (1968).

(11) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768, 1471 (1959).

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(18) R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc., Ser. A*, **269**, 385 (1962).

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