Though this symmetrical interaction is higher in energy, it seems to be a very favorable transition state or intermediate for the observed intramolecular rearrangement according to eq 1, *i.e.*, $G \rightleftharpoons G'$. At least it is superior to that of a largely intermolecular dissociation–recombination mechanism, as shown by the differences in activation energies for both processes (Table IV).

The presence of two methyl groups in the 2 and 7 positions of the ligands are likely to preclude a coplanar arrangement of the planar dimethylgold (pseudo)halide unit and the ligand. The relative orientation of the two parts of the complexes during the intramolecular rearrangement process is not known, however. It is possible that a perpendicular orientation is preferred. A determination of the crystal structure of one of the compounds should provide at least indirect information on that point.

Acknowledgment. This work has been supported by Fonds der Chemischen Industrie, Frankfurt, Germany. K. C. D. thanks the Deutsche Akademische Austauschdienst, Bonn, Germany, for a postdoctoral fellowship and the authorities of Utkal University for leave of absence. The authors are also grateful to Dr. W. Buchner and Mr. C. P. Kneis for obtaining most of the nmr spectra.

Orbital Noninteraction in Bridged Cyclohexanes

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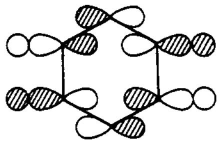
Abstract: The highest occupied σ orbitals in six-membered rings possess interesting symmetry properties. In the bicyclo[2.2.1]heptane skeleton the consequent inability of these levels to interact with any orbitals of the one-carbon bridge results in an unusual destabilization of the 7-norbornyl cation and a stabilization of the oxygen p-type lone pair of 7-oxanorbornane.

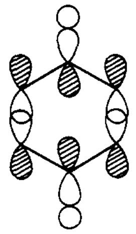
Diverse are the spectroscopic and chemical consequences of orbital interaction through space and through bonds.[2] In this contribution we discuss a curious case of structurally enforced absence of orbital interaction, with significant chemical implications.

In benzene there is found a high-lying degenerate set of σ orbitals, e_{2g} in D_{6h} symmetry. In the notation of Lindholm,[3] these are a mixture of radial and tangential C 2p orbitals. In the photoelectron spectrum of benzene, the 11.4 eV ionization potential is assigned to this e_{2g} orbital set.[3] The e_{2g} orbitals can be represented in various ways but are most easily spotted and remembered as a set of horizontal and vertical waves (**1** and **2**). We have come to term them "ribbon orbitals."[4]



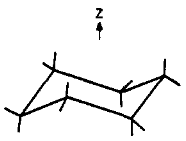
AA

1



SS

2



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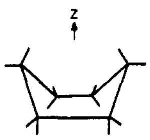

4

The ribbon orbitals are not peculiar to benzene but recur in any system with a six carbon cycle. They are the highest lying molecular orbitals, e_g in D_{3d} symmetry, in a chair cyclohexane structure (**3**). In the boat cyclohexane structure (**4**), the lowered C_{2v} symmetry finally forces a splitting of the formerly degenerate levels. SS (**2**, a_1 in C_{2v}) comes below AA (a_2, **1**) by 0.26 eV in an extended Hückel[5a] or 0.34 eV in a CNDO/2[5b] calculation. The primary determinant of the observed level ordering appears to be the antibonding H–H interaction among the side equatorial hydrogens in AA. Both AA and SS ribbon orbitals acquire some z component in the chair and boat cyclohexane structures, but their inplane nature, as represented by the structures **1** and **2**, remains dominant. Indeed, the ribbon orbitals persist in any molecule which incorporates a six-membered ring, and representations of them may be found in the literature for molecules as diverse as **5**, triasterane,[6] the

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[1] Part 49 of "Applications of Photoelectron Spectroscopy." Part 48: M. Beez, G. Bieri, H. Bock, and E. Heilbronner, *Helv. Chim. Acta*, in press.

[2] (a) See previous papers in the series "Applications of Photoelectron Spectroscopy." (b) R. Hoffmann, *Accounts Chem. Res.*, 4, 1 (1971); R. Hoffmann and W.-D. Stohrer, "Special Lectures at XXIIIrd International Congress of Pure and Applied Chemistry," Vol. 1, Butterworths, London, 1971, p 157.

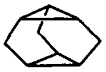
[3] B.-Ö. Jonsson and E. Lindholm, *Ark. Fys.*, **39**, 65 (1969); *Chem. Phys. Lett.*, **1**, 501 (1967).

[4] Still better representations of these orbitals may be found in W. L. Jorgensen and L. Salem, "The Organic Chemist's Book of Orbitals," Academic Press, New York, N. Y., 1973.

[5] (a) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); R. Hoffmann and W. N. Lipscomb, *ibid.*, **36**, 2179, 3489 (1962); **37**, 2872 (1962). A hydrogen exponent of 1.3 was used. (b) J. A. Pople, D. P. Santry, and G. A. Segal, *ibid.*, **43**, S129 (1965); J. A. Pople and G. A. Segal, *ibid.*, **43**, S 136 (1965) and subsequent papers.

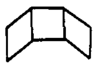
[6] E. Haselbach, E. Heilbronner, H. Musso, and A. Schmelzer, *Helv. Chim. Acta*, **55**, 302 (1972).

tricyclic isomers **6** and **7**,[7] bicyclo[2.2.0]hexane[8] (**8**), and the various azabenzenes.[9]



5

6



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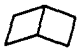
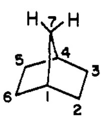


8

The AA ribbon orbital in a boat cyclohexane structure is not very much destabilized in energy, but it is the highest occupied molecular orbital. It occurred to us that the combination of high energy and d-type symmetry of this orbital could have some operational consequences.

Consider the molecules of norbornane (**9**), the classical 7-norbornyl cation (**10**), and the 7-oxanorbornane (**11**). The 7 position of the norbornane skeleton is



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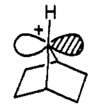
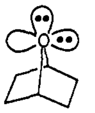


10



11

poised at the intersection of the two mirror planes of these structures. The result is that no valence orbital of the CH$_2$ in **9**, nor the CH$^+$ group in **10**, nor the oxygen in **11** can interact at all with the high-lying σ orbital. The latter is AA or d type, whereas the orbitals at the 7 position are AS or SS, p or s type, respectively.

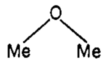
For norbornane the symmetry-enforced absence of interaction between a high-lying molecular orbital of the boat cyclohexane substructure and the methylene at the 7 position has no significant consequences. But in the carbonium ion and the ether the missing interaction makes the C$_7$ or O$_7$ 2p orbital lie abnormally low in energy. And this would make the 7-carbonium ion *less* stable than it should be, and the 7-oxanorbornane oxygen 2p ionization potential greater in magnitude than it should be.

The above conclusions were supported by a computational comparison of a 7-norbornyl cation with a diisopropyl carbonium ion. The latter duplicates the extent of carbon substitution in the 7-norbornyl species; to take account of the obvious influence of angle strain on carbonium ion stability, we constructed the diisopropyl model with a C$_1$C$_7$C$_4$ angle of 94.5°, matching that in our model norbornane.[10]

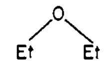
In the extended Hückel and CNDO/2 calculations which we carried out every indicator showed more interaction in the model than in the norbornyl system: in the diisopropyl carbonium ion the carbonium center vacant p orbital was at higher energy, and less localized; the positive charge at the 7 position less; the C$_1$–C$_7$ and C$_4$–C$_7$ overlap populations greater; the C$_1$–C$_2$, C$_1$–C$_6$, C$_4$–C$_3$, C$_4$–C$_5$ populations smaller. The conclusion that the 7-norbornyl cation is destabilized is obvious. The analysis of the 7-oxanorbornane follows similar lines. The oxygen p-type lone pair interacts less and lies at lower energy than the corresponding lone pair of a model diisopropyl ether.

Experimental Evidence

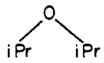
Let us first take the 7-oxanorbornane. Its photoelectron spectrum has been recently reported by Bain, *et al.*[11] The first ionization potential, unambiguously assigned to the oxygen p-type lone pair, of this and some related ethers[12–15] is shown below (all ionization potentials are quoted with a conservative error estimate of ±0.05 eV).



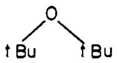
9.9$_5$



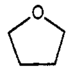
9.5$_0$-9.5$_5$



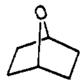
9.3$_5$



8.9$_5$



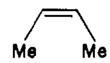
9.5$_0$-9.5$_5$



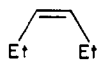
9.5$_0$-9.5$_5$

Note that an increase in the length of the attached carbon chain leads to a decrease in the magnitude of the ionization potential.

But that anticipated effect is not observed in the step from tetrahydrofuran to 7-oxanorbornane, as already noted by Bain, *et al.*[11] Perhaps the effect becomes more striking when it is compared to an analogous and well-behaved series of molecules in which an ethylene π level is affected by alkyl substitution.[16–18]

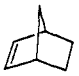


9.1$_0$



8.9$_0$

9.2$_0$



8.9$_5$

It is clear that the oxygen lone pair in the 7-oxanorbornane **11** is at lower energy than it should be. The ionization potential of a model for **11**, diisopropyl ether,[13] is 9.35. If "ring closure" were to have a negligible effect, as it seems to have in the diethyl ether–tetrahydrofuran case, the expected ionization potential of **11** would also be 9.35 instead of the observed 9.50 to 9.55. The magnitude of the effect would thus seem to be of the order of 0.2 eV.

Examination of the photoelectron spectrum of **11** also shows that the first ionization potential band is

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[7] R. Hoffmann and R. B. Davidson, *J. Amer. Chem. Soc.*, **93**, 5699 (1971); R. Gleiter, E. Heilbronner, M. Heckman, and H.-D. Martin, *Chem. Ber.*, in press.

[8] W. Schmidt and B. T. Wilkins, *Tetrahedron*, **28**, 5649 (1972).

[9] J. Almlöf, H. Johansen, B. Roos, and U. Wahlgren, *J. Electron Spectrosc. Relat. Phenomena*, in press.

[10] (a) The structure of norbornane was based on the average bond lengths and angles reported by G. Dallinga and L. Toneman, *Recl. Trav. Chim., Pays-Bas*, **87**, 795 (1968). See also J. Chiang, C. Wilcox, and S. Bauer, *J. Amer. Chem. Soc.*, **90**, 3149 (1968); Y. Morino, K. Kuchitsu, and A. Yokozeki, *Bull. Chem. Soc. Jap.*, **40**, 1552 (1967). (b) The numbering system in the model diisopropyl carbonium ion follows that of the norbornane.

[11] A. D. Bain, J. C. Bünzli, D. C. Frost, and L. Weiler, *J. Amer. Chem. Soc.*, **95**, 291 (1973).

[12] Dimethyl ether: (a) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, **No. 26**, 124 (1969); (b) B. J. Cocksey, J. H. D. Eland, and C. J. Danby, *J. Chem. Soc. B*, 790 (1971).

[13] Diethyl ether: 9.55 from ref 12a and K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957); 9.50 from ref 12b. Di-*tert*-butyl ether from ref 12b. Diisopropyl ether from H. Kaiser, Dissertation, University München, 1970. Tetrahydrofuran: 9.55 from ref 11, 9.50 from ref 14.

[14] C. Batich, D. O. Cowan, and E. Heilbronner, unpublished results.

[15] 7-Oxanorbornane: 9.55 from ref 11, 9.50 from ref 14.

[16] Dimethylethylene (butene-2) *cis* and *trans*: (a) E. Haselbach and E. Heilbronner, *Helv. Chim. Acta*, **53**, 684 (1970); (b) M. J. S. Dewar and S. D. Worley, *J. Chem. Phys.*, **50**, 654 (1969); (c) P. A. Clark, *Theor. Chim. Acta*, **28**, 75 (1972), who also reports the value for *trans*-diethylethylene.

[17] P. Bischof and E. Heilbronner, *Helv. Chim. Acta*, **53**, 1677 (1970).

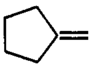
[18] P. Bischof, J. A. Hashmall, E. Heilbronner, and V. Hornung, *ibid.*, **52**, 1745 (1969).

unusually sharp, in accord with our conclusion that the oxygen 2p orbital in **11** is interacting less than normal with the skeletal σ orbitals.

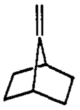
The 7-norbornyl carbonium ion is a favorite of rate enhancers, making frequent appearances as "[1]" in compilations of relative rate data. The exceptional unreactivity of its solvolytic precursors has long been noted.[19] The change in angle strain upon solvolysis has been believed to be responsible for this inertness.[20] Yet there are a number of indications that there may be other factors contributing to the destabilization of **10**. Tanida and Tsushima[21] have made a detailed study of the linear free energy relationships in substituted α-arylcycloalkyl chlorides.[22] The electron demand of the 7-norbornyl system is enormous. It has a Hammett ρ value of -5.64, by far the largest in the cycloalkyl series.[23] The methyl/H and phenyl/H acceleration ratios are similarly the highest known.[21,23,24] Model systems which would incorporate a similar angle strain as in **10** are hard to come by. Cyclobutyl cation would be a suitable model, but the solvolysis of its precursors is anchimerically assisted.[25] A better comparison may be obtained between tertiary cyclobutyl cations and tertiary 7-norbornyl cations. Despite the greater angle strain in the cyclobutyl case, the 7-norbornyl derivatives solvolyze some 10^3 slower.[21,24,26] We believe the available evidence, though indirect, supports the presence of a special destabilizing factor in the 7-norbornyl cation, which we believe is the symmetry enforced absence of a stabilizing interaction with high-lying σ orbitals of the cyclohexane structure.

In the chemistry of the 7-norbornyl cation a highly interesting finding is the large degree of retention of configuration in the solvolysis of precursors of the cation.[27] Our calculations, which perforce refer to a hypothetical nonsolvated cation, unfortunately do not explain this unusual result.[28]

A third manifestation of the ribbon orbital returns us again to photoelectron spectroscopy, now that of olefins. We compare the methylenecyclopentane (**12**) with the 7-methylenenorbornane (**13**). The anticipated trend in going from **12** to **13** (*cf.* the ionization potentials for cyclopentene and norbornene given above) would be a decrease in the magnitude of the ionization potential. In fact, an opposite increase of 0.25 eV occurs, from 9.15 in methylenecyclopentane[30] to 9.40 in methylenenorbornane.[31] The perturbed, or rather unperturbed, orbital is in this case the ethylene π level, but its symmetry properties are identical with those of the vacant cation orbital in **10** or the oxygen lone pair in **11**.



12



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Acknowledgment. We are grateful to the George Fisher Baker Lectureship which brought Edgar Heilbronner to Ithaca. Professor P. v. R. Schleyer was very helpful in providing us with some leading references and commentary in the carbonium ion field. The research of Roald Hoffmann and Phillip D. Mollère was supported by the National Science Foundation (GP 28137) and the National Institutes of Health (GM 13468).

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(19) J. D. Roberts, F. O. Johnson, and R. A. Carboni, *J. Amer. Chem. Soc.*, **76**, 5692 (1954); S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *ibid.*, **77**, 4183 (1955); E. E. van Tamelen and C. I. Judd, *ibid.*, **80**, 6305 (1958).

(20) P. v. R. Schleyer and R. C. Nicholas, *ibid.*, **83**, 182 (1961); P. v. R. Schleyer, *ibid.*, **86**, 1854 (1964); C. S. Foote, *ibid.*, **86**, 1853 (1964).

(21) H. Tanida and T. Tsushima, *ibid.*, **92**, 3397 (1970).

(22) See also P. G. Gassman and A. F. Fentiman, *ibid.*, **92**, 2549 (1970).

(23) A more extensive comparison is made by W. F. Sliwinski, T. M. Su, and P. v. R. Schleyer, *ibid.*, **94**, 133 (1972).

(24) D. E. Sunko, I. Szele, and M. Tomić, *Tetrahedron Lett.*, 1827 (1972).

(25) K. B. Wiberg, B. A. Hess, Jr., and A. J. Ashe, III, in "Carbonium Ions," Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1972, p 1295.

(26) K. L. Servis, S. Borčić, and D. E. Sunko, *Tetrahedron*, 24, 1247 (1968).

(27) P. G. Gassman and J. M. Hornback, *J. Amer. Chem. Soc.*, **89**, 2487 (1967); F. B. Miles, *ibid.*, **89**, 2488 (1967); **90**, 1265 (1968); P. G. Gassman, J. M. Hornback, and J. L. Marshall, *ibid.*, **90**, 6238 (1968).

(28) A MINDO/2 calculation of the 7-norbornyl cation has been published (ref 29). It predicts a significant tilting of the bridging group from a symmetrical position.

(29) M. J. S. Dewar and W. W. Schoeller, *Tetrahedron*, **27**, 4401 (1971).

(30) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," Wiley-Interscience, London, 1970.

(31) R. W. Hoffmann, R. Schüttler, W. Schäfer, and A. Schweig, *Angew. Chem.*, **84**, 533 (1972).