

product of the polyhedral expansion reaction,^{5,8} and structurally characterized⁹ as 2,3-(η -C₅H₅)₂-2,3-Co₂-1,7-C₂B₈H₁₀ by X-ray diffraction. The metal atoms occupy adjacent vertices in this isomer. While a large number of possible structures exist for I, II, IV, and V, we tentatively propose the following atomic arrangements based on a number of empirical observations of their spectral and physical properties; the carbon atoms are in 1,7 positions in all isomers, and cobalt positions are: I, 6,9; II, 3,9; IV, 2,5; and V, 3,6.¹⁰

Thermal polyhedral rearrangements of carboranes and metallocarboranes have been known for a number of years, but this is the first example of the preparation of an ($n + 1$)-vertex bimetallocarborane by pyrolysis of an n -vertex monometallocarborane. The synthesis of 12-vertex neutral species by pyrolysis of the cobalticinium salt of the commo-11-vertex complex is even more surprising.

Previous syntheses of (C₅H₅)₂Co₂C₂B₈H₁₀ isomers by polyhedral expansion^{5,8} or contraction¹² produced at most two isomers. The thermal intermolecular metal transfer process described here occurs in an energetically rich environment and would be expected to afford a diversity of products. The predominant production of icosahedral bimetallocarboranes indicates the greater kinetic or thermodynamic stability of 12-vertex polyhedra and also expands the range of isomeric (C₅H₅)₂-Co₂C₂B₈H₁₀ species available for further investigation. Generalization of this method to other metallocarboranes is under investigation and may afford a new source of heretofore unknown polymetallocarboranes of diverse structures.

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(8) W. J. Evans and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 611 (1972).

(9) K. P. Callahan, C. E. Strouse, A. L. Sims, and M. F. Hawthorne, manuscript in preparation.

(10) Isomers II and V are also formed^{2,11} by thermal rearrangement of 3,6-(π -C₅H₅)₂-3,6-Co₂-1,2-C₂B₈H₁₀¹² and similar rearrangements of the other isomers of (C₅H₅)₂Co₂C₂B₈H₁₀ are being examined to confirm the above assignments.

(11) B. Stibr, private communication.

(12) C. J. Jones and M. F. Hawthorne, *Inorg. Chem.*, 12, 608 (1973).

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Interconverting Cyclopropylcarbinyl Cations

Sir:

One of the longest sought after goals in mechanistic carbonium ion chemistry has been the nature of the intermediate involved in the rapid equilibration of cyclopropylcarbinyl, cyclobutyl, and homoallyl derivatives in protic solvents.¹ The suggestion, made more than a quarter of a century ago by Winstein and Adams,² that a cation might be involved has received

(1) For an excellent recent review see: K. B. Wiberg, B. A. Hess, Jr., and A. J. Ashe, III, in "Carbonium Ions," G. A. Olah and P. v. R. Schleyer, Ed., Vol. 3, Wiley, New York, N. Y., 1972, p 1295.

(2) S. Winstein and R. Adams, *J. Amer. Chem. Soc.*, 70, 838 (1948).

overwhelming support and has led to two schools of thought. Reasoning primarily from product and rate data, the first preferred the existence of either one of the cyclopropylcarbinyl (I), cyclobutyl (II), or homoallyl cations or a rapid equilibration among two or more of them. More recently, however, Olah and his collaborators³ have suggested the inadequacy of these "classical" representations.

While all indications point to classical structures for methyl and (geminally) dimethyl-substituted cyclopropylcarbinyl cations, with no sign of either degenerate rearrangement processes or equilibration with other forms taking place, the data seem not to be interpretable as such for the parent species. Rather, Olah best represents his (¹H and ¹³C) nmr data in terms of a rapidly equilibrating set of σ delocalized structures.



It strikes these authors that Olah's strongest argument for such an assignment (or rather for deviation from a classical picture) rests not so much on direct structural evidence gathered for parent C₃H₇⁺, but more on the observed lack of consistency between the nmr parameters for methyl-substituted ions and that for the parent itself.

In this communication we present evidence, resulting from theoretical *ab initio* molecular orbital calculations,⁴ for a classical bisected cyclopropylcarbinyl type structure for all three ions. We suggest, moreover, that while parent C₃H₇⁺ may readily undergo facile degenerate rearrangement interconverting the three equivalent cyclopropylcarbinyl valence tautomers, the introduction of either one or two (geminal) methyl substituents greatly enhances the stability of but one cyclopropylcarbinyl form effectively blocking the possibility of further rearrangement.

Recently we reported that all forms of the homoallyl cation collapsed without activation energy to bisected cyclopropylcarbinyl (I).⁸ We have now resolved the structure of the puckered cyclobutyl cation (II) on this same potential surface. We find that like the homoallyl systems, the puckered cyclobutyl cation is unstable with respect to distortion in the direction of bisected cyclopropylcarbinyl, and hence may be thought of as one possible transition state to degenerate cyclopropylcarbinyl-cyclopropylcarbinyl rearrangement. 4-31G level calculations indicate an activation of 9.4 kcal/mol (the difference in stabilities between ground-state cyclopropylcarbinyl and the puckered cyclobutyl

(3) G. A. Olah, C. L. Jeuell, D. P. Kelly, and R. D. Porter, *J. Amer. Chem. Soc.*, 94, 146 (1972).

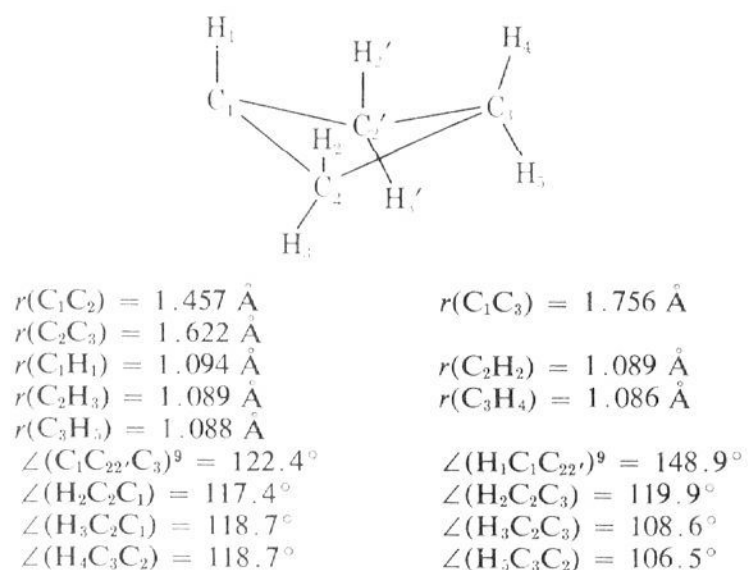
(4) The minimal STO-3G basis⁵ has been used to calculate equilibrium and transition state geometries. Computations at interesting points on the resulting potential surface are then performed using the 4-31G extended basis set⁶ in order to more accurately access relative molecular energetics. All calculations have been carried out using the GAUSSIAN 70 series of computer programs.⁷

(5) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, 51, 2657 (1969).

(6) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, 54, 724 (1971).

(7) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Ind., program no. 236.

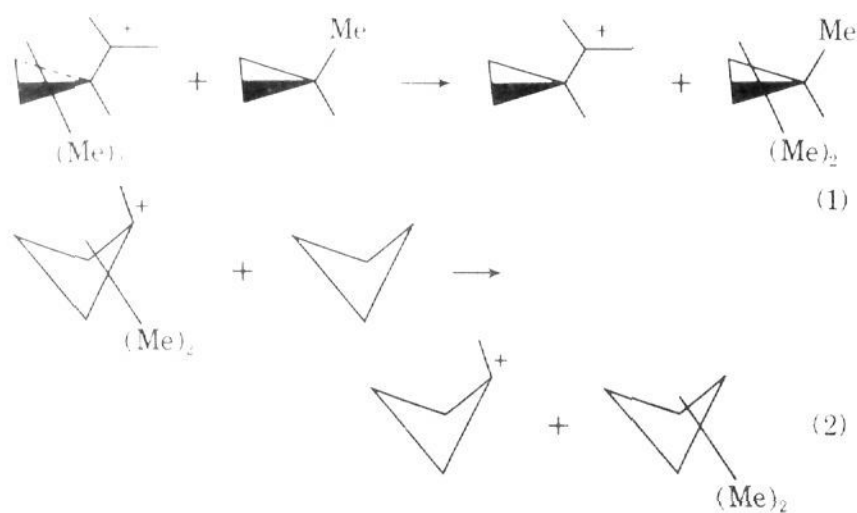
(8) W. J. Hehre and P. C. Hiberty, *J. Amer. Chem. Soc.*, 94, 5917 (1972).



cation); however, this value is probably subject to some modification in light of known deviations of theory from experiment in the comparison of the relative energies of similar tautomeric pairs in the neutral hydrocarbons.¹⁰

For example, the theory underestimates the stability of cyclobutene with respect to methylenecyclopropane by 5.1 kcal/mol. On the other hand saturated cyclobutane is calculated by 4-31G to be 1.8 kcal/mol lower in energy than methylcyclopropane, while in fact the latter is energetically the favored (by 0.7 kcal/mol). The spectrum of probable rearrangement energies is given in Figure 1. The error range is admittedly wide; however, it does indicate that while the activation required for degenerate rearrangement through a puckered cyclobutyl cation is indeed small it is probably not zero, and that bisected cyclopropylcarbinyl is likely the theory's choice for the $C_4H_7^+$ ground state.

Consider now what happens to this interconversion potential when we introduce a geminal pair of methyl substituents. In cyclopropylcarbinyl itself, it is apparent that substituent groups directly bonded to the positively charged center will have a much greater stabilizing effect than those further removed. Similarly, because the (formal) location of the positive charge in puckered cyclobutyl cation is not accessible to our pair of substituent groups, their effect here is not expected to be as great as in the optimum cyclopropylcarbinyl case. We may estimate the stabilizing effects of geminal methyl substituents on the bisected cyclopropylcarbinyl and puckered cyclobutyl cations by use of *isodesmic*¹¹ reactions 1 and 2, the energies of which



(9) C_{mid} is the midpoint of the line connecting carbons 2 and 2'.

(10) W. J. Hehre and J. A. Pople, manuscript in preparation.

(11) W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 4796 (1970).

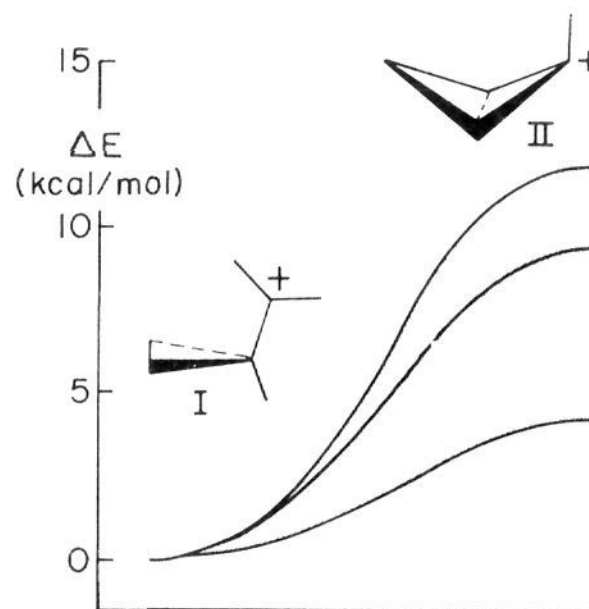


Figure 1. Interconversion of cyclopropylcarbinyl and cyclobutyl cations. The coordinate is the angle $C_2C_1C_3$.

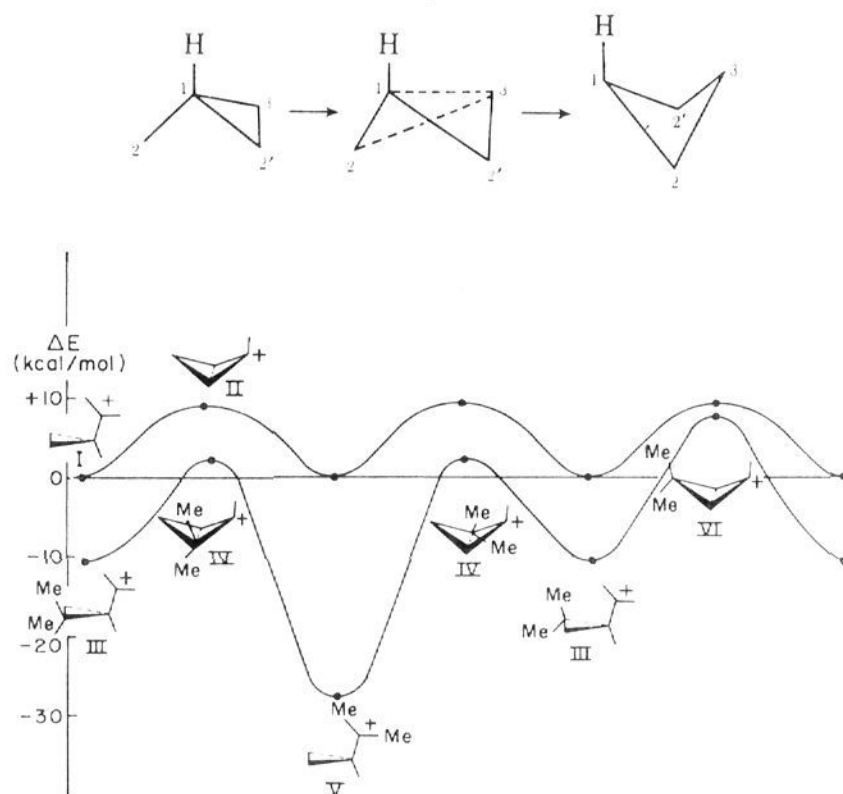


Figure 2. Rearrangement in cyclopropylcarbinyl (upper curve) and dimethylcyclopropylcarbinyl (lower curve). Reaction coordinate as above. See text for details.

are expected to be reasonably well described by simple levels of *ab initio* molecular orbital theory (STO-3G basis). Combining these methyl stabilization data with our theoretical potential for rearrangement in parent $C_4H_7^+$ the scheme depicted in Figure 2 results. Whereas interconversion of parent cyclopropylcarbinyl is a facile process (and at the lower theoretical estimate, resolution within the normal nmr time scale of the individual forms is not likely) the picture presented here for the dimethyl-substituted ions is quite different. Indeed, dimethylcyclopropylcarbinyl (V) itself is predicted to lie some 30 kcal/mol below the 2,2-dimethylcyclobutyl cation transition states (IV), effectively blocking any possible exit.¹²

(12) The observation of hindered rotation in dimethylcyclopropylcarbinyl¹³ is entirely in keeping with our findings, and is a process which certainly could occur without the energy required for rearrangement to other structures. Thus, both the experimental and theoretical barriers hindering rotation about the cyclopropyl cationic center bond (13.7 and 16.6 kcal/mol, respectively) are well below the depth of the potential to rearrangement. Restricted rotation in the parent (requiring a predicted 31 kcal/mol), however, is not likely to be observed due to intervention of the much more facile rearrangement process.

(13) D. S. Kabakoff and E. Namanworth, *J. Amer. Chem. Soc.*, **92**, 3234 (1970).

In conclusion we suggest that there is no fundamental difference between the structure of dimethyl-substituted cyclopropylcarbinyl and that of the parent ion,¹⁴ but rather prefer to interpret the contrasting experimental observations on the two in terms of a difference in dynamical behavior. Whereas the unsubstituted ion may pass with little hindrance from one cyclopropylcarbinyl-like structure to another, the potential surrounding dimethylcyclopropylcarbinyl is much deeper and passage to the outside much the more unlikely. We suggest furthermore that the experiment of choice to resolve the controversy is one with a very much shorter time scale than the nmr. Electron spectroscopy may possibly fill that gap.¹⁵

(14) Preliminary investigations on the geometrical structures of bisected mono- and dimethyl-substituted cyclopropylcarbinyls indicate a gradual change from the parent. Thus, for example, the ring-exocyclic methylene bond increases from 1.384 Å in the parent⁸ to 1.416 Å in methylcyclopropylcarbinyl to 1.426 Å in the dimethyl-substituted ion; P. C. Hiberty, Thèse de Troisième Cycle, Université de Paris-Sud, Orsay, 1973.

(15) G. A. Olah, G. D. Mateescu, L. A. Wilson, and M. H. Gross, *J. Amer. Chem. Soc.*, **92**, 7231 (1970); G. A. Olah, G. D. Mateescu, and J. L. Riemenschneider, *ibid.*, **94**, 2529 (1972); G. D. Mateescu, J. L. Riemenschneider, J. J. Svoboda, and G. A. Olah, *ibid.*, **94**, 7191 (1972).

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Infrared Spectroscopic Evidence for "Nitrogen Hypofluorite," an Isomer of Nitrosyl Fluoride, in Inert Gas Matrices

Sir:

The gas-phase reaction of nitric oxide and fluorine is known to proceed vigorously and quantitatively^{1,2} even under mild conditions³ to produce nitrosyl fluoride, FNO, which contains a fluorine atom bound to the more electropositive nitrogen. The FNO molecule is generally depicted as a loosely bound combination of a fluorine atom and the NO radical,⁴⁻⁶ owing to the unusually low N-F force constant (2.3 mdyne Å⁻¹)⁷ and an N-O force constant (15.9 mdyne Å⁻¹) which is virtually the same as that of free NO (15.5 mdyne Å⁻¹).⁸ Various bonding studies have supported this interpretation.⁹⁻¹³

(1) H. S. Johnston and H. J. Bertin, *J. Amer. Chem. Soc.*, **81**, 6402 (1959).

(2) R. Schmutzler, *Angew. Chem., Int. Ed. Engl.*, **7**, 440 (1968).

(3) H. S. Johnston and H. J. Bertin, *J. Mol. Spectrosc.*, **3**, 683 (1959).

(4) J. Mason and W. VanBronswijk, *J. Chem. Soc. D*, 357 (1969).

(5) L. O. Anderson, J. Mason, and W. VanBronswijk, *J. Chem. Soc. A*, 296 (1970).

(6) K. Ramaswamy and R. Namasivayan, *Z. Phys. Chem., (Leipzig)*, **245**, 224 (1970).

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(9) S. D. Peyerimhoff and R. J. Buenker, *Theor. Chim. Acta*, **9**, 103 (1967).

(10) C. Petrongolo, E. Scrocco, and J. Tomasi, *J. Chem. Phys.*, **48**, 407 (1968).

(11) M. S. Gordon and J. A. Pople, *J. Chem. Phys.*, **49**, 4643 (1968).

(12) B. Tinland, *J. Mol. Struct.*, **3**, 256 (1969).

(13) R. D. Brown, F. R. Burden, and G. R. Williams, *Theor. Chim. Acta*, **18**, 98 (1970).

In a recent *ab initio* molecular orbital study of the FNO molecule,¹⁴ and an earlier description of its bonding,¹⁵ the possibility of its OF-bonded hypofluorite isomer, NOF, existing under certain conditions was raised. Although predicted to be less stable than the FNO form, it seemed to us that the kinetic stability of the isomeric NOF might be enhanced at extremely low temperatures (8–20°K) in an unreactive matrix.

Separate samples of nitric oxide and fluorine at high dilution in argon and nitrogen were simultaneously deposited onto a cesium iodide window at 8°K through separate spray-on lines (316 SS) oriented at 45° to the window and 90° to each other. Deposition rates through each spray-on line were monitored at *ca.* 0.5–1.0 mmol/hr by previously calibrated thermocouple readings downstream of the vernier metering valves. Prior to deposition, all sample manipulations were carried out in a passivated 316 SS vacuum manifold with Teflon seals.

When a sample of fluorine in nitrogen at an *M/R* = 250 (molar ratio of matrix to reactant gas) was simultaneously codeposited with an equivalent sample of NO in nitrogen (*M/R* = 250) onto an 8°K CsI window, a total of three new major absorption bands appeared in the infrared spectrum in addition to those normally attributed to NF-bonded FNO.¹⁶ These new bands, depicted in Figure 1a, consist of a weak feature in the vicinity of 1900 cm⁻¹ ($\nu(\text{N}=\text{O})$ region) and two stronger doublets centered at *ca.* 725 and 480 cm⁻¹, the $\delta(\text{FNO})$ and $\nu(\text{N}-\text{F})$ regions, respectively, of FNO.⁷ A similar experiment with argon as the matrix material produced three similar bands which were, however, unsplit, suggesting that the doublet structure of the lower frequency bands in the nitrogen matrix, with splittings of only 3–4 cm⁻¹, is the result of a matrix site effect. Absorption frequencies are listed in Table I. As is

Table I. Infrared Absorptions (cm⁻¹) of F(NO) Isomers

Assignment	Ar Matrix	N ₂ Matrix
FNO $\nu(\text{N}=\text{O})$	1852.1 vs	1869.7 vs
$\delta(\text{FNO})$	751.4 s	740.9 vs 737.5 m, sh
$\nu(\text{N}-\text{F})$	510.1 ms	497.0 vs 494.3 w, sh
NOF $\nu(\text{N}=\text{O})$	1886.6 w	1904.1 m
$\delta(\text{NOF})$	735.1 ms	724.6 ms 721.8 m
$\nu(\text{O}-\text{F})$	492.2 m	485.4 s, sh 480.9 s

normally the case, trace amounts of various noncondensable (at -196°) impurities were present in the fluorine samples (N₂, O₂, OF₂), but these did not interfere in the spectra.

Photolysis ($\lambda \geq 200$ nm) of the nitrogen matrix sample resulted in a noticeable decrease in intensity of these three new features, while those associated with FNO increased in intensity (Figure 1b). Even under conditions of lower energy radiation (λ 360 nm) and shorter periods of photolysis (*i.e.*, 15 min), the bands in

(14) J. Peslak, D. S. Klett, and C. W. David, *J. Amer. Chem. Soc.*, **93**, 5001 (1971).

(15) R. D. Spratley and G. C. Pimentel, *J. Amer. Chem. Soc.*, **88**, 2394 (1966).

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