diation) indicated that the crystals were triclinic, and the successful refinement of the structure has confirmed the space group as $P\bar{1}$. Reduced cell parameters were obtained from precession photographs which were corrected for shrinkage by superposition of a previously oriented NaCl lattice. Measurements were made directly from the photographs using a film measuring device supplied by Charles Supper Co. A total of 30 reflections were used to obtain reduced cell parameters of a = 7.564 (7) Å, b = 9.547 (8) Å, c = 9.575 (8) Å, α = 111.83 (10)°, β = 96.32 (8)°, and γ = 100.25 (9)°; the density calculated for one trimer per unit cell, 1.64 g cm^{-3}, agrees well with the experimental value, 1.62 g cm^{-3}, obtained by the flotation method in a mixture of methyl iodide and carbon tetrachloride. Intensity data were collected on a Philips PAILRED diffractometer using equiinclination geometry and a continuous ω-scan technique. Cu Kα radiation (λ 1.5418 Å) and a graphite monochromator crystal (d(002) = 3.3539 Å) were used. A total of 2057 reflections were chosen as above background on the basis of the acceptance criterion that $\sigma(I)/I < 0.5$. The reflections were corrected for Lorentz and polarization effects as well as for absorption. The standard heavy atom technique was employed to locate the positions of all non-hydrogen atoms. Full-matrix least-squares refinement of the coordinates and anisotropic temperature factors of all the non-hydrogen atoms have resulted in a conventional R value,

$$R = (\Sigma|F_o - F_c|)/(\Sigma|F_o|)$$

of 0.042 and a weighted R_w value

$$R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2\}^{1/2}$$

of 0.073 using a weighting scheme in which the weights, $w = 1.0/|\Delta\bar{F}|^2$, were obtained from a plot of $|\Delta\bar{F}|$ vs. $|\bar{F}_o|$. Further refinement is in progress, but the main features of the structure are apparent at this stage.

The unit cell contains only one trimeric unit and is illustrated with an atomic numbering scheme in Figure 1. The central copper atom, Cu1 rests on a site of inversion in the space group $P\bar{1}$, which for simplicity was arbitrarily chosen to be the origin of the cell. Copper ions 2 and 2′, which occupy general positions, are centrosymmetrically related to one another and, consequently, lie in a straight line relationship thru the origin defined at Cu1. The copper ions are held together by μ_2-bridging oxygens, O3, O3′, O6, and O6′, from the propoxide portions of the trinegative diimine ligand. The coordination about Cu2 is square planar, and consists of two bridging propoxide oxygens and two imine nitrogen atoms from the same ligand; no donor atom deviates from the coordination plane by more than 0.04 Å (N5, −0.02 (1) Å; N4, 0.02 (1) Å; O3, 0.02 (1) Å; O6, −0.03 (1) Å; and Cu2, 0.02 (1) Å). The four coordination about Cu1 is strictly planar as required by symmetry and consists of four μ_2-bridging propoxide oxygens, two from each of the two tetradentate diimine ligands of the trimer.

Although both Cu1 and Cu2 have square planar coordination, this does not give rise to an entirely planar trimeric unit. Instead, there is a noticeable bend in the Cu_2O_2 four-membered ring as measured by the dihedral angle, 10.2 (4)°, between the Cu1-O3-O6 and Cu2-O3-O6 planes. This nonplanarity in the Cu_2O_2 ring is evident from Figure 1 in that the propanolamine carbons (C16, C17, C15 and C7, C8, C9) are tilted in the same direction away from the coordination plane about Cu2. It is interesting to note that the ligand atoms of the six-membered ring (N5, C13, C12, C11, and N4) are also tilted (in the opposite direction) out of the coordination plane about Cu2, even though the bond lengths, angles, and planarity of the six-membered ring are indicative of a delocalized π-system.

The copper-copper distance of 3.017 (1) Å is only slightly shorter than that reported,[11] 3.026 (6) Å, for the parent dinuclear complex, $[Cu(PIA)]_2$, and is likely due to the bending of the Cu_2O_2 ring. Despite the nonplanarity of the Cu_2O_2 ring, it is evident from the magnetic moment at room temperature, 1.09 BM/(g atom of Cu), that strong antiferromagnetic interactions are operating within the Cu_2O_2 ring. This follows from the fact that there are no intertrimer contacts within 4 Å of either copper atom. Consequently, the principal coupling interaction cannot be interclusteral, but intramolecular. In addition, the bent Cu_2O_2 bridge is indicative of indirect coupling via a σ-pathway, since the effectiveness of a π-pathway would be greatly diminished. The efficiency of a predominately σ-pathway is evidenced in the nearly invariant magnetic moment below room temperature; the magnetic moment per copper drops only 0.04 BM (from 1.09 to 1.05 BM) on lowering the temperature from 296 to 35°K. In effect, two of the three electrons of the copper trimer are paired, and only the spin-doublet state is populated. This behavior is analogous to that found for the copper complexes, $Cu_3(PAO)_3(OH)(SO_4)\cdot 16.3H_2O$ and $Cu_3(PrAO)_3(H_2O)_3O_{0.5}(OH)_{0.5}(ClO_4)_{1.5}\cdot 4H_2O$, whose molecular structures[8,9] have revealed an equilateral triangular array of copper ions (PAO = pyridinaldoxime, and PrAO = 2-propylamino-2-methyl-3-butanone oxime; both PAO and PrAO are minus the oxime proton).

Further work on the synthesis, structure, and magnetic properties of other metal complexes containing diimine ligands is in progress.

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References and Notes

(1) R. Beckett, R. Colton, B. B. Hoskins, R. L. Martin, and D. G. Vince, *Aust. J. Chem.*, **22**, 2527 (1969).
(2) J. O. Miners, E. Sinn, R. B. Coles, and C. M. Harris, *J. Chem. Soc., Dalton Trans.*, 1149 (1972).
(3) S. J. Gruber, C. M. Harris, and E. Sinn, *J. Chem. Phys.*, **49**, 2183 (1968).
(4) C. B. Singh and B. Sahoo, *J. Inorg. Nucl. Chem.*, **36**, 1259 (1974).
(5) S. J. Gruber, C. M. Harris, and E. Sinn, *J. Inorg. Nucl. Chem.*, **30**, 1805 (1968).
(6) J. G. Mohanty, S. Baral, R. P. Singh, and A. Chakravorty, *Inorg. Nucl. Chem. Lett.*, **10**, 655 (1974).
(7) J. M. Epstein, B. N. Figgis, A. H. White, and A. C. Willis, *J. Chem. Soc., Dalton Trans.*, 1954 (1974).
(8) P. R. Ross, R. K. Murmann, and E. O. Schlemper, *Acta Crystallogr. Sect. B*, **30**, 1120 (1974).
(9) R. Beckett and B. F. Hoskins, *J. Chem. Soc., Dalton Trans.*, 291 (1972).
(10) E. Sinn, *Coord. Chem. Rev.*, **5**, 313 (1970).
(11) J. A. Bertrand and J. A. Kelley, *Inorg. Chim. Acta*, **4**, 203 (1970).

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Frontier Orbital Resolution of the Quadricyclyl Cation Puzzle[1]

Sir:

A cyclopropane ring is known to enhance the rate of solvolysis at an adjacent incipient carbocation center by a factor of ~10^9. This enhancement is consistent with the rate of solvolysis for norticyclyl cation (**2**) relative to the unstabilized[2] 7-norbornyl cation (**1**).[3] Furthermore, these stabilizations have been shown to be largely additive upon multiple

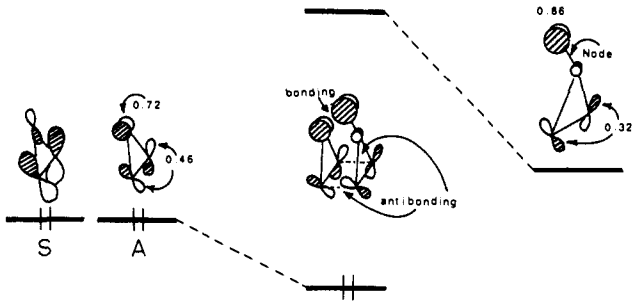
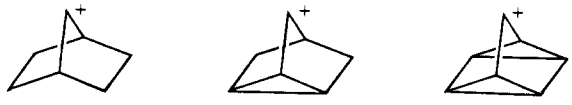


Figure 1. Interaction diagram for formation of quadricyclyl cation.

cyclopropyl substitution [an experimental observation[4] which can be explained by the high concentration of charge at the carbinyl carbon in the LUMO (lowest unoccupied molecular orbital) of the parent cyclopropyl carbinyl cation].[5] This generalization finds an exception in the rate enhancement because of introduction of a second cyclopropane in the nortricyclyl skeleton to form the quadricyclyl system (**3**); this second cyclopropane provides a mere 20-fold rate increase, whereas strict additivity of stabilization energies would dictate a 6×10^8-fold enhancement relative to **2**.[3] This puzzle has been explained by noting that only one of the two equivalent groups in **3** can be interacting with the cationic center.[6] It is the purpose of this communication to shed new light on this old problem via an elaboration of the simple "frontier orbital"[7] ideas which have recently been applied to carbocation substituent effects.[2,5,8]



1 k_{rel}: 1 | **2** 6×10^8 | **3** 10^{10}

The most important contribution in the perturbation theory[9] expression for stabilization of a cation by a substituent is the interaction of the unsubstituted cation LUMO with the substituent HOMO (highest occupied MO).[7] The magnitude of this interaction is given by (1), where H_{L-H} is

$$\frac{(H_{L-H})^2}{\Delta E} \approx \frac{K\left(\sum_{ij} C_H{}^i C_L{}^j\right)^2}{\Delta E} \qquad (1)$$

the resonance integral between cation LUMO and substituent HOMO, ΔE is the energy difference between these MO's, $C_H{}^i$ is the coefficient of atomic orbital i in the substituent HOMO, $C_L{}^j$ is the coefficient of atomic orbital j in the cation LUMO, K is a proportionality constant, and the summation is taken over only adjacent atoms, i and j.

The combination of the HOMO of cyclopropane with the LUMO[10] of cyclopropyl carbinyl cation to form the quadricyclyl cation is depicted in Figure 1. A large bonding interaction between the carbinyl carbon and the adjacent cyclopropane carbon predominates; however, this is substantially counteracted by the two antibonding interactions across the base of the tetracyclic ring system. The net effect is a small stabilization upon introduction of this second cyclopropane.[11]

In the quadricyclyl cation, the secondary destabilizing interaction may be traced, therefore, to the phase reversal between the carbinyl carbon and the cyclopropane ring in the cation fragment (Figure 1). This destabilization can be overcome simply by insulating the interacting centers from each other via inserted methylene groups as in **4**.[12] More cleverly, one may introduce a second phase reversal in the

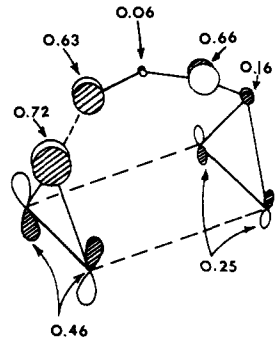
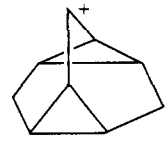


Figure 2. Interaction of the HOMO of cyclopropane with the LUMO of cyclopropylallyl cation.



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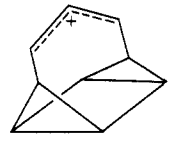
LUMO and thus produce a stabilizing secondary interaction. This can be realized in cation **5** as seen in Figure 2.[13]



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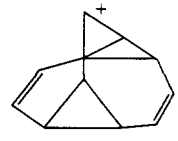
Similarly reversal of phase in the cyclopropane HOMO can be achieved by appending two vinyl groups as in **6**. This is not expected to offer quite as dramatic a stabilization as **5**, however.



6

Finally, it is of interest to compare these complex tetracyclic through bond interactions with their through-space bicyclic (i.e., longicyclic)[14] counterparts. Synthetically, the cations **3**, **5**, and **6** may all be, in principle, prepared by photochemical ring closure of a bicyclic π system (**7**, **8**, and **9**,

7 **8** **9**

respectively). The bicyclic cations thus identified display stabilities[14] antiparallel to those of their tetracyclic counterparts (a phenomenon which may be generalized).

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References and Notes

(1) A portion of this work is detailed in L. M. Loew, Ph.D. Thesis, Cornell University, 1974.
(2) R. Hoffmann, P. D. Mollère, and E. Heilbronner, *J. Am. Chem. Soc.*, **95**, 4860 (1973).
(3) H. G. Richey, Jr., and N. C. Buckley, *J. Am. Chem. Soc.*, **85**, 3057 (1963).

(4) H. Hart and J. M. Sandri, *J. Am. Chem. Soc.*, **81**, 320 (1959); H. Hart and D. A. Law, *ibid.*, **86**, 1957 (1964); L. Birladeanu, T. Hanafusa, B. Johnson, and S. Winstein, *ibid.*, **88**, 2316 (1966).
(5) C. F. Wilcox, L. M. Loew, and R. Hoffmann, *J. Am. Chem. Soc.*, **95**, 8192 (1973).
(6) P. R. Story and S. R. Fahrenholtz, *J. Am. Chem. Soc.*, **86**, 527 (1964); R. E. Leone, J. C. Barborak, and P. v. R. Schleyer in "Carbonium Ions", Vol. IV, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1973, p 1860.
(7) K. Fukui, *Fortschr. Chem. Forsch.*, **15**, 1 (1970), and references cited therein.
(8) C. F. Wilcox, Jr., L. M. Loew, R. G. Jesaitis, S. Belin, and J. N. C. Hsu, *J. Am. Chem. Soc.*, **96**, 4061 (1974).
(9) R. Hoffmann, *Acc. Chem. Res.*, **4**, 1 (1970); M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New York, N.Y., 1969; E. Heilbronner and H. Bock, "Das HMO-Modell und seine Anwendung", Verlag Chemie, Weinheim/Bergstr., Germany, 1968.
(10 Calculational methods are described in ref 5.
(11) Using perturbation expression 1, one finds:

$$\text{stabilization} \propto \frac{[(0.72)(0.86) - 2(0.46)(0.32)]^2}{\Delta E_{2\text{-}3}} = \frac{0.11}{\Delta E_{2\text{-}3}}$$

This is to be compared with the stabilization of nortricyclyl which can be thought of as simply the interaction of methyl cation LUMO with cyclopropane HOMO

$$= \frac{[(1.00)(0.72)]^2}{\Delta E_{1\text{-}2}} = \frac{0.52}{\Delta E_{1\text{-}2}}$$

Thus the stabilization energy due to the second cyclopropane in quadricyclyl should be no greater than 0.11/0.52 = 0.21 of the initial stabilization in nortricyclyl. This fraction is reduced still further since $|\Delta E_{1\text{-}2}| < |\Delta E_{2\text{-}3}|$ (i.e., the methyl cation LUMO is lower than the cyclopropyl carbinyl LUMO). This simple perturbation theory result is to be compared with the experimental relative rates

$$\frac{\log\left(\frac{k_3}{k_2}\right)}{\log\left(\frac{k_2}{k_1}\right)} = \frac{1.2}{8.8} = 0.14$$

(12) This species is stabilized yet further, of course, because of relief of angle strain at the cationic center. It is the intention of this paper to focus on only electronic effects, however.
(13) Using the procedure of ref 11, $(H_{L-H})^2 \propto 0.47$ for the interaction of cyclopropane with the already strongly stabilized cyclopropyl allyl cation; this represents 90% of the stabilization due to interaction of cyclopropane with methyl cation.
(14) M. J. Goldstein, *J. Am. Chem. Soc.*, **89**, 6357 (1967); M. J. Goldstein and R. Hoffmann, *ibid.*, **93**, 6193 (1971).

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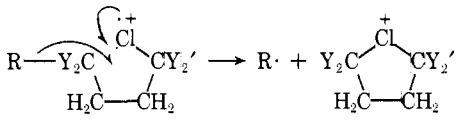
The Gaseous Tetramethylenechloronium Ion[1]

Sir:

The formation of chloronium and bromonium ions in the gas phase was postulated[2] to explain the dominant peaks in the mass spectra of higher 1-haloalkanes (eq 1). Despite the apparent general acceptance of this rationalization,[3] and the postulation of similar cyclization-displacement reactions involving anchimeric assistance to explain[3] unusual



(1)

1, R = C_2H_5; Y = Y′ = H
1a, R = C_2H_5; Y = H; Y′ = D
1b, R = C_2H_5; Y = D; Y′ = H

2

Table I. Partial Mass Spectra of Labeled 1-Chlorohexanes

Compound	m/e	90	91	92	93	94	95
		Relative abundance					
1-Chlorohexane		0.3	72.	3.6	23.	1.3	
1-Chlorohexane-*1,1*-d_2			0.2	1.9	70.	3.8	23
1-Chlorohexane-*4,4*-d_2			0.5	1.6	71.	3.8	22

Table II. Collisional Activation Spectra of $C_4H_8{}^{35}Cl^+$ and $C_4H_6D_2{}^{35}Cl^+$ Ions[13]

m/e	1-Chloroheptane[a]	1-Chlorohexane[a]	1-Chlorohexane, 18 eV[a]	1-Chlorohexane-*1,1*-d_2[b]	1-Chlorohexane-*4,4*-d_2
27	16	15	16	8.0	7.4
28	4	4	4	8.5	8.0
29	9.2	10	9.1	5.4	5.5
30				5.6	5.0
31				3.4	3.3
39	14	15	14	7.5	7.1
40	2	2.	2	7.2	7.1
41	9.6	9.5	8.3	5.9	5.7
42				3.7	3.6
43				4.0	4.0
47	1.1	1.2	1.5	1.0	1.0
48	0.5	0.5	0.5	0.5	0.5
49	12	12	10	5.7	5.2
50	1.	1.	1.	2.6	2.7
51	3.4	3.3	3.6	5.5	5.2
52	0.5	0.5	0.5	1.5	2.0
53	7.2	6.5	6.7	1.7	1.5
54	<2	<2	<3	3.0	3.0
(55)	(140)	(180)	(110)	3.5	3.5
61	4.3	4.3	4.1	2.	2.
(62)	(15)	(16)	(13)	(7)	(7)
(63)	(19)	(21)	(16)	(8)	(8)
73	1.	1.0	1.1	0.4	0.4
74		0.1	0.1	0.4	0.3
75	4.	3.5	4.3	1.0	0.9
76		0.5	1.	1.3	1.3
77				1.2	1.2
78				0.2	0.2
90	10	11	12	0.2	0.3
91				0.7	1.1
92				5.5	7.6

[a] Abundances are relative to the total ion abundance = 100, excluding m/e 55, 62, and 63 which arise in part from metastable ion decompositions. [b] Abundances are relative to the total = 100 for the ions used in footnote *a* and their deuteriated derivatives; contribution of such ions to m/e 62 and 63 is assumed to be 3/100.

peaks in the spectra of *n*-alkyl amines, thiols, nitriles, and ketones,[4] no direct evidence for such ion structures has yet been presented. Cyclic halonium ions have been identified in SbF_5-SO_2 solution by Olah, Peterson, and their coworkers,[5] supporting previous postulates of 1,2- and 1,4-halonium ion participation in solvolysis. However, although relatively high stabilities are found for tetramethylenehalonium (Cl, Br, I) and ethylenehalonium ions in solution,[5] mass spectral examples in which high ion abundance indicates such special stabilization have been found only for $C_4H_8Cl^+$ and $C_4H_8Br^+$ ions and not for gaseous ions such as $C_4H_8I^+$, $C_2H_4Cl^+$, or $C_2H_4Br^+$. Recent ion-molecule reaction studies[6] indicate that $C_4H_8Br^+$ ions are substantially more stable than $C_2H_4Br^+$ ions. Theoretical studies[7] utilizing ab initio calculations, which neglect solvent effects, also predict the ethylenehalonium ions to be stable. Thus we felt that unequivocal evidence for the structure of the parent tetramethylenechloronium ion **1** in the gas phase was necessary before further comparisons of gas and solution phase behavior of these ions was warranted.

The base peak in the spectrum of 1-chlorohexane, **1**, has the composition $C_4H_8Cl^+$. In the mass spectra of both 1-