

Structure and Stability of the Carbocations $C_2H_3^+$ and $C_2H_4X^+$, X = H, F, Cl, and CH_3 . Ab Initio Investigation Including Electron Correlation and a Comparison with MINDO/3 Results

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Abstract: Ab initio calculations both at the SCF level and with inclusion of electron correlation in the framework of the IEPA-PNO, PNO-Cl, and CEPA-PNO methods were performed for the title molecules. The geometries were taken from previous ab initio calculations. Electron correlation turns out to be crucial for a satisfactory description of relative stabilities. For $C_2H_3^+$ and $C_2H_5^+$ we compute, with the CEPA method, the nonclassical structures to be more stable than the classical ones by 4.0 and 6.4 kcal/mol, respectively. $CH_2FCH_2^+$ (nonclassical) is only slightly more stable than $CH_2FCH_2^+$ (classical) ($\Delta E(\text{CEPA}) = 1.4$ kcal/mol) whereas for the analogous chlorine compounds $\Delta E(\text{CEPA}) = 30.0$ kcal/mol. The most stable $C_3H_7^+$ isomer is the isopropyl cation. We find edge-protonated cyclopropane more stable than corner-protonated cyclopropane by 5 kcal/mol. For the pure hydrocarbon systems MINDO/3 results are in good agreement with the CEPA values. In the case of the haloethyl cations the MINDO/3 method exaggerates by far the stability of the nonclassical structure. In the MINDO/3 calculations all structures were characterized by the matrix of force constants.

I. Introduction

The widespread occurrence of carbocations as reaction intermediates in many organic reactions¹⁻⁶ and their preparation in superacid media⁷ have stimulated a large number of theoretical investigations by semiempirical⁸⁻¹⁵ and ab initio methods.¹⁶⁻³⁴ The addition of protons and halogens to olefins has long been known to be electrophilic³⁵ producing intermediate carbenium or carbonium ions.³⁶ For the ions $C_2H_3^+$ (vinyl cation) and $C_2H_4X^+$ (ethyl cation or haloethyl cation) the classical structures (carbenium ions) Ia, IIa, and IIc and the nonclassical ones (carbonium ions) Ic and IIb are considered (see Figure 1). From experimental evidence^{37,38} it is impossible to decide whether the classical or nonclassical structure of isolated $C_2H_5^+$ is more stable.

NMR investigations of haloethyl cations in solvents of low nucleophilicity show that the position of equilibrium depends strongly on the halogen substituent: iodine and bromine compounds are cyclic.^{7,40-45} Substituted chloroethyl cations are also usually cyclic but the parent (unsubstituted) cation forms an equilibrium mixture of the cyclic and open structures IIb and IIc.^{46,47} The open fluorine compounds IIc which rapidly exchanges fluorine with the superacid solvent was observed^{46,48} but no cyclic structure has been found to date.

The nature of bonding in the haloethyl cations is still a matter of considerable dispute. In recent works^{27,41} direct analogy with conventional three-membered heterocycles was favored.

Protonated cyclopropane has been studied intensively both by experimental⁴⁹⁻⁵⁴ and theoretical methods.^{13,14,21,29,30} In spite of the great efforts it is still unclear whether the edge-protonated form V or the corner-protonated structure VI is more stable. Experimental evidence is not conclusive. Thus both alternatives have been employed for the interpretation of kinetic data.^{49,50} The theoretical investigations lead to contradictory results: the ab initio SCF calculations by Hariharan et al.³⁰ using 6-31G* basis sets including d functions predict the corner-protonated structure VI to be more stable than the edge-protonated structure V. The MINDO/3 cal-

culations by Bischof and Dewar¹³ give the reversed order of stability.

It is now well known that a flexible basis set including polarization functions⁵⁵ and the consideration of electron correlation effects^{25,32,34} are crucial for an accurate ab initio computation of differences in stability between classical and nonclassical structures. Calculations of this type have so far been confined to the relatively small systems $C_2H_3^+$ and $C_2H_5^+$.^{25,32,34} From the experience gained in this investigations one is led to expect significant electron correlation effects also in other similar cases. On the other hand, it is very difficult to estimate the reliability of the MINDO/3 results. Because of the lack of accurate experimental data it is not possible to check the MINDO/3 calculations for some typical test cases. Thus no molecular data concerning the structures of interest here could be included in the parametrization procedure.⁶⁴ Therefore it is not clear whether the extrapolation to a new class of compounds is reasonable within the MINDO/3 approximation.

In view of the present situation it is the purpose of our work to study systematically a series of molecules ($C_2H_3^+$, $C_2H_5^+$, $C_2H_4F^+$, $C_2H_4Cl^+$, and $C_3H_7^+$) at the SCF level using flexible basis sets and to compute electron correlation energies. Furthermore we want to see how MINDO/3 performs in the case of carbocations and eventually want to combine ab initio and semiempirical methods. By this we mean a strategy in which an energy hypersurface is computed by semiempirical methods in detail and only critical regions are then examined with accurate ab initio methods. Since semiempirical calculations are much faster than ab initio techniques one should save a considerable amount of computer time without losing too much information. However, much care has to be taken in choosing an appropriate semiempirical method. For example, several cases are now known where MINDO/3 is not adequate.^{66,67,70} Some deficiencies of MINDO/3 are corrected in the MNDO theory of Dewar and Thiel.⁷¹ However, in contrast to MINDO/3 and to ab initio methods including electron correlation this method fails to reproduce the relative stability of the classical and nonclassical ethyl cations. The classical cation is predicted to be more stable than the nonclassical one by MNDO calculations.⁷²

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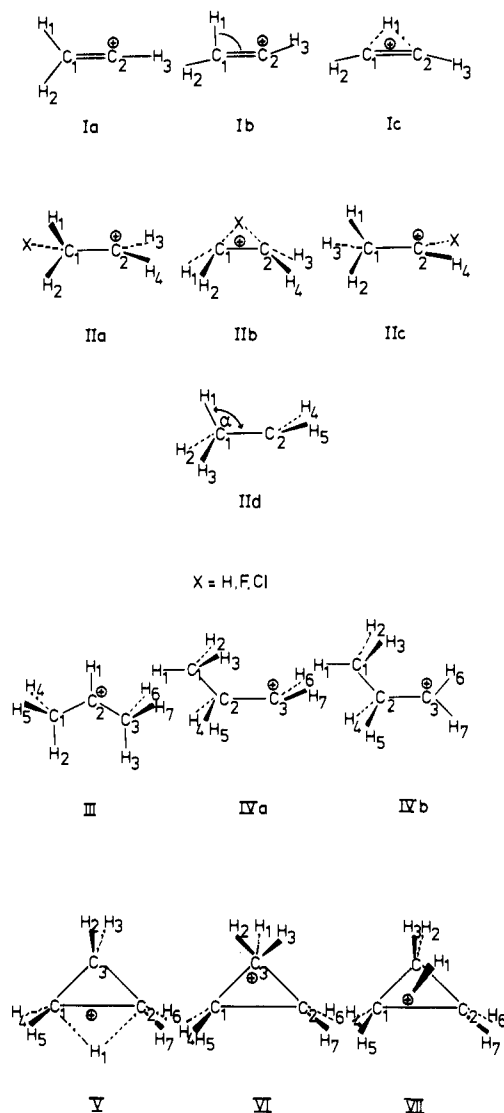


Figure 1. The structures investigated in this work.

II. Method of Calculation

The ab initio computations were performed both at the SCF level and with inclusion of valence shell electron correlation energy. Starting from localized SCF MOs⁵⁶ we calculate electron correlation effects in the framework of the IEPA-PNO, PNO-CI, and CEPA-PNO methods.^{57,58} We consider the CEPA-PNO results to be the most reliable ones and report IEPA-PNO and PNO-CI values only for the purpose of reference to previous work.

Since we use localized orbitals for the evaluation of the pair correlation energies we obtain a large number of relatively small interpair interactions between nonneighboring bonds. In the case of $C_2H_4F^+$, $C_2H_4Cl^+$, and $C_3H_7^+$ we calculated these contributions only by IEPA making use of local C_{3v} symmetries and added the resulting terms to the CEPA energies of the more strongly interacting pairs. The overall sum is reported only in the subsequent tables under the heading of "CEPA". By neglecting thus a number of very small nondiagonal blocks in the CI matrix we save a large amount of computer time. Considering still existing basis set deficiencies and changes due to geometry relaxation these effects are certainly not important.

The MINDO/3 computations were performed with the program no. 279 distributed by QCPE.⁶⁵ This program was extended by one of us (H.-J.K.) so as to calculate also the matrix of force constants (matrix of second derivatives with

Table I. Basis Sets^a

basis no.	atom	primitive set ^b	polarization functions ^c
1	C	7s3p	
	H	3s	
2	C	7s3p	1d (1.0)
	H	3s	1p (0.65)
3	C	8s4p	1d (1.0)
	H	4s	1p (0.65)
4	F	7s3p	
	C	7s3p	
	H	3s	
	F	8s4p	
	C	7s3p	
5	F	8s4p	
	C	7s3p	
	H	3s	
	F	8s4p	1d (1.5)
	C	7s3p	1d (1.0)
6	F	8s4p	
	C	7s3p	
	H	3s	
	F	8s4p	1d (1.5)
	C	7s3p	1d (1.0)
7	F	8s4p	
	C	8s4p	
	H	3s	
	F	8s4p	1d (1.5)
	C	7s3p	1d (1.0)
8	F	8s4p	
	C	7s3p	
	H	3s	
	F	8s4p	1d (1.5)
	C	8s4p	1d (1.0)
9	H	3s	
	F	8s4p	1d (1.5)
	C	8s4p	1d (1.0)
10	H	3s	
	Cl	10s6p	
	C	7s3p	
11	H	3s	
	Cl	10s6p	1d (0.6)
	C	7s3p	1d (1.0)
	H	3s	1p (0.65)

^a S. Huzinaga, "Approximate Atomic Functions I", University of Alberta, Canada, 1971. ^b The 7s3p, the 8s3p, and the 10s6p sets were contracted to [4111/21], [41111/211], and [511111/3111], respectively. The orbital exponents of the 3s and 4s sets on hydrogen were scaled with $\eta^2 = 1.44$ and contracted to [21] and [211], respectively. ^c Orbital exponents are given in parentheses.

respect to Cartesian coordinates) according to the McIver-Komornicki treatment.⁶¹

III. Basis Sets and Geometries

The Gaussian basis sets constructed from lobes as described in ref 60 are collected in Table I. Basis set no. 2 is essentially the "hydrocarbon" set used successfully by Zurawski et al.²⁵ for $C_2H_5^+$. Several other sets were used to study the effect of enlarging the s and p basis and of adding polarization functions.

The carbocation structures investigated are shown in Figure 1. The geometries were taken from ab initio calculations in the literature ($C_2H_3^+$, ref 32; $C_2H_5^+$, ref 23; $C_2H_4F^+$, ref 31; $C_2H_4Cl^+$, ref 27; $C_3H_7^+$, ref 29). We did not perform any reoptimization of these geometries. Especially for the larger systems $C_2H_4F^+$, $C_2H_4Cl^+$, and $C_3H_7^+$ a systematic variation of geometry is impossible with the computer capacity available. However, we calculated a few test cases within the IEPA method and found that energy differences between the structures IIa and IIb of the $C_2H_5^+$ molecule were practically the same using either ab initio or MINDO/3 geometries. Similar results were obtained for $C_2H_3^+$. We think that a further optimization of the geometries with larger basis sets will certainly have some effect on the numerical values of the computed stabilities but not on their relative order.

The MINDO/3 geometries were optimized with respect to all geometrical variables without applying any symmetry constraints. At this point we want to stress that it is necessary to verify whether the result found by the automatic geometry optimization procedure implemented in the QCPE program

Table II. Ab Initio Energies (au) and MINDO/3 Results for $C_2H_3^+$ ^d

	basis set no.	-E			ΔE_{1a-1b}	ΔE_{1a-1c}
		Ia	Ib	Ic		
SCF	2	77.034 05	77.027 30	77.026 59	-4.23	-4.68
IEPA	2	77.334 98	77.336 43	77.346 59	0.91	7.28
PNO-CI	2	77.267 29	77.264 78	77.270 00	-1.57	1.71
CEPA	2	77.288 51	77.286 55	77.292 37	-1.23	2.43
SCF	3	77.092 97	77.087 11	77.086 94	-3.68	-3.78
IEPA	3	77.403 47	77.406 38	77.417 84	1.83	9.02
PNO-CI	3	77.332 84	77.331 55	77.337 82	-0.81	3.12
CEPA	3	77.355 34	77.354 66	77.361 63	-0.43	3.95
IEPA ^a		77.326 3		77.338 1		7.41
SCF ^b		77.103 91	77.097 40	77.095 36	-4.09	-5.36
CI ^b		77.344 92	77.342 4	77.344 91	-1.58	-0.01
MINDO/3					1.05 ^c	5.32

^a Reference 25. ^b Reference 32. ^c Value for a CCH angle of 90.8° (see Figure 1, Ib). ^d The energy differences are given in kcal/mol.

is really a minimum, a transition state, or a maximum at all. An example where a hilltop instead of a local minimum was reported in the literature is described in section IV for $C_3H_7^+$. Therefore, we characterize the stationary points obtained in the MINDO/3 approximation by the eigenvalues of the matrix of force constants.^{62,63}

IV. Results

A. Energies and Relative Stabilities. $C_2H_3^+$. The results of calculations using two different basis sets are shown in Table II. They are also compared with our MINDO/3 values and previous IEPA²⁵ and CI³² computations. Structure Ib corresponds to the transition state at the CI level of ref 32. In the SCF approximation the classical structure Ia is more stable than the nonclassical one Ic. However, inclusion of electron correlation effects (IEPA, PNO-CI, and CEPA) makes the nonclassical structure more stable. The energy barrier is decreased by electron correlation and is almost negligible with basis no. 3. On further optimization of the geometry this barrier will probably disappear completely.

The qualitative trends of correlation effects in our work agree with that reported by Weber et al.³² However, the numerical values are somewhat different. Already at the SCF level the nonclassical structure is favored in comparison to Weber's result. This latter trend persists in the correlation energies. In contrast to our own calculations Weber et al. find a small but significant energy barrier. The classical and nonclassical structures have practically the same energy. The CI calculations by Weber et al. should be compared with our PNO-CI results and not with CEPA since in the former treatment no higher order effects (quadruple excitations, etc.) are included. Both the increase of the flexibility of the s and p set (basis no. 2/3) and the inclusion of unlinked cluster contributions by CEPA confirm the aforementioned trend. From this we conclude that our results are the more reliable ones. However, one should not forget that the differences in question are very small (only a few kcal/mol). More investigations are still necessary to settle this question finally.

The MINDO/3 method also shows the nonclassical structure more stable than the classical one. The numerical value is close to our CEPA result. Both species, Ia and Ic, correspond to local minima in MINDO/3 (i.e., only positive eigenvalues exist for the matrix of force constants). The computed energy difference of the structure Ia and the transition state structure with a $\angle CCH$ angle equal to 115° (Figure 1) is negligible.

Recently, the same results have been obtained by Dewar and Řzepa⁷⁴ from their MINDO/3 calculations on the systems $C_2H_3^+$ and $C_2H_5^+$. The PNO-CI and CEPA-PNO calculations performed by Kollmar⁷⁵ agree nicely with ours.

$C_2H_5^+$. SCF²³ and IEPA²⁵ investigations have already been performed previously. The SCF calculations (see Table III)

Table III. Ab Initio Energies (au) Obtained with Basis No. 2 and MINDO/3 Results for $C_2H_5^+$ ^c

	-E		$\Delta E_{11a-11b}$
	IIa	IIb	
SCF	78.254 02	78.256 80	1.74
SCF ^a	78.316 88	78.318 31	0.90
SCF ^b	78.2525	78.2547	1.38
IEPA	78.581 34	78.596 10	9.26
PNO-CI	78.513 73	78.523 99	6.44
CEPA	78.537 37	78.549 04	7.33
IEPA ^b	78.5794	78.5934	8.79
MINDO/3			8.00

^a Reference 23. ^b Reference 25. ^c The energy differences are given in kcal/mol.

show the nonclassical structure to be only slightly more stable than the classical one. As in the case of $C_2H_3^+$ electron correlation effects stabilize the bridged geometry. Our CEPA values are quite close to the IEPA results obtained by Zurawski et al.²⁵ MINDO/3 also reproduces the relative stabilities satisfactorily.

The structure of $C_2H_5^+$ in the gas phase has not been identified experimentally.^{37,38} Comparison with experimental data from solution is difficult because of considerable solvent effects. From theoretical and experimental considerations^{15,26,39,73} it is estimated that the classical structure is preferentially stabilized by solvation. We believe that our CEPA calculations are sufficiently accurate to show that the nonclassical structure is the most stable one for the isolated molecule. For $C_2H_5^+$ there is no barrier along the minimum energy path between structures IIa and IIb in MINDO/3 calculations. The structure IIa corresponds to a saddle point.¹²

The $\angle HCC$ angle α chosen as reaction coordinate. An analysis of the reaction path starting from structure IIa shows³⁴ that already for $\alpha \sim 105^\circ$ the symmetrical structure IIc (Figure 1) is obtained. In order to test the MINDO/3 results we thought it sufficient to recompute, with ab initio methods, several points of that part of the reaction coordinate which is represented by structure IIc. The results obtained from the MINDO/3 geometries are illustrated in Figure 2. The SCF curve is more or less horizontal with an extremely flat barrier. The shapes of the CEPA and MINDO/3 curve are very similar. Both curves show a steady decrease in energy going from the classical to the nonclassical structure, the MINDO/3 curve being somewhat steeper.

$C_2H_4F^+$ and $C_2H_4Cl^+$. The haloethyl cations have been investigated by a number of ab initio SCF calculations.^{26,27,31,33} Basis set effects are documented in ref 31 and can also be studied in Table IV. The main point for the com-

Table IV. A Comparison of SCF Calculations with Different Basis Sets for $C_2H_4X^+$, $X = F, Cl$

basis no.	$-E_{SCF}$			$\Delta E_{IIa-IIb}$	$\Delta E_{IIc-IIb}$
	IIa	IIb	IIc		
X = F					
4	176.867 149	176.865 839	176.898 016	-0.82	-20.20
5	177.000 179	176.987 175		-8.16	
6	177.060 763	177.046 929	177.099 043	-8.68	-32.71
7	177.072 126	177.058 417		-8.61	
8	177.076 237	177.059 986	177.113 343	-10.20	-33.49
9	177.125 584	177.110 538		-9.44	
STO-3G ^a	174.840 83	174.872 14	174.898 80	19.65	-16.74
22-SP ^b	176.525 45	176.531 15	176.588 18	3.58	-35.80
4-31G ^a	176.889 77	176.871 46	176.918 97	-11.49	-29.82
6-31G ^c	177.073 457	177.061 747		-7.35	
DZ(38-SP) ^c	177.110 340	177.093 932		-10.30	
X = Cl					
10	536.897 941	536.914 596	536.919 077	10.45	-2.81
11	536.973 896	537.000 120	537.006 230	16.46	-3.84
STO-3G ^a	531.379 44	531.409 78	531.408 08	19.05	1.07
26-SP ^d	536.473 02	536.498 20	536.519 44	15.81	-13.33
4-31G ^a	536.572 75	536.587 38	536.594 60	9.18	-4.53
4-31G ^e	536.578 465	536.597 077		11.68	
DZ(43-SP) ^e	537.145 365	537.160 274		9.36	

^a Reference 27 (based on STO-3G optimized geometries). ^b Reference 17b. ^c Reference 31 (based on 6-31G optimized geometries). ^d Reference 26. ^e Reference 33 (based on 4-31G optimized geometries). ^f Total energies are given in au, differences in kcal/mol.

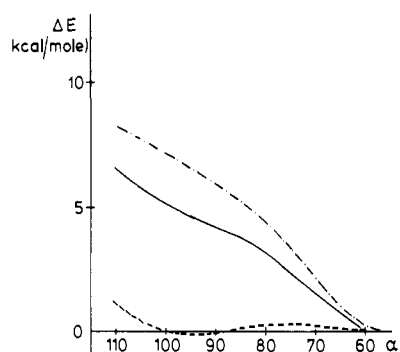


Figure 2. Energy profile for the conversion of the classical into the non-classical structure of $C_2H_5^+$ (see Figure 1, structure II d). MINDO/3 geometries are used. —, CEPA; ---, SCF (basis set no. 2); - · - ·, MINDO/3.

putation of energy differences is to have a sufficiently flexible s and p basis. Our basis no. 4 as well as the STO-3G sets is not adequate for that purpose since the stability of the bridged structure of the fluorine compound is strongly exaggerated. As one would expect it is necessary to increase the number of s and p groups on fluorine. Basis set no. 5 which still has a 7s3p basis on carbon but a 8s4p set on fluorine does not show the aforementioned deficiencies and is adequate for our purpose. A further increase of the carbon basis of 8s4p (basis set no. 7) shows only minor additional changes. Interestingly, the effect of d functions is relatively small for the fluorine compounds.

For the chlorine compounds basis set no. 10 reproduces the double ζ results³³ quite well. Again, the STO-3G basis is not satisfactory. The relative stability of IIb vs. IIa is here much more sensitive to polarization functions than in the fluorine case.

As it can be seen from Tables IV and V the electron correlation contributions to $\Delta E(IIa-IIb)$ are large (11–14 kcal/mol). In the SCF approximation structure IIa ($X = F$) is more stable than IIb by 10.2 kcal/mol whereas the CEPA results show a corresponding energy difference of 1.4 kcal/mol favoring the structure IIb. Considering the accuracy of our computations we do not regard this small energy difference to be significant.

In the case of chlorine the bridged structure IIb is more stable than IIa already at the SCF level. Inclusion of electron correlation pronounces this difference even more. On the contrary, the stability relations between structures IIa and IIc (which is always the most stable one) are not very much affected by electron correlation. The reason for this behavior is discussed in the following section.

The MINDO/3 results show some of the deficiencies of the method mentioned in the Introduction.⁶⁷ In contrast to the CEPA results the bridged fluoronium and chloronium ion structures IIb are the most stable ones. The energy difference of 31.1 kcal/mol between the fluoroethyl cations IIa and IIb is probably arising from an inadequate fluorine parametrization. The structure IIa ($X = F, Cl$) corresponds to a transition state whereas the remaining structures represent minima.

The experimental results for the haloethyl cations have already been described in the Introduction. We note again that these data refer to solutions. Still, our results for F and Cl follow the general trend that the bridged structure becomes more stable in the series F, Cl, Br, and I.⁴⁵

The question whether a cyclic fluorine compound does exist cannot be answered conclusively from our data. Hehre and Hiberty²⁷ report a local minimum for the cyclic haloethyl compounds. They also studied the reaction to the more stable structure IIc. The transition state for this process was approximated by the staggered conformation of structure IIa. A detailed analysis assuming a plausible reaction coordinate for the interconversion IIa/IIb was given by Hopkinson et al.³¹ The resulting barrier height in going from IIb to IIa is about 9 kcal/mol. Since structure IIb is stabilized even more in our calculations than in previous ones we should also expect a local minimum for the cyclic fluoroethyl cation IIb. For the same reasons as in the case of $C_2H_3^+$ electron correlation effects will probably decrease the energy barrier. So the cyclic structure might easily isomerize to the more stable product IIc. In the case of the chlorine compounds the situation is not so delicate because the nonclassical cation IIb is much more stable than the open structure IIa and a deep local minimum is found for IIb. The numerical values for the barrier height given by Hopkinson et al.³³ will be changed significantly by electron correlation in the case of chlorine too.

$C_3H_7^+$. The ab initio calculations on the $C_3H_7^+$ system

Table V. IEPA and CEPA Results for $C_2H_4X^+$, X = F, Cl, Obtained with Basis Sets No. 8 and 11, Respectively, in Comparison with MINDO/3 Results^b

	-E			$\Delta E_{11a-11b}$	$\Delta E_{11c-11b}$
	IIa	IIb	IIc		
X = F					
IEPA	177.623 90	177.631 20	177.681 76	4.58	-31.77
CEPA ^a	177.538 42	177.540 68	177.591 22	1.41	-31.72
MINDO/3				31.14	1.77
X = Cl					
IEPA	537.453 47	537.502 40	537.506 36	30.71	2.59
CEPA ^a	537.383 91	537.431 72	537.432 33	30.00	-0.38
MINDO/3				29.28	8.46

^a For the evaluation of the CEPA correlation energies see section II. ^b Total energies are given in au, differences in kcal/mol.

Table VI. Energies (au) and Relative Stabilities (kcal/mol) with Respect to Structure III for $C_3H_7^+$

Structure	-E				ΔE				MIN-DO/3	exp ^a
	SCF		IEPA	CEPA ^c	SCF		IEPA	CEPA ^c		
	basis no. 1	basis no. 2	basis no. 2	basis no. 2	basis no. 1	basis no. 2	basis no. 2	basis no. 2		
III	117.221 66	117.294 43	117.800 32	117.728 56	0	0	0	0	0	0
IVa	117.195 44	117.267 54	117.776 29	117.702 19	16.45	16.88	15.08	16.54		16 ^a
IVb	117.191 84	117.265 35	117.771 39	117.698 99	18.71	18.25	18.15	18.55	18.87	
V	117.173 95	117.263 84	117.795 76	117.724 58	29.94	19.20	2.86	2.49	7.81	8 ^b
VI	117.192 74	117.267 68	117.786 18	117.716 58	18.15	16.79	9.01	7.52	12.96	
VII	116.992 92	117.091 88	117.649 42	117.569 68	143.55	127.12	94.70	99.71	88.41	

^a F. P. Lossink and G. P. Semeluck, *Can. J. Chem.*, **48**, 955 (1970). ^b Reference 52. ^c For the evaluation of the CEPA correlation energies see section II.

provide another illustrative example of how much care and computational effort is necessary in order to get reliable ab initio results. An analysis of basis set effects has been given by Hariharan et al.³⁰ (see also Table VI). There is no question about the fact that the isopropyl cation (structure III) is the most stable species. In MINDO/3 structure III as calculated by Bischof and Dewar¹³ corresponds to a hilltop (the matrix of the force constants has two negative eigenvalues). The true minimum structure is found by rotation of the two methyl groups clockwise and counterclockwise to one another (the heat of formation of the minimum structure is 183.9 kcal/mol).

The *n*-propyl cation IVa is 16.5 kcal/mol (CEPA value) less stable than the isopropyl cation. The basis set effect and the influence of electron correlation on this difference are relatively small. The same is true for structure IVb. Structure IVa is not at all a stationary point in MINDO/3 whereas structure IVb corresponds to a transition state (the matrix of force constants has one negative eigenvalue).

The calculated stabilities of the protonated cyclopropane structures are very sensitive to the basis set and to electron correlation effects. All methods agree that the face-protonated structure VII cannot compete with the other ones. In fact, this has already been shown at an early stage of the theoretical investigations (see, e.g., ref 21). By addition of polarization functions the stability of the edge-protonated structure is increased relative to the corner-protonated one. At near Hartree-Fock level structures IV, V, and VI are practically equal in energy. This situation is changed in the CEPA approximation. Both bridged structures appear stabilized with respect to IV, the edge-protonated configuration V even more so than the corner-protonated geometry VI. V is now about 5 kcal/mol more stable than VI. This means that on the basis of our CEPA calculations we predict that the edge-protonated form is the one which is experimentally observed. This is in contradiction to the SCF results but in agreement with MINDO/3. The force constant matrix for structure V (edge-protonated cyclopropane) shows only positive eigenvalues in the MINDO/3 approach (minimum); for structure VI (corner-protonated

cyclopropane) one negative eigenvalue is found (saddle point). In the case of face-protonated cyclopropane two negative eigenvalues are obtained and the structure is therefore classified as a hilltop.^{62,63}

The experimental investigations^{52,54} show that the protonated cyclopropane should be about 8 kcal/mol less stable than the isopropyl cation. The CEPA method gives an energy difference of 2.5 kcal/mol. From this we compute within the rigid rotator/harmonic oscillator approximation a ΔH value using geometries and zero-point energies calculated by MINDO/3.^{77,78} In view of the large computational effort for an ab initio calculation of the harmonic force field we regard it as useful to correct ab initio ΔE 's with the semiempirically computed vibrational frequencies. Such a procedure has been applied successfully in the case of $C_2H_7^+$.⁷⁶ Here we arrive at $\Delta H_{298.16}$ (calcd) = 3.78 kcal/mol, which is still ~ 4 kcal/mol off from the experimental value.

B. Localized Orbitals and Pair Correlation Energies. After having discussed the molecular energies we now turn to the question of chemical bonding. The bonding properties can, of course, be discussed in several ways. Here we want to concentrate on localized orbitals and on population analysis data. In our cases localized orbitals allow a straightforward rationalization of electron correlation effects and, together with atomic charges, give an instructive picture of chemical bonds.

The localization procedure has been performed in the following way. For the $C_2H_3^+$ system the σ/π separation between orbitals symmetrical with respect to the molecular plane and the antisymmetric orbital was maintained. In the other cases all the valence orbitals were subjected to transformation.

The nonclassical $C_2H_3^+$ structure shows a three-center bond closely similar to the one in $C_2H_5^+$. Since the population analysis for the structures Ia-c has also been discussed by Weber et al.³² we need not further comment on that molecule. Localization of nonclassical $C_2H_5^+$ yields conventional CH and CC σ bonds and a three-center bond. The latter orbital is illustrated by a contour diagram in Figure 3. It clearly dem-

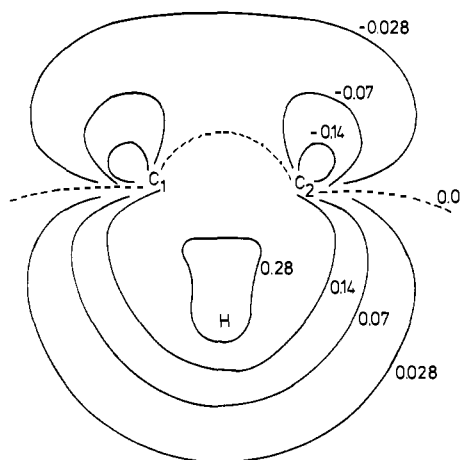


Figure 3. Contour lines (in au) for the three-center bond in nonclassical $C_2H_5^+$

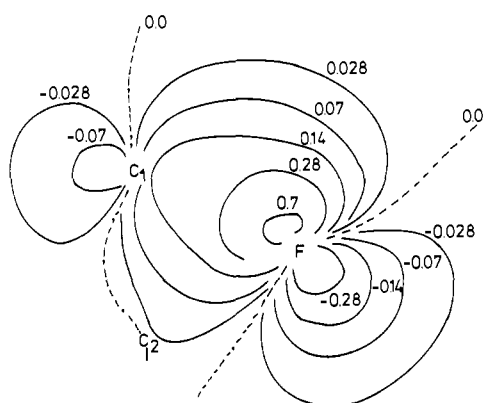


Figure 4. Contour lines for the localized C_1-F bond orbital in nonclassical $C_2H_4F^+$.

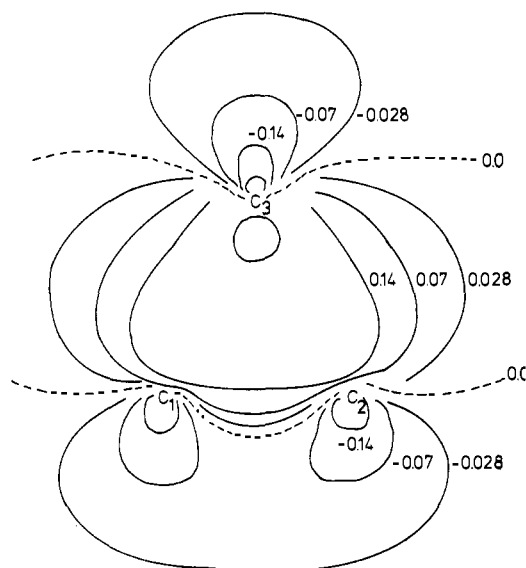


Figure 5. Contour lines for the three-center bond in corner-protonated cyclopropane.

onstrates the extension of the orbital over all three atomic centers involved in the bond. If the bridging hydrogen is replaced by halogen as in structure IIb, $X = F$ or Cl , a new feature appears. Since the halogen atom has lone pair orbitals available, these become involved in the process of "back-

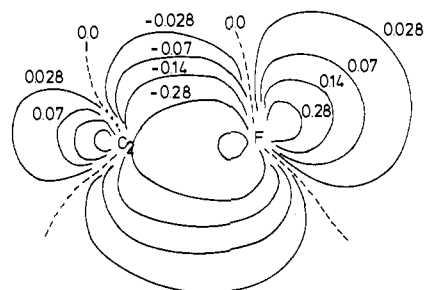


Figure 6. Contour lines for the localized CF σ bond orbital in structure IIc. The plane of intersection contains the $C-F$ intermolecular axis and is perpendicular to the C_1C_2F plane.

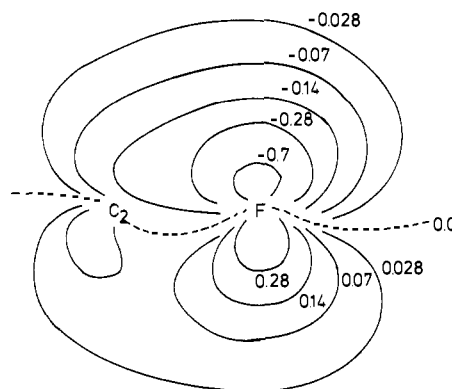


Figure 7. Contour lines for the localized π orbital in structure IIc. The same plane as in Figure 5 was chosen.

donation". Depending on the importance of this effect a situation may arise where the bonding is better characterized by two covalent bonds than by one three-center orbital and a lone pair orbital. In fact, recent experimental and theoretical investigations^{27,41,45} support the analogy to conventional three-membered heterocycles like ethylene oxide.

The localized orbital concerning the $C-F$ bonding in question is shown in Figure 4. It is an orbital mainly situated in the region between C_1 and F . A second, equivalent orbital was obtained for the C_2-F bond. Owing to the large electronegativity difference of fluorine and carbon the orbital in Figure 4 is highly polarized toward F . Furthermore, significant three-center contributions can also be recognized. Thus we find a situation intermediate between a strong π complex with a three-center interaction and two covalent bonds. A clear distinction between these two alternatives appears somewhat arbitrary.

The results for the analogous chloronium compound are similar to those for fluorine. The orbitals containing contributions from the chlorine atom are more diffuse and less polar.

A different situation arises when the halogen atom is replaced by CH_3 , leading to the corner-protonated cyclopropane VI. Since the CH_3 group has no lone pair orbitals available, back-donation is not important. Therefore, we find a delocalized three-center bond (see Figure 5).

The carbon-halogen bond in structure IIc is significantly shorter than a normal single bond.²⁷ This partial double bond character⁴⁶ is clearly shown by the two localized orbitals (Figures 6 and 7). One orbital is of σ type in the direction of the $C-F$ bond; the other one is a π -type orbital. Again the chlorine analogue parallels the situation found for fluorine.

The remaining orbitals which were not discussed here do not show any new features. We find either a conventional two-electron two-center bond, lone pairs, or the three-center bond

Table VII. Gross Atomic Populations of Different Structures of the $C_2H_4X^+$ Cations, with X = H, F, Cl, as Calculated with Basis Sets No. 2, 8, and 11, Respectively^a

structure	C ₁	C ₂	X	H ₁	H ₂	H ₃	H ₄
X = H							
IIa	6.2740	5.6531	0.8354	0.8098	0.8098	0.8060	0.8119
IIb	5.9545	5.9545	0.9106	0.7951	0.7951	0.7951	0.7951
X = F							
IIa	5.7932	5.6795	9.3537	0.8074	0.8074	0.7685	0.7904
IIb	5.7700	5.7700	9.3167	0.7858	0.7858	0.7858	0.7858
IIc	6.2517	5.3100	9.1897	0.8170	0.8170	0.8189	0.7957
X = Cl							
IIa	6.2087	5.6244	17.0073	0.7864	0.7864	0.7857	0.8012
IIb	5.9961	5.9961	16.8848	0.7807	0.7807	0.7807	0.7807
IIc	6.1941	5.7021	16.8298	0.8273	0.8273	0.8395	0.7799

^a For numbering of the atoms see Figure 1.**Table VIII.** Gross Atomic Populations of Different Structures of the $C_3H_7^+$ Cations (III-VII) as Calculated with Basis Set No. 2^a

structure	C ₁	C ₂	C ₃	H ₁	H ₂	H ₃	H ₄	H ₅	H ₆	H ₇
III	6.1755	5.7704	6.1755	0.8079	0.8608	0.8608	0.8372	0.8372	0.8372	0.8372
IVa	6.1172	6.3347	5.6368	0.8407	0.8965	0.8965	0.8219	0.8219	0.8169	0.8169
IVb	6.0651	6.3543	5.6160	0.8806	0.9166	0.9166	0.8101	0.8101	0.8168	0.8140
V	6.0752	6.0752	6.1406	0.8953	0.8170	0.8170	0.7950	0.7950	0.7950	0.7950
VI	6.0297	6.0297	6.2875	0.8134	0.8181	0.8181	0.7996	0.8021	0.7996	0.8021
VII	6.2010	6.2010	6.2010	0.5261	0.7786	0.8450	0.7786	0.8450	0.7786	0.8450

^a For numbering of the atoms see Figure 1.

in edge-protonated cyclopropane which is similar to the one in Figure 3 for $C_2H_5^+$.

The gross atomic populations derived from the total densities are given in Tables VII and VIII. Because of the deficiencies of the Mulliken population analysis it is certainly problematic to discuss details in both tables. However, general trends like the changes in electronegativity are correctly reproduced. The electrophilic carbon center in the classical structures carries a positive net charge of 0.3 e_0 . The neighboring carbon atoms are negatively charged (0.1–0.2 e_0). Only in the case of $C_2H_4F^+$, structure IIa, the fluorine atom is able to withdraw electrons from center C₁ resulting in a positive charge practically equal to the one on C₂. Fluorine is negatively charged in the nonclassical structure IIb whereas chlorine is positive. Although the net charge of the carbon atom no. 3 in corner-protonated cyclopropane is negative ($\sim 0.3 e_0$), the total net charge of the CH₃ group is positive (+0.3 e_0).

As already stated at the beginning of this section localized orbitals provide a good basis for the discussion of pair energies. Comparing a number of previous results⁵⁹ the transferability of IEPA pair energies is well established. In CEPA the non-diagonal terms taken into account in addition to the IEPA diagonal blocks effectively couple only neighboring pairs, so a local character of the CEPA pair energies must still be expected. Since we have available with approximately equal accuracy a relatively large amount of data, we investigated the transferability of pair energies in a systematic way. In Table IX mean values and standard deviations for typical pair interactions are collected. In constructing this table the $C_2H_3^+$ system was excluded because the type of localization (σ/π separation) for this molecule was not quite compatible with the localization used for the others. For a discussion of the effect of localization on the pair energies for CC multiple bonds see ref 59. In the case of local symmetry for bond or lone pairs (e.g., CH₃, lone pairs) the interaction between these pairs and neighboring ones was averaged so that finer details like rotation barriers cannot be discussed on the basis of the correlation energy values of Table IX. The interaction energies between nonneighboring pairs are derived from widely varying values as may be seen from the standard deviation, which is large in

relation to the mean value. Although these contributions are very small, one must not neglect them totally, owing to their large number. From our analysis it turned out that it is not necessary to split these interactions into more subgroups. It is sufficient to take them into account globally.

The averaged pair correlation energies allow us to compute within the basis used the total correlation energy of the systems investigated here within an error of only a few percent. This will certainly be true for compounds of similar type also. However, an error of several kcal/mol in the total correlation energies (within the basis set used) still remains which may or may not be subject to error cancellation when energy differences are computed. Nevertheless we think that we have a reliable procedure for estimating the main characteristics of electron correlation effects. This may be especially useful in cases where it is still possible to perform reliable SCF calculations but, because of the size of the molecule, correlation energy computations are no longer feasible. Of course it is important to verify whether the chemical bonds for which the pair correlation energies are transferred from one molecule to the other are of similar nature.

The way in which electron correlation stabilizes bridged structures in comparison to open ones has already been analyzed for $C_2H_3^+$ and $C_2H_5^+$ by Zurawski et al.²⁵ The same arguments apply for $C_3H_7^+$ as well. The sum of the intrapair correlation remains practically constant for the structures III–VII. The main point is that in the case of bridged structures the number of next neighbor interpair interactions is larger than for the open structures. Thereby the absolute value of the correlation energy of the nonclassical structures, and thus also their stability with respect to the open structures, is increased. The fact that edge-protonated cyclopropane has more bonds close to each other than corner-protonated cyclopropane explains the enhanced stabilization of the former molecule by electron correlation.

For the molecules without heteroatoms the near constancy of the total intrapair correlation energy comes from the fact that the intrapair energies for CC and CH single bonds and the respective three-center bonds are almost equal. However, when a lone pair orbital of fluorine in structure IIa is changed

Table IX. Mean IEPA and CEPA Pair Correlation Energies ϵ_{μ} (au) and Standard Deviations Based on the Cations $C_2H_4X^+$ with $X = H, F, Cl,$ and $C_3H_7^+$, Respectively

μ	$-\epsilon_{\mu}$	
	IEPA	CEPA
intrapair		
CH	0.0296 ± 0.0006 ^a	0.0283 ± 0.0005 ^a
C ⁺ H	0.0317 ± 0.0002	0.0304 ± 0.0001
CC	0.0252 ± 0.0008	0.0231 ± 0.0006
CCH ^b	0.0292	0.0279
CCH ^c	0.0291	0.0275
CCC ^d	0.0236	0.0216
CF _σ	0.0285 ± 0.0019	0.0248 ± 0.0014
CF _π	0.0240	0.0214
F _{1p}	0.0214 ± 0.0001	0.0200 ± 0.0008
CCl _σ	0.0206 ± 0.0014	0.0192 ± 0.0013
CCl _π	0.0194	0.0178
Cl _{1p}	0.0194 ± 0.0003	0.0181 ± 0.0004
interpair		
CH,CH	0.0160 ± 0.0006	0.0122 ± 0.0004
CH,CC	0.0149 ± 0.0010	0.0114 ± 0.0007
CC,CC	0.0152 ± 0.0024	0.0116 ± 0.0018
CC,CCH ^b	0.0262	0.0204
CH,CCH ^b	0.0117	0.0087
CC,CCH ^c	0.0131	0.0098
CH,CCH ^c	0.0122	0.0093
CC,CCC ^d	0.0244	0.0188
CH,CCC ^d	0.0145	0.0111
CH,CCC ^d	0.0111	0.0082
F _{1p} ,F _{1p} ^e	0.0280	0.0218
F _{1p} ,F _{1p} ^f	0.0255 ± 0.0003	0.0196 ± 0.0005
F _{1p} ,CF _σ	0.0293 ± 0.0010	0.0224 ± 0.0022
F _{1p} ,CF _π	0.0308	0.0237
CF _σ ,CH	0.0073 ± 0.0023	0.0053 ± 0.0010
CF _π ,CH	0.0043	0.0032
CF _σ ,CC	0.0075 ± 0.0001	0.0059 ± 0.0002
CF _π ,CC	0.0039	0.0030
CF,CF ^g	0.0386	0.0258
CF _σ ,CF _π	0.0390	0.0279
F _{1p} ,CH ^h or CC ^h } CF _σ or CF _π ,CH ^h } Cl _{1p} ,Cl _{1p} ^h	0.012 ± 0.0006	0.0159
Cl _{1p} ,Cl _{1p} ⁱ	0.0182 ± 0.0002	0.0139 ± 0.0002
CCl _σ ,Cl _{1p}	0.0159 ± 0.0022	0.0129 ± 0.0017
CCl _π ,Cl _{1p}	0.0226	0.0179
CCl _σ ,CH	0.0120 ± 0.0020	0.0083 ± 0.0015
CCl _π ,CH	0.0052	0.0036
CCl _σ ,CC	0.0112 ± 0.0007	0.0084 ± 0.0005
CCl _π ,CC	0.0046	0.0032
CCl,CCl ^j	0.0198	0.0144
CCl _σ ,CCl _π	0.0257	0.0187
Cl _{1p} ,CH ^k or CC ⁺ } CCl _σ ,CH ^k } CH,CH ^k } CH,CC ^k }	0.0019 ± 0.0004	0.0011 ± 0.0004
	0.0015 ± 0.0006	0.0011 ± 0.0004
	0.0016 ± 0.0009	0.0011 ± 0.0008

^a Standard deviation. ^b Three-center LMO of $C_2H_5^+$ (IIb). ^c Three-center LMO of edge-protonated cyclopropane (V). ^d Three-center LMO of corner-protonated cyclopropane (VI). ^e 2-Fluoroethyl cation (IIa). ^f Fluoronium ion and 1-fluoroethyl cation (IIb, IIc). ^g Fluoronium ion (IIb). ^h 2-Chloroethyl cation (IIa). ⁱ Chloronium ion and 1-chloroethyl cation (IIb, IIc). ^j Chloronium ion (IIb). ^k Interaction between non-nearest neighbors. ^l CH bond of CH_3^+ in corner-protonated cyclopropane.

to a CF σ or π bond, in structures IIb and IIc an increase in absolute value of the intrapair correlation energy is found for the individual bond as well as for the total sum. In the case of chlorine the difference between lone pair and C-Cl σ pair is negligible. Owing to the partial double bond in structure IIc the number of next neighbor pairs is comparable to that in structure IIb. Although the type of interaction is quite different in both cases, the final results are about the same. Thus,

structures IIb and IIc are equally stabilized by electron correlation. These results and a number of others⁶⁸ demonstrate that in the case of molecules containing heteroatoms and polar bonds the interpretation of electron correlation effects is much more complicated than in the case of pure hydrocarbon systems.

V. Conclusions

Our calculations show that the contribution of electron correlation energies is very important for an ab initio treatment of classical and nonclassical structures of carbocations. We find not only a change in the numerical values by electron correlation but also a reordering of relative stabilities. The SCF approximation alone is clearly not sufficient. From the experience with previous calculations (see, e.g., ref 25, 68, and 69) we expect that our basis sets are flexible enough to give the correct order of stabilities with the CEPA method. However, extensions of the basis sets and further geometry optimization will still have an influence on the numerical results.

The MINDO/3 method works well in the case of the pure hydrocarbon systems, but cannot be used for the haloethyl cations since the stability of the nonclassical structure IIb is largely overestimated. Thus the danger of applying a semi-empirical method like MINDO/3 to new classes of molecules is clearly demonstrated. On the other hand we find MINDO/3 a useful tool for the computation of carbocations without heteroatoms present and we intend to proceed further in a combination of both quantum chemical approaches.

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References and Notes

- (1) P. D. Bartlett, "Nonclassical Ions", W. A. Benjamin, New York, N.Y., 1965.
- (2) B. Capon, *Q. Rev., Chem. Soc.*, **18**, 45 (1964).
- (3) R. Breslow in "Molecular Rearrangements", Part I, Interscience, New York, N.Y., 1963, pp 233-294.
- (4) M. Hanack and H. J. Schneider, *Angew. Chem., Int. Ed. Engl.*, **6**, 666 (1967).
- (5) G. A. Olah and P. v. R. Schleyer, Ed., "Carbonium Ions", Vol. III, Interscience, New York, N.Y., 1972.
- (6) P. J. Stang, *Prog. Phys. Org. Chem.*, **10**, 205 (1973).
- (7) G. A. Olah and J. M. Bollinger, *J. Am. Chem. Soc.*, **89**, 4744 (1967).
- (8) R. Hoffmann, *J. Chem. Phys.*, **40**, 2480 (1964).
- (9) R. Sustmann, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **91**, 5350 (1969).
- (10) H. Kollmar and H. O. Smith, *Theor. Chim. Acta*, **20**, 65 (1971).
- (11) R. D. Bach and H. Henneke, *J. Am. Chem. Soc.*, **92**, 5589 (1970).
- (12) D. Heidrich, M. Grimmer, and H.-J. Köhler, *Tetrahedron*, **32**, 1193 (1976).
- (13) P. K. Bischof and M. J. S. Dewar, *J. Am. Chem. Soc.*, **97**, 2278 (1975).
- (14) H. Kollmar and H. O. Smith, *Tetrahedron Lett.*, 1833 (1970).
- (15) D. Heidrich and M. Grimmer, *Int. J. Quantum Chem.*, **9**, 923 (1975).
- (16) G. F. Pfeiffer and J. G. Jewett, *J. Am. Chem. Soc.*, **92**, 2143 (1970).
- (17) (a) D. T. Clark and D. M. J. Lilley, *Chem. Commun.*, 549 (1970); (b) *ibid.*, 603, 1043 (1970).
- (18) J. E. Williams, V. Buss, L. C. Allen, P. v. R. Schleyer, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 2141 (1970).
- (19) W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 808 (1971).
- (20) J. E. Williams, V. Buss, and L. C. Allen, *J. Am. Chem. Soc.*, **93**, 6867 (1971).
- (21) J. P. Pette and J. L. Whitten, *J. Am. Chem. Soc.*, **90**, 3338 (1968).
- (22) V. Buss, P. v. R. Schleyer, and L. C. Allen, *Top. Stereochem.*, **7**, 253 (1972).
- (23) P. C. Hariharan, W. A. Lathan, and J. A. Pople, *Chem. Phys. Lett.*, **14**, 385 (1972).
- (24) P. A. Dixon and W. N. Lipscomb, *J. Am. Chem. Soc.*, **95**, 2853 (1973).

- (25) B. Zurawski, R. Ahlrichs, and W. Kutzelnigg, *Chem. Phys. Lett.*, **21**, 309 (1973).
- (26) D. T. Clark and D. M. J. Lilley, *Tetrahedron*, **29**, 845 (1973).
- (27) W. J. Hehre and P. C. Hlberty, *J. Am. Chem. Soc.*, **96**, 2665 (1974).
- (28) V. Dyczmons, and W. Kutzelnigg, *Theor. Chim. Acta*, **33**, 239 (1974).
- (29) L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **94**, 311 (1972).
- (30) P. C. Hariharan, L. Radom, J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **96**, 599 (1974).
- (31) A. C. Hopkinson, M. H. Lien, K. Yates, and I. G. Csizmadia, *Theor. Chim. Acta*, **38**, 21 (1975).
- (32) (a) J. Weber and A. D. McLean, *J. Am. Chem. Soc.*, **98**, 875 (1976); (b) J. Weber, M. Yoshimine, and A. D. McLean, *J. Chem. Phys.*, **64**, 4159 (1976).
- (33) A. C. Hopkinson, M. H. Lien, K. Yates, and I. G. Csizmadia, *Theor. Chim. Acta*, **44**, 385 (1977).
- (34) H.-J. Köhler, D. Heidrich, and H. Lischka, *Z. Chem.*, **17**, 67 (1977).
- (35) I. Roberts and G. E. Kimball, *J. Am. Chem. Soc.*, **59**, 947 (1937).
- (36) G. A. Olah, *J. Am. Chem. Soc.*, **94**, 808 (1972).
- (37) J. H. Vorachek, G. G. Meisels, R. H. Geanangel, and R. N. Emmel, *J. Am. Chem. Soc.*, **95**, 4078 (1973).
- (38) H. H. Jaffé and S. Billets, *J. Am. Chem. Soc.*, **94**, 674 (1972).
- (39) J. L. Beauchamp, *J. Am. Chem. Soc.*, **96**, 7552 (1974).
- (40) G. A. Olah and J. M. Bollinger, *J. Am. Chem. Soc.*, **90**, 947 (1968).
- (41) G. A. Olah, J. M. Bollinger, and J. Brinich, *J. Am. Chem. Soc.*, **90**, 2587 (1968).
- (42) G. A. Olah and A. M. White, *J. Am. Chem. Soc.*, **91**, 5801 (1969).
- (43) G. A. Olah and R. D. Porter, *J. Am. Chem. Soc.*, **93**, 6877 (1971).
- (44) G. A. Olah, J. M. Bollinger, Y. K. Mo, and J. M. Brinich, *J. Am. Chem. Soc.*, **94**, 1164 (1972).
- (45) R. H. Staley, R. D. Wieling, and J. L. Beauchamp, *J. Am. Chem. Soc.*, **99**, 5964 (1977).
- (46) G. A. Olah, D. A. Deal, and P. W. Westerman, *J. Am. Chem. Soc.*, **95**, 3387 (1973).
- (47) G. A. Olah, Y. K. Mo, and Y. Halpern, *J. Org. Chem.*, **37**, 1169 (1972).
- (48) R. C. Fahey, *Top. Stereochem.*, **3**, 237 (1968).
- (49) C. J. Collins, *Chem. Rev.*, **69**, 543 (1969), and references cited therein.
- (50) M. Saunders, P. Vogel, E. L. Hagen, and R. Rosenfeld, *Acc. Chem. Res.*, **6**, 53 (1973).
- (51) G. P. K. Smith, J. Weiner, M. Saunders, and R. J. Cross, Jr., *J. Am. Chem. Soc.*, **97**, 3593 (1975).
- (52) S.-L. Chong and J. L. Franklin, *J. Am. Chem. Soc.*, **94**, 6347 (1972).
- (53) D. J. McAdoo, F. W. McLafferty, and P. F. Bente, III, *J. Am. Chem. Soc.*, **94**, 2027 (1972).
- (54) P. P. Dymerski, R. M. Prinstein, P. F. Bente, III, and F. W. McLafferty, *J. Am. Chem. Soc.*, **98**, 6834 (1976).
- (55) P. C. Hariharan and J. A. Pople, *Chem. Phys. Lett.*, **16**, 217 (1972).
- (56) S. F. Boys in "Quantum Theory of Atoms, Molecules and the Solid State", P. O. Löwdin, Ed., Interscience, New York, N.Y., 1967, p 253.
- (57) (a) W. Meyer, *Int. J. Quantum Chem., Symp.*, **1**, 59 (1971); (b) *J. Chem. Phys.*, **58**, 1017 (1973).
- (58) R. Ahlrichs, H. Lischka, V. Staemmler, and W. Kutzelnigg, *J. Chem. Phys.*, **62**, 1225 (1975).
- (59) R. Ahlrichs, H. Lischka, B. Zurwaski, and W. Kutzelnigg, *J. Chem. Phys.*, **63**, 4685 (1975), and references cited therein.
- (60) R. Ahlrichs and F. Driessler, *Chem. Phys. Lett.*, **23**, 571 (1973).
- (61) J. W. McIver, Jr., and A. Komornicki, *J. Am. Chem. Soc.*, **94**, 2625 (1972).
- (62) R. E. Stanton and J. W. McIver, Jr., *J. Am. Chem. Soc.*, **97**, 3632 (1975).
- (63) P. G. Mezey, *Chem. Phys. Lett.*, **47**, 70 (1977), and references cited therein.
- (64) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1294 (1975).
- (65) Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind., Program No. 279.
- (66) (a) J. A. Pople, *J. Am. Chem. Soc.*, **97**, 5306 (1975); (b) W. J. Hehre, *ibid.*, **97**, 5308 (1975).
- (67) E.g., polyhalogen compounds: H. J. Köhler, unpublished work, and H. Kollmar, private communication.
- (68) F. Kell and R. Ahlrichs, *J. Am. Chem. Soc.*, **98**, 4787 (1976).
- (69) H. Lischka, P. Carsky, and R. Zahradnik, *Chem. Phys.*, **25**, 19 (1977).
- (70) S. Bantle and R. Ahlrichs, *Chem. Phys. Lett.*, **53**, 148 (1978).
- (71) M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **99**, 4899 (1977).
- (72) M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **99**, 4907 (1977); see footnotes of Table VI.
- (73) W. L. Jorgensen and J. E. Munroe, *Tetrahedron Lett.*, 581 (1977).
- (74) M. J. S. Dewar and H. S. Rzepa, *J. Am. Chem. Soc.*, **99**, 7432 (1977).
- (75) H. Kollmar, private communication.
- (76) H.-J. Köhler and H. Lischka, *Chem. Phys. Lett.*, in press.
- (77) M. J. S. Dewar and G. P. Ford, *J. Am. Chem. Soc.*, **99**, 1685 (1977).
- (78) M. J. S. Dewar and G. P. Ford, *J. Am. Chem. Soc.*, **99**, 7822 (1977).

The Bonding Capabilities of Transition Metal Clusters

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Abstract: The bonding capabilities of various transition metal clusters and the resulting stoichiometries of transition metal cluster compounds have been estimated, based upon extended Hückel calculations of the isolated metal clusters. It has been found that the molecular orbitals of each cluster may be readily divided into two classes: the high lying antibonding orbitals (HLAOs) and the cluster valence molecular orbitals (CVMOs). Only the CVMOs are suitable energetically for ligand bonding or for containing metal electrons. Each cluster of a given size and geometry has a particular number of CVMOs which may be used for reliable predictions of compound stoichiometries. A wide range of cluster geometries with up to 15 atoms has been explored including common geometries such as the tetrahedron and octahedron found for known cluster compounds, as well as other less conventional geometries for which there are no known examples.

Transition metal cluster compounds lie at the focus of two converging lines of study. Synthetic chemists are continually preparing new cluster compounds of increasing nuclearity and complexity,^{1,2} while at the same time chemists concerned with catalysis are devoting more study to the important roles of small metal clusters or particles as the active sites in heterogeneous catalysts.^{3,4} Clusters have also been used as models for bulk metals and metal surfaces. This interrelationship becomes more evident when one considers the high nuclearity clusters prepared by Chini and co-workers,¹ clusters which greatly resemble small fragments of bulk metals. Indeed the metal cores of nearly all known organometallic clusters can be considered to be derived from a bulk close packed structure.

Theories of bonding within metal cluster compounds are still primitive. Theoretical analyses have been of necessity primarily of a qualitative nature owing to the complexity of the problem.

Discrete cluster compounds have been approached with varying degrees of success by various empirical rules including the quite successful polyhedral skeletal electron pair theory developed by Wade and Mingos.^{5,6} A few semiempirical LCAO-MO treatments have also been applied to specific systems.^{7,8} The bonding within bare metal clusters, primarily as models for surface and bulk metal phenomena, has also been examined. Included are numerous LCAO-MO calculations⁹⁻¹¹ as well as a number of more sophisticated X- α calculations.¹²

In our studies we have also made semiempirical LCAO-MO calculations for a number of bare metal clusters, but our objectives have been slightly different from those of previous studies. We are not particularly concerned with the electronic properties of a bare metal cluster itself, but are instead concerned with certain aspects of its chemistry. We wish to answer