trobenzyl acetate (which seems uniformly to behave anomalously) no significant effect of substituent on the thermodynamic quantities exists for either reaction, but a difference does seem to exist between the values for each reaction. Further comment on this observation is not warranted at present.

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The Cyclopropylmethyl Cation Series Subjected to the Complete Neglect of Differential Overlap Approximation (CNDO)

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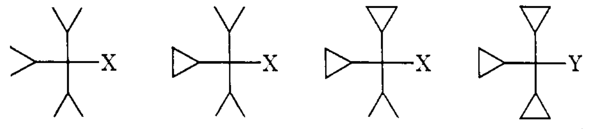
Abstract: The calculations show that the introduction of one cyclopropyl group on methyl cation does not appreciably diminish the charge density on the central carbon atom, but the charge densities on the ring carbons are changed dramatically. The variation of the charge on the ring carbon atoms with successive replacement of hydrogen atoms of methyl cation by cyclopropyl groups suggests a homoallylic type structure. This effect is most pronounced for tricyclopropylmethyl cation.

It is well known that a cyclopropyl group is unusually effective in stabilizing a positive charge on an adjacent carbon. Although the nonclassical explanation for this unusual stabilizing ability is attractive, it has not received unquestioned acceptance.[2] Hart has shown that the replacement of an isopropyl group by a cyclopropyl group in triisopropylmethyl esters increases the solvolysis rate in a regular fashion.[3] The magnitude of the effect produced by successively substituting a cyclopropyl for an isopropyl group becomes more dramatic when one considers that (a) cyclopropyl groups are inductively electron withdrawing relative to an isopropyl group,[4] (b) the steric requirements of the cyclopropyl group are less than of an isopropyl group. Thus, one would expect a slower rate of solvolysis for the cyclopropyl analogs because of less nonbonded repulsions in the ground state relative to the planar transition state for a first-order reaction. A qualitative explanation proposed by Hart to explain the unusual solvolysis rates was set forth in terms of electron delocalization into the cyclopropyl rings.[3b]

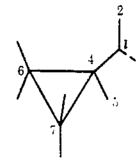


K_{rel} 1 246 2.4×10^4 $\sim 2.0 \times 10^7$

80% aqueous dioxane at 60°

X = *p*-nitrobenzoate; Y = benzoate

In order to ascertain whether this qualitative explanation is consistent with molecular orbital calculation using a fairly sophisticated method, an electron density study was undertaken on the cyclopropyl methyl cation system using the CNDO/2 approximation (complete neglect of differential overlap).[5] Wiberg has applied this approximation to the unsubstituted cyclopropylmethyl cation in both the "bisected" and "in-plane" conformations.[6a] It was concluded from these calculations that the "bisected" conformation (one in which the plane of atoms 1, 2, 3, 4, and 5 bisects the C_6–C_7 bond) was preferred by 8 kcal/mol and that 51.3% of the charge remained outside of the ring. Similar results were obtained by the extended Hückel method.[7]



In view of these findings, our CNDO/2 calculations were carried out on the methyl cation, the cyclopropylmethyl cation with C_s symmetry, the dicyclopropylmethyl cation with both C_s and C_{2v} symmetry, and the tricyclopropylmethyl cation with C_{3h} symmetry. The results of this study are shown in Figures 1–5.

Experimental Section

The computations were carried out on a Burroughs B5500 computer using a Burroughs-ALGOL translation of the CNDO/2 program No. 91, obtained from the Quantum Chemistry Program Exchange (University of Indiana).[8] Although the program was

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[1] (a) Phillip F. du Pont Predoctoral Fellow, 1968–1969; (b) National Institutes of Health Predoctoral Fellow, 1968–1969.

[2] Review article: M. Hannack and H. J. Schneider, *Angew. Chem. Intern. Ed. Engl.*, **6**, 666 (1967).

[3] (a) H. A. Hart and J. M. Sandri, *J. Amer. Chem. Soc.*, **81**, 320 (1959); (b) H. A. Hart and P. A. Law, *ibid.*, **84**, 2462 (1962); **86**, 2957 (1964).

[4] T. L. Brown, J. M. Sandri, and H. A. Hart, *J. Phys. Chem.*, **61**, 698 (1957).

[5] (a) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965); (b) J. A. Pople and G. A. Segal, *ibid.*, **43**, S136 (1965); **44**, 3289 (1966).

[6] (a) K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968); (b) K. B. Wiberg, *J. Amer. Chem. Soc.*, **90**, 59 (1968).

[7] J. E. Baldwin and W. D. Foglesong, *ibid.*, **90**, 4311 (1968).

[8] (a) The description of the method is given in an article by J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966); (b) O. Bastiansen, F. Fritsch, and K. Hedberg, *Acta Crystallogr.*, **17**, 538 (1964); (c) "Tables of Interatomic Distances and Configuration in Molecules

originally written for the IBM 7040-44, our translation is logically identical, except for one modification which was made by Mr. B. R. Gilson of this laboratory. That is, we found that due to our machine limit of eleven significant figures, we were unable to diagonalize the energy matrix for molecules containing threefold rotation axes to within 10^{-8} as required by the original program. Hence, for those molecules containing a threefold axis, such as methyl cation, we relaxed the diagonalization tolerance to 10^{-6}. For molecules not possessing a threefold axis we used the 10^{-8} tolerance. We do not consider this change a serious threat to the qualitative results obtained from the computations, but we make note of this change with regard to machine dependence of the single precision program. Our total processor times varied from 27 sec for methyl cation to 32 min for tricyclopropylmethyl cation.

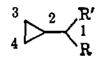
The coordinates of the atoms were calculated using experimental bond lengths and angles wherever possible,[8b] and using idealized sp^2 and sp^3 angles with average bond lengths as given in ref 8c. In cases where a group of atoms repeated in the molecule, such as the cyclopropyl group, the coordinates of the atoms in one group were transformed by a unitary transformation matrix to the second or third position so as to exactly preserve the relative conformation of the atoms within the group.

Results and Discussion

The charge densities in Table I show that the effect of adding two or three cyclopropyl groups lowers the bare charge on the central carbon only by 0.03 and 0.04 e, respectively. With the exception of a 0.159-e decrease by the introduction of one cyclopropyl group, these results do not support the tentative suggestion by Hart. These results are, however, comparable to the effect reported by Baird and Whitehead for a series of alkyl carbonium ions using the SGOBE method of orbital electronegativity equalization to estimate electron densities in nonconjugated systems.[9] These results demonstrate that successive replacement of hydrogen by a methyl group in methyl cation does not drastically affect the electron density of the central carbon after the introduction of one methyl group.

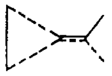
Closer examination of the results reveals an interesting trend in the cyclopropylmethyl cation series. Although successive addition of cyclopropyl groups to the methyl cation does not lower the bare charge at the central atom to any appreciable extent, the electron densities of the cyclopropyl ring carbons do change in an unusual fashion (Table I). The electron densities of the ring carbons of the parent compound (cyclopropylmethyl cation) are approximately equal. Successive replacement of hydrogen by a cyclopropyl moiety on the cyclopropylmethyl cation produces a shift of electron density away from the apex carbon toward the outer-ring carbons. This shift of electron density is dramatically demonstrated in the tricyclopropylmethyl cation, in which the charge on the apex ring carbons is almost zero (electron density approaches that of a neutral carbon atom).

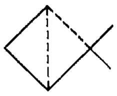
Table I

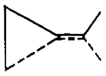


R	R′	Symmetry	C_1	C_2	C_3	C_4	% charge per ring
H	H	C_s	0.276	0.014	0.040	0.040	48.70
H	Cyclopropyl	C_{2v}	0.245	0.016	0.025	0.025	33.75
H	Cyclopropyl	C_s	0.247	0.014	0.025	0.025	33.45
Cyclopropyl	Cyclopropyl	C_{3h}	0.238	0.003	0.017	0.017	25.40

The CNDO/2 calculations tend to support the symmetrical homoallylic intermediate or transition state concept for the cyclopropylmethyl cation (**1**) as suggested by Bergstrom and Siegel.[10] This concept has received continued support recently. Stereochemical studies have been performed by several groups[11,12] using optically active 1-methylcyclopropylcarbinyl derivatives which give unrearranged products. A carbonium ion formed from one of these might maintain optical activity if it had a bicyclobutonium (**2**) or unsymmetrical (**3**) structure. However, a symmetrical homoallylic cation with a bisected structure would be completely racemized. In each of the reactions studied essentially complete racemization took place. Schleyer[13] has provided further evidence for a symmetrical intermediate by examining the effects of one or more methyl substituents on the outer ring carbons. He found a remarkably constant multiplicative effect, for each additional methyl group enhanced the rate of solvolysis, independent of the number and location of its neighbors. The symmetrical effect of the substituents at the corners of the cyclopropyl ring is strong evidence for the symmetrical homoallylic structure. The equality of the electron density of the ring carbons in the cyclopropylmethyl cation seems fortuitous, but the regular decrease in electron density at the apex ring carbon in this series supports the symmetrical homoallylic structure over the bicyclobutonium structure.


1


2


3

In the dicyclopropylmethyl and tricyclopropylmethyl cations (see Table II), the homoallylic structure becomes more classical in nature; that is, there is more double-bond character in the transition state. The partial double bond formed in one ring can now be stabilized by the remaining rings. Ultraviolet studies of cyclopropyl moiety impart a bathochromic shift from 8 to 15 mμ to the π → π* transition when compared to the corresponding isopropyl substitution.[14] The double-bond character in the transition state is born out by formolysis studies by Roberts and Servis[15] on cyclopropylmethyl tosylates which have shown that a considerable amount of ring opening occurs when the carbinyl carbon is substituted.

Thus it seems to us that the cyclopropyl moiety is a "semiolefin"[16] in the sense that in different electronic

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and Ions," L. E. Sutton, Ed., The Chemical Society, London, 1958 and 1965.

(9) N. C. Baird and M. A. Whitehead, *Theor. Chim. Acta*, **6**, 167 (1966).

(10) C. G. Bergstrom and S. Siegel, *J. Amer. Chem. Soc.*, **74**, 145 (1952).

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(12) M. Vogel and J. D. Roberts, *ibid.*, **88**, 2262 (1966).

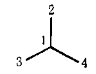
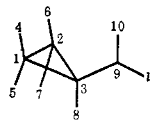
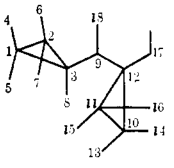
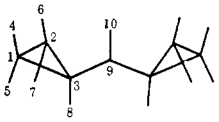
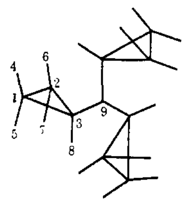
(13) P. von R. Schleyer and G. W. Van Dine, *ibid.*, **88**, 2321 (1966).

(14) C. H. Heathcock and S. R. Poulter, *ibid.*, **90**, 3766 (1968).

(15) K. L. Servis and J. D. Roberts, *ibid.*, **86**, 3773 (1964).

(16) J. M. Stewart and G. K. Pagenkopf, *J. Org. Chem.*, **34**, 7 (1969).

Table II

Atom	q, e	Coordinates x	y	z
				
1	0.435	0	0	0
2	0.188	1.088	0	0
3	0.188	−0.544	0.9422	0
4	0.188	−0.544	−0.9422	0
				
1	0.040	−1.2264	−0.1636	2.2934
2	0.040	−2.2934	−0.1636	1.2264
3	0.041[a]	−0.9406	−0.7680	0.9406
4	0.060	−0.7516	0.7855	2.5336
5	0.084	−1.352	−0.8426	3.1342
6	0.060	−2.5336	0.7855	0.7516
7	0.084	−3.1342	−0.8426	1.3522
8	0.079	−0.8750	−1.8520	0.8749
9	0.276	0	0	0
10	0.116	0	1.080	0
11	0.121	0.6614	−0.540	−0.6614
				
1	0.025	−0.7545	−2.1310	−1.2962
2	0.025	0.7545	2.1310	−1.2962
3	0.014	0	−0.8242	−1.2962
4	0.046	−1.2601	−2.4228	−0.3781
5	0.064	−1.2601	−2.4228	−2.2143
6	0.046	1.2601	−2.4228	−0.3781
7	0.064	1.2601	−2.4228	−2.2143
8	0.050	0	−0.2404	−2.2143
9	0.247	0	0	0
10	0.025	120° rotation of the above 9 atoms		
11	0.025			
12	0.017			
13	0.040			
14	0.066			
15	0.040			
16	0.066			
17	0.059			
18	0.084	0	−0.6984	1.3388
				
1	0.025	−1.2264	−0.1636	2.2934[b]
2	0.025	−2.2934	−0.1636	1.2264
3	0.016	−0.9406	−0.7680	0.9406
4	0.044	−0.7516	0.7855	0.5336
5	0.064	−1.352	−0.8426	3.1342
6	0.044	−2.5336	0.7855	0.7516
7	0.064	−3.1342	−0.8426	1.3522
8	0.056	−0.8750	−1.8520	0.8749
9	0.245	0	0	0
10	0.080	0	1.080	0
				
1	0.017	−0.7545	−2.1310	−1.2962
2	0.017	0.7545	−2.1310	−1.2962
3	0.003	0	−0.8242	−1.2962
4	0.034	−1.2601	−2.4228	−0.3781
5	0.055	−1.2601	−2.4228	−2.2143
6	0.034	0.2601	−2.4228	−0.3781
7	0.055	1.2061	−2.4228	−2.2143
8	0.040	0	−0.2404	−2.2143
9	0.238	0	0	0

[a] Results agree with those calculated previously by Wiberg[6] except for the methine ring carbon (atom 3) in which Wiberg reports 0.036 e as compared to our 0.041 e. [b] For the second ring Z becomes $-Z$.

environments it can behave as a symmetrical, nonclassical homoallylic type structure when delocalization is limited to its immediate environment or as a homoallylic group capable of substantial delocalization when combined with another moiety capable of sharing electrons (*i.e.*, methyl or olefin). We believe the series of compounds for which we have performed CNDO/2 calculations illustrate the ambivalence of the cyclopropyl group in this regard, and may aid in interpreting kinetic results for compounds containing this group.

Acknowledgment. We thank Professor Francis A. Carey, Professor John E. Bloor, Mr. Bruce Gilson, and Mr. Frank Billingsley for their assistance. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.