Iminium Salts in Organic Chemistry

Edited by

H. BÖHME

and

H. G. VIEHE

ADVANCES IN ORGANIC CHEMISTRY

Methods and Results

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ADVANCES IN ORGANIC CHEMISTRY: Methods and Results
E. C. TAYLOR, *Editor*

Iminium Salts in Organic Chemistry
Part 1

Edited by

H. BÖHME

Universität Marburg/Lahn, Germany

H. G. VIEHE

Université de Louvain, Belgium

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Foreword

The exceptional role of the iminium grouping in many reactions that occur both in the laboratory and in nature has been recognized for a long time. Since then, however, organic chemistry has become such an extremely broad and diversified science that the enormous progress attained meanwhile in iminium chemistry, including new methods, reagents, ideas, new ways, and fields of application, may have escaped general attention. People engaged in this area have become aware that an urgent need exists for a book which not only gathers the vast amount of new material but reintegrates all of the recent achievements into a more general framework in terms of modern concepts of organic chemistry.

I strongly believe that the present work fulfills these requirements. Although I was engaged in the early discussions during the conception of this book I am now very impressed at seeing the final result. Both the editors and the authors have succeeded in creating a book from which, I am sure, the chemical community will profit for a long time.

Z. ARNOLD

Prague, Czechoslovakia,
February 1976

Series Editor's Note

Although most volumes in the *Advances in Organic Chemistry* series will continue to be multiauthored works presenting authoritative, critical, and timely discussions of new developments in synthetic and instrumental methodology, in line with the general objectives of the series as set forth in the Preface to previous volumes, the present volume, which will appear in two parts, marks a further expansion of the concept of *Advances*. The first departure from the normal format, as outlined above, will be found in Volume 7, which was a single-authored research monograph. The present volume is likewise devoted to a single topic, but is multiauthored and prepared under the general editorship of outside experts in the field. We hope that the rapidity of publication of the two types of research monographs in the *Advances* series will be attractive both to readers and to authors, and that the series as a whole will continue to present in a challenging, provocative, and stimulating manner new ideas, new techniques, and new methods that will become part of the classical repertoire of the practicing organic chemist.

EDWARD C. TAYLOR
Series Editor
Advances in Organic Chemistry

Preface

Research workers in nitrogen chemistry have felt the need for an adequate coverage of modern iminium salt chemistry. This book, we think, will satisfy this need.

Many discussions preceded the 1972 meeting in Marburg at which it was decided to "launch" this book. The project started with an encounter of H. G. Viehe with Z. Arnold in Prague, 1972, followed by others with L. Ghosez in Louvain, with H. Eilingsfeld, H. Pommer, and M. Pape in BASF-Ludwigshafen, with H. Bredereck in Stuttgart, with E. Küle and E. Grigat in Bayer-Leverkusen, and with C. Jutz in Munich. We feel honored and thank the authors for their extensive work and for their trust and confidence. To Prof. E. C. Taylor, the series editor, we address our repeated thanks for his masterly streamlining of this book.

May all the work serve well now!

H. BÖHME
H. G. VIEHE

Marburg, Germany
Louvain-la-Neuve, Belgium
August 1976

Contents

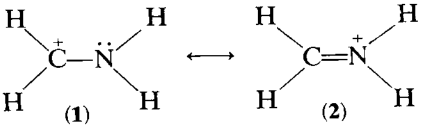
THE ELECTRONIC STRUCTURE OF IMINIUM IONS

By P. A. KOLLMAN, *Department of Pharmaceutical Chemistry, School of Pharmacy, University of California, San Francisco, California* 94143

CONTENTS

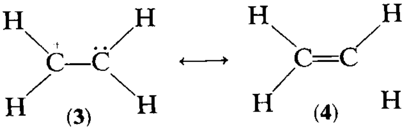
I. Introduction

The iminium ion, $CH_2NH_2^+$, considered from the point of view of valence bond theory, contains contributions from the two resonance structures **1** and **2**:



(1) (2)

The ion is isoelectronic with ethylene and has many physical properties that are qualitatively similar to those of C_2H_4. From the point of view of the simple valence bond description above, however, the molecules differ somewhat, ethylene being predominately in resonance structure **4** and iminium containing significant contributions from structures **1** and **2**:



(3) (4)

In any practical sense the chemistry of the two is very different; for example, a simple method of preparing alkenes is dehydration of alcohols, whereas iminium ions can be formed most simply by protonation of imines or by dissociation: $R_2NCH_2X \rightleftharpoons R_2N{=}CH_2^+ + X^-$.

In this chapter we examine the properties of iminium from the point of view of modern electronic structure theory. We address ourselves to two main questions. First, what do quantum-mechanical calculations predict for the structural and spectral properties of iminium? Second, what do these calculations predict for the relative stabilities, rotational barriers, and electronic structures of substituted iminium ions?

II. Description of Methods

All of the calculations described in this chapter solve the quantum-mechanical Schrödinger equation variationally, using an atomic orbital basis to represent molecular orbitals. The wave function is a single Slater determinant constructed from these molecular orbitals. This type of calculation is often referred to as LCAO-MO-SCF (Hartree-Fock): Linear Combination of Atomic Orbitals-Molecular Orbitals-determined via a Self-Consistent Field procedure. The optimum molecular energy determined that constrains the wave function to be a single determinant is called the Hartree-Fock energy; this is always greater than the exact molecular total energy. The difference between the exact (nonrelativistic) molecular energy and the Hartree-Fock energy is termed the correlation energy.

Here we consider semiempirical and nonempirical LCAO-MO-SCF solutions of the Schrödinger equation. There are many all-valence electron semiempirical methods, but the one discussed in this chapter is the CNDO/2 procedure described by Pople and Beveridge (1). This method was parameterized to reproduce charge distributions predicted from nonempirical calculations on simple molecules. Other methods, such as INDO (1), MINDO (2), and NDDO (3) are parameterized in a different fashion, include other terms in the Hamiltonian, and differ in the experimental properties they reproduce most successfully. It is a reasonable generalization that semiempirical molecular orbital methods are reliable in reproducing some molecular properties but are rarely predictive (2b).

The nonempirical calculations (often referred to as *ab initio*) are generally more reliable, but there is a great variation in their reliability, depending on the size of the atomic orbital basis set used to determine the molecular orbitals. In this chapter we consider mainly two types of basis sets, a single Slater (STO) to represent every atomic orbital, and a "double zeta" set, which uses two orbitals in the basis set per atomic orbital. Hehre, Pople, Ditchfield, and Stewart (4) have developed Gaussian representations of these two types of basis sets, and their STO-3G

(4a) and 431G (4b) bases are used for many of the calculations described below (5).

In general, for the molecules considered here, one would expect the CNDO/2 procedure to yield a reasonable representation of their electronic structures, and STO basis *ab initio* calculations to predict qualitatively correct molecular structures. The double zeta basis *ab initio* calculations allow one to predict with confidence electronic and molecular structures and the energetics of some reactions. Obviously the double zeta *ab initio* calculations are the most reliable, but they are also the most time consuming. For example, a CNDO/2 calculation on methyleniminium takes 0.2 sec, an STO-3G calculation 2 sec, and a 431G calculation 10 sec (all on a CDC 7600 computer). However, it must be emphasized that there are a number of interesting chemical properties which any Hartree-Fock calculation cannot adequately represent, such as dissociation energies, $\Delta E(\text{HF} \rightarrow \text{H} + \text{F})$, and activation energies for chemical reactions ($H_2 + F \rightarrow HF + F$). Calculations that include part of the "correlation energy" are capable of precisely representing some of these very important properties, but as yet only for quite small molecules (6).

III. The Parent Iminium Ion

It may be instructive to begin by comparing the basicity of imines and other heterocyclic compounds. The calculated proton affinity of methylenimine, CH_2NH, is 226 kcal/mole (7); similar calculations on formaldehyde [predicted proton affinity (PA) = 180 kcal/mole, compared with the experimental value of 161 kcal/mole] (8) lead to expectations that the experimental proton affinity of H_2CNH is ~207 kcal/mole. We expect from our calculations that CH_2NH will have a proton affinity similar to that of ammonia (experimental PA = 207 kcal/mole) and less than that of methylamine (PA = 216 kcal/mole) (9). Since a comparable inductive effect might be expected for a CH_2 and a CH_3 group, the difference between the proton affinities of methylamine, methylenimine, and HCN (PA = 180 kcal/mole) (10) follows the trend expected, decreased basicity paralleling the "%*s* character" of the nitrogen lone pair.

The calculated ground-state geometry of iminium appears to be quite similar to that of C_2H_4. The geometrical parameters for each are summarized in Table I. As one can see, the evidence is strong that the iminium ion contains a $C{-}N^+$ double bond ($R = 1.26$ Å) intermediate in length between the C–C double bond (1.32 Å) and the C–O double bond [for formaldehyde $R(C{=}O) = 1.21$ Å]. The more accurate and flexible 431G calculation (4b) predicts a somewhat smaller C–N distance than the minimal basis STO-3G calculation (4a), probably because the former can represent the C=N bond more accurately; for neutral hydrocarbons,

TABLE I

Geometries[a] for CH_2NH, $CH_2NH_2^+$, and CH_2CH_2

	$CH_2NH_2^+$		CH_2NH			CH_2CH_2	
	STO-3G	431G	431G	Experimental		STO-3G	Experimental (13)
R(C—N)	1.29	1.26	1.26	1.30	R(C—C)	1.31	1.34
R(C—H)	1.11	(1.11)	(1.09)	(1.09)	R(C—H)	(1.09)	1.09
R(N—H)	1.04	(1.04)	(1.00)				
θ(HCH)	118	118	(118)	(118)[b]	θ(HCH)	116	117
θ(HNH)	116	115	(113)[c]				
ν(C—N)[d]	1910	1980	1760		ν(C—C)	1950	1620–1680 (14)

[a] Distances in angstroms, and angles in degrees; parameters in parentheses were not optimized.

[b] The two hydrogens were assumed to be of equivalent length and NCH to be the same for each; the microwave spectrum was consistent with slightly different structural parameters for the two hydrogens (see ref. 12).

[c] CNH angle determined by Lehn (11).

[d] Stretching frequencies calculated.

however, the minimal basis does very well in predicting geometrical parameters (6). X-ray structural evidence (15) on $(CH_3)_2C$—$N(CH_3)_2$ indicates a $\overset{+}{\mathrm{C}}$—N bond length of 1.30 Å. Guanidinium, $(NH_2)_3C^+$, has a C—N bond length of 1.32 Å (16); a 431G calculation on guanidinium predicts a bond length of 1.30 Å (17). In the tetramethyl-substituted iminium ion, one might expect a longer C–N distance than in the unsubstituted compound because of methyl hyperconjugation with the carbonium ion center and C· · ·C repulsions. The comparison between the calculated and experimental guanidinium values supports a prediction of ~1.28 Å for the C–N bond length in iminium, CNH_4^+. The fact that the methyleniminium ion is predicted to have about the same bond length as methylenimine is further support for the "double-bonded" nature of CNH_4^+.

The predicted C–H and N–H bond lengths are in reasonable accord with what one expects for isoelectronic neutral species, although probably somewhat greater than the experimental values. The fact that the HCH angle in $CH_2NH_2^+$ is predicted to be 2° larger than the HCH angle in ethylene appears to be inconsistent with the prediction by a number of authors that AB_2 bond angles in similar systems can be predicted from electronegativity effects: the more electronegative the external atom, the smaller the BAB angle (18,19). However, if one looks at the Mulliken atomic populations in C_2H_4 and $CH_2NH_2^+$ (relatively insensitive to the HCH angle), one finds that $\overset{\delta-}{\mathrm{C}}$–$\overset{\delta+}{\mathrm{H}}$ polarity is greater in the iminium ion and thus the relative bond angles are consistent with the electronegativity picture.

Rationalization of the relative HCH and HNH angles in iminium is not obvious via the same model; one would expect θ(HNH) to be greater than θ(HCH) if electronegativity effects were the key. It may be, however, that the greater π occupancy on the nitrogen half of the molecule shrinks the N–H bond hybrids to smaller angles,[†] but a more complete study of $CH_2NH_2^+$ and CH_2NH is needed for a better understanding of the bond angles found in these molecules.

As would be expected (6), the predicted stretching frequencies are uniformly higher than those found experimentally. The prediction that the stretching frequency of the $C{=}N^+$ linkage in iminium is approximately equal to that of the ethylenic C=C and imine C=N is consistent with experimental observations on substituted (14,20) C=C, C=N, and $C{=}N^+$ linkages, where $\nu(C{=}C) = 1620–1680\ cm^{-1}$, $\nu(C{=}N) = 1640–1690\ cm^{-1}$, and $\nu(C{=}N^+) = 1660–1690\ cm^{-1}$.

The orbital energies and atomic populations for the three species C_2H_4, CNH_3, and CNH_4^+ are presented in Table II. The orbital energies are

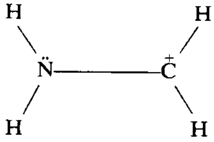
TABLE II

Mulliken Populations and Orbital Energies of C_2H_4, CNH_3, and CNH_4^+[a]

Ethylene		Methyleniminium		Methylenimine	
Orbital energy, au	Atomic population	Orbital energy, au	Atomic population	Orbital energy, au	Atomic population
−11.2072	C: 6.34	−15.8854	C: 5.88	−15.5421	C: 6.08
−11.2056	C(π): 1.00	−11.5833	C(π): 0.53	−11.2660	C(π): 0.89
−1.0376	H: 0.83	−1.5696	N: 7.72	−1.2253	N: 7.55
−0.7821		−1.1686	N(π): 1.47	−0.8482	N(π): 1.11
−0.6388		−1.0313	H_N: 0.52	−0.6884	$H_{cis\text{-}N—H}$ 0.85
−0.5870		−0.9757	H_C: 0.68	−0.6118	H: 0.82
−0.4913		−0.8185		−0.4462	H_N: 0.70
−0.3772 (π)		−0.7907 (π)		−0.4147 (π)	
0.1875 (π^*)		−0.1336 (π^*)		0.1608 (π^*)	
0.2651 (σ^*)		−0.0168 (σ^*)		0.2375 (σ^*)	

[a] 431G basis set; minimum energy geometry.

[†] The extreme case of



(both π electrons on nitrogen)

would lead to a predicted HCH angle of 120° (as in CH_3^+) and an HNH angle near 107° (NH_3).

similar in the ionic and neutral compounds, with the highest occupied and lowest unoccupied orbitals being of π symmetry. The orbital energies for CNH_4^+ are of much lower energy because of the positive charge. In CNH_4^+ the highest occupied and lowest empty orbitals are also of π symmetry. Comparing ethylene and methyleniminium, one finds a smaller π-π^* gap in ethylene, despite the fact that the iminium $\pi \rightarrow \pi^*$ transition appears to be at a longer wavelength (220–235 nm) (21) than the ethylene $\pi \rightarrow \pi^*$ (171 nm) (14). This is not very surprising, however, since experimentally one is observing the spectrum of the iminium ion in the vicinity of an anion, whereas the calculations described in Table II were done on the isolated cation. In view of the polarities predicted for the iminium ion (Table II), one might expect that the anion would be, on the average, nearer the NH_2 protons, and would destabilize the π ground state more than the π^* excited state (the ground-state π orbital contains 1.5 electrons on nitrogen and 0.5 on carbon; the π^*, the reverse polarity), and thus cause a red shift in the $\pi - \pi^*$ transition.

One of the curious features of methyleniminium is the fact that the Mulliken population on the nitrogen *increases* on protonation. Comparing methylenimine and methyleniminium, one finds that on protonation the total charge on the three protons in CNH_3 (2.37) is shared among the four in CNH_4^+ (2.40) and that the nitrogen and carbon lose only 0.03 electron on protonation. The C–N bond length causes us to conclude that the π bond is equally strong in the ion and in the imine, but far more ionic in CNH_4^+, where the nitrogen has 1.47 of the total of 2 π electrons. However, the Mulliken overlap population for the C–N bond is significantly smaller for the iminium ion than for the imine (0.66 versus 0.99). Thus the use of overlap populations to predict bond strength and length will not work with the two molecules CNH_3 and CNH_4^+. The very small populations on the hydrogens indicate that they should be quite far downfield in proton NMR, and this is what is observed (22).

The rotational barrier in the iminium ion is significant. With optimization of the parallel and perpendicular forms, one predicts a barrier of 71 kcal/mole for methyleniminium, which is significantly higher than the value predicted for methylenimine (57 kcal/mole) (11). The barrier for iminium appears to be lower than that of ethylene at the SCF level, but the important role of configuration interaction (*correlation energy*) in determining the barrier in C_2H_4 has been emphasized (23). On the basis of Buenker's calculations (23) one expects that the calculated values cited above are upper bounds for the actual barriers.

Why is the rotational barrier larger in $CH_2NH_2^+$ than in CH_2NH? In CH_2NH there is still a lone pair to stabilize the C^+ center in the perpendicular form, even though this "lone pair" is of a σ variety and much more tightly bound than the nitrogen π lone pair (thus the large barrier), the lone pair is more easily donated to the carbon than are the N–H bonding electrons of methyleniminium.

What makes iminium ions such relatively stable ions? We have compared (7) the stabilities of CH_2R^+, where $R = H$, CH_3, NH_2, and F, in an attempt to answer this question. Looking at the rotational barriers would give only a partial answer to this question, since for $R = H$ and $R = F$ there is obviously no (in the case of CH_3, very small) dependence of the energy on rotation of the R group. Comparing $R = NH_2$ and $R = OH$, it is clear that the π electrons of the nitrogen are more effective at stabilizing the carbonium ion center, since the rotational barriers of $CH_2NH_2^+$ and of CH_2NH are greater than the value for CH_2OH^+.

One way to compare the stabilization effect of the R group on the CH_2^+ carbonium ion fragment is to look at the energy for hydride transfer:

$$CH_3X + CH_2Y^+ \rightarrow CH_3Y + CH_2X^+ \qquad (1)$$

Since the heats of formation of a number of these species are known, one can determine ΔH for reaction 1 with different X and Y.

Similarly, one can carry out quantum-mechanical calculations on CH_3X and CH_2X^+ and compare the energy differences (ΔE) for the various substituent groups. The experimental and theoretically calculated differences for the various groups (relative to $X = H$) are presented in Table III. As one can see, the stabilizing influence on the carbonium ions follows the order $X = NH_2 > OH > CH_3 > F$.

It is also important to mention here that Radom et al. (24) have given extensive numerical support to the suggestion by Snyder (25) that the energies for reactions such as reaction 1 can be well described within the

TABLE III

Carbonium Ion Stabilization Energies

R	ΔH_{stab}[a]	ΔE_{stab}[b]	ΔE_{res}	ΔE_{induct}
R	0	0	0	0
CH_3	31–42	27	11	16
NH_2	96.5	89	66	23
OH	32–57	45	48	−3
F	4	−5	31	−36

[a] ΔH for the reaction $CH_2R^+ + CH_4 \rightarrow CH_3R + CH_3^+$, determined for heat of formation data for the above species; see ref. 10.

[b] ΔE calculated for the reaction of footnote a, evaluated from the total energies for the species.

Hartree-Fock framework; the agreement between theory and experiment in Table III is further support for this view. These types of reactions involve the same number of electron pairs in both reactants and products, and thus both reactants and products would be expected to have similar correlation energies (6).

We have further separated (7) the "resonance" and "inductive" effects on carbonium ion stability by carrying out SCF calculations with and without the $p\pi$ orbitals on the carbon to determine the "resonance" stabilization of these carbonium ions, and have attributed the remainder of the stability or instability to inductive effects, that is,

$$\Delta E_{\text{stab}}\{[E(\text{CH}_4) - E(\text{CH}_3^+)] - [E(\text{CH}_3\text{X}) - E(\text{CH}_2\text{X}^+)]\}$$
$$= \Delta E_{\text{res}}[E(\text{CH}_2\text{X}^+ \text{ with } p\pi \text{ orbital on C})$$
$$- E(\text{CH}_2\text{X}^+ \text{ without C } p\pi \text{ orbital})] + \Delta E_{\text{induct}} \qquad (2)$$

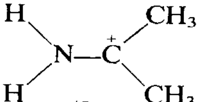
These results are presented in Table III and clearly indicate that CH_3 and NH_2 groups are inductively stabilizing, OH is inductively neutral, and F is inductively destabilizing. The "inductive effect" for OH and NH_2 is somewhat surprising until one looks at the Mulliken populations and realizes that the *hydrogens* are playing an important role in "absorbing" the positive charge, thus compensating for the inductive withdrawing power of nitrogen and oxygen. Hence the iminium ion is stabilized in relation to the simplest carbonium ion, CH_3^+, by a substantial amount of resonance and inductive stabilization.

IV. Substituted Iminium Ions

A. ELECTRONIC STRUCTURE AND ISOMERIZATION ENERGIES

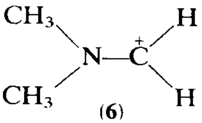
Since the iminium ion $CH_2NH_2^+$ has never been chemically isolated, one is naturally interested in the effects of various substituents on the electronic structure and properties of the parent iminium fragment. Here we consider the effects of substitution of CH_3, NH_2, OH, SH, F, Cl, —C=O, and —C=C groups on the iminium ion structure (26).

What is the effect of a methyl substituent on the iminium ion? We have examined two possibilities of dimethyl substitution and carried out electronic structure calculations at the CNDO/2 (1) and STO-3G *ab initio* (4a) level for two isomers **5** and **6**:



(5)

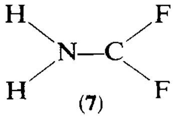
and



(6)

The difference in energy calculated for these two species is considerable, the C—CH_3 species being favored by 21 kcal/mole at the STO-3G level (the CNDO/2 calculations predict the N—CH_3 substituent to be more stable by 1 kcal/mole). The more trustworthy STO-3G results are consistent with one's intuition that the CH_3 groups play an important role in stabilizing the carbonium ion center, but comparison of the Mulliken populations for the CH_3-substituted species with the value for the parent species shows that the C—Me stabilizing effect comes, not from more net electrons in the carbonium carbon π orbital, but from an increase in the total nitrogen electron population (7.32) and in the nitrogen π population (1.52). In the parent compound these populations are $N(\text{total}) = 7.28$ and $N(\pi) = 1.43$; in the N-CH_3-substituted compound, $N(\text{total}) = 7.16$ and $N(\pi) = 1.35$. The carbon π populations are 0.57 in the parent and C—CH_3-substituted compounds and 0.66 in the N—CH_3-substituted compound. Our general working model is as follows: methyl groups attached to the positively charged carbon donate electrons into the C^+ π orbital and allow the nitrogen to retain more of its lone pair (1.52) than in the parent compound (1.43). In the N—CH_3 compound the interaction is a repulsive one between the C–H bond and the iminium $\ddot{N}$, forcing electrons from the nitrogen lone pair to the carbon, which ends up with 0.65 electron.

We have also examined the effects of difluorosubstitution on the iminium fragment and have considered the relative energies of the four difluorosubstituted compounds. The results are consistent with what one would predict: the CF_2 isomer **7**:

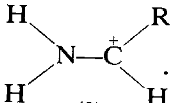


(7)

is the most stable, with the cis and trans 1,2-difluoro compounds of roughly equal energies and 45 kcal/mole less stable than the CF_2 isomer; the NF_2 isomer is an additional 34 kcal/mole higher in energy. The Mulliken populations on the C^+ for the CF_2 species indicate a large π population (0.77) but a quite small total population (5.33), indicating that these fluorosubstituted compounds are probably quite unstable (recall the inductive destabilizing effect of a fluoro group, discussed in Section III).

The fact that the cis and trans 1,2-isomers are very similar in energy is expected, considering the two 1,2-fluoro isomers of ethylene (27), where the cis is favored over the trans by ~0.3 kcal/mole. There is very little difference in the electronic structures of the two 1,2-difluoro isomers, and the carbon π population is 0.71, between the values for the CF_2 iminium ion (0.77) and the NF_2 isomer (0.63). The other populations are also close to "averages" of the values found for the CF_2 and NF_2 isomers.

One now inquires about the general effect of the substitution of π-donating groups such as NH_2, OH, F, SH, and Cl on the iminium ion fragment **8**:



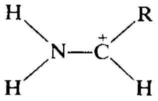
(8)

There is a significant donation into the carbon π orbitals from these groups; the Mulliken populations on the C—N fragment for the various substitutions are present in Table IV. As one can see, these groups have a significant electron-donating effect on the carbon π orbital, but it is interesting that this effect is very similar for all the R's (0.10–0.13 electron).

How well does a double bond conjugate with the iminium fragment? We have examined the conjugation of C=C and C=O linkages with the $C{=}\overset{+}{N}$ fragment, carrying out the theoretical calculations on the isoelectric analogues of butadiene and acrolein. In these cases we found relatively little energy difference between species in which the double bond is attached to the nitrogen and those in which it is attached to carbon. Since complete geometry searches were not carried out, one should not overemphasize the absolute energy difference, but this difference is small. The results are summarized in Tables V and VI. The C=C-substituted iminium ions are similar to the Me-substituted compounds, carbon substituted ones being more stable than nitrogen-substituted by about 12 kcal/mole. This difference is *not* reflected in the $\overset{+}{C}$ π population, since the more stable compound has fewer (0.63) electrons in its π orbitals than does the less stable (0.65). Once again, the nitrogen π population is

TABLE IV

Mulliken Populations for the Substituted Iminium Ions



	R					
	H	NH_2	OH	F	SH	Cl
C:	5.70	5.66	5.68	5.63	5.90	5.79
C(π):	0.57	0.70	0.70	0.68	0.69	0.67
N:	7.28	7.34	7.31	7.30	7.32	7.27
N(π):	1.43	1.65	1.52	1.46	1.54	1.43