acetate); *N*-methylaniline (Matheson Coleman and Bell) was distilled prior to use. *N*-Methyl-2,2,2-trifluoroacetanilide was synthesized from trifluoroacetic anhydride and *N*-methylaniline in ether according to Bourne, Henry, Tatlow, and Tatlow.[18] The substituted anilides were available from previous work.[6a]

Kinetics. Rate constants were determined spectrophotometrically employing a Cary Model 16 (with Sargent recorder, Model SRL) or Beckman DB spectrophotometer. An increase in absorbance (typically 0.2–0.4 absorbance unit) with time was followed at either 285 or 238 nm, the product ultraviolet maxima. Faster reactions were carried out directly in a quartz cuvette secured in a constant-temperature cell holder. Slower reactions were carried out with aliquot sampling from solutions in a 100-ml volumetric flask held in a constant-temperature bath. The data were treated in two ways: for approximately one-half of the runs a Guggenheim procedure[19] was employed in which two sets of an equal number of measurements spaced at a constant time interval were taken, the first set during the first half-life and the second after 3 half-lives. Rate constants for the remaining runs were derived from the points taken during the first half-life and an experimental infinity point. The Guggenheim-calculated rate constant values were approximately 6–8% higher than the infinity point values for the slower glycylglycine runs, due presumably to a small amount of oxidation of *N*-methylaniline which occurred in allowing the solution to stand for the longer times required for the hydrolysis to go to completion (4–5 days). First-order rate coefficients were obtained from a computer calculation of the slope of the least-squares regression line for a plot of $\ln (A - A_t)/(A - A_0)$ *vs.* time. A least-squares program was also applied in the reduction of Guggenheim data.

pK_a Determination. The pK_a values for the catalyst species were derived from potentiometric titration experiments following the procedure of Albert and Serjeant.[20] Measurements of pH were made with an Instrumentation Labs Digimatic pH meter equipped with a combination silver|silver chloride electrode. The values obtained are included in Table II.

Table II. Ionization Constants of Buffer Species at 25°

	Buffer (BH)	pK_a (μ = 0.05)[a]	pK_a[b]
(1)	*N*-Glycylglycine	8.25 ± 0.01	8.25
(2)	Ammonium	9.24 ± 0.02	9.24
(3)	Benzylammonium	9.41 ± 0.02	9.35
(4)	Glycine	9.70 ± 0.02	9.78
(5)	Trimethylammonium	9.81 ± 0.01	9.80
(6)	*N*,*N*-Dimethylglycine	9.92 ± 0.04	9.94[c]
(7)	Sarcosine	10.04 ± 0.02	9.92[d]
(8)	β-Alanine	10.16 ± 0.02	10.24[c]
(9)	L-Proline	10.54 ± 0.02	10.64
(10)	*n*-Butylammonium	10.62 ± 0.02	10.60

[a] Constant ionic strength maintained by addition of KCl. [b] Literature values of thermodynamic ionization constants from L. Meites, Ed., "Handbook of Analytical Chemistry," McGraw-Hill, New York, N. Y., 1963, pp 1-21, unless otherwise indicated. [c] J. P. Greenstein and M. Winitz, "Chemistry of the Amino Acids," Vol. I, Wiley, New York, N. Y., 1961, p 492. [d] R. C. Weast, Ed., "Handbook of Chemistry and Physics," 50th ed, Chemical Rubber Co., Cleveland, Ohio, 1969–1970, pp 1-118.

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The Methylenimmonium Ion and the Role of Resonance and Inductive Stabilization in Carbonium Ions

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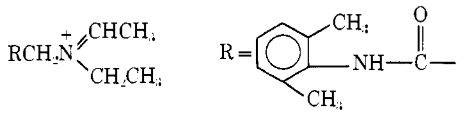
Abstract: The electronic structure and rotational barrier of the methylenimmonium ion and the proton affinity of methylenimine are examined with high quality molecular orbital wave functions. The electronic properties of this resonance stabilized carbonium ion, $CH_2NH_2^+$, are compared with its neutral precursor, CH_2NH, with its neighbors in the periodic table, formaldehyde and protonated formaldehyde, and with methyl, fluoromethyl, and ethyl carbonium ions. CH_2F^+, CH_2OH^+, and $CH_2NH_2^+$ are computed to be resonance stabilized by 31, 48, and 66 kcal/mol, respectively, relative to the methyl cation. The rotational barrier of $CH_2NH_2^+$ is found to be higher than its neutral precursor, CH_2NH. $CH_2NH_2^+$ is also *inductively* stabilized relative to CH_3^+.

The role of resonance in the stabilization of carbonium ions has not as yet been examined quantitatively; the calculations reported here on the methylenimmonium ion and other resonance stabilized carbonium ions will allow us to compare simple carbonium ions, such as ethyl and methyl cation[2] with resonance stabilized ions $CH_2NH_2^+$, CH_2OH^+, and CH_2F^+.

The methylenimmonium ion $(CH_2NH_2)^+$ is a prototype of postulated intermediates in biologically important N-dealkylation reactions. The structure



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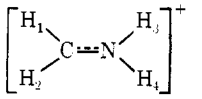
[2] (a) J. E. Williams, V. Buss, L. C. Allen, P. v. R. Schleyer, W. Latham, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 2141 (1970); J. E. Williams, V. Buss, and L. C. Allen, *ibid.*, **93**, 6867 (1971); (b) J. E. Williams, R. Sustmann, L. C. Allen, and P. v. R. Schleyer, *ibid.*, **92**, 1038 (1970).

has been proposed as a key intermediate in the dealkylation of lidocaine.[3] Thus, it is important to examine how well semiempirical molecular orbital methods like CNDO/2[4] can represent the energetics and charge distribution of the small methylenimmonium ion in order to assay the usefulness of these MO methods in studying larger immonium intermediates. $CH_2NH_2^+$ should be a relatively stable ion (it is often observed in mass spectral fragmentation[5]) and thus is of interest in its own right. In addition, a variety of immonium ions have been studied by nmr spectroscopy.[6]

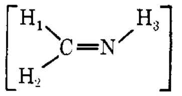
Computational Details

For $CH_2NH_2^+$, the results of a complete geometry search (assuming the carbon and nitrogen lie in a plane of symmetry) with the CNDO/2 semiempirical molecular orbital method are listed in Table I, along with the Mulliken[7] atomic populations at the minimum energy geometry. The C–H, N–H, and C–N distances were the reoptimized using an STO-3G basis set[8] and the total energies found in these *ab initio* calculations are listed in Table II. Next, "double zeta"[9] *ab initio* calculations were carried out at the STO-3G optimized geometries of methylenimmonium (Table III) and previously reported geometries of methylenimine[10] (Table III), formaldehyde and protonated formaldehyde[11] (Table IV), methylamine and methyl alcohol (Table V),[12] ethyl cation[1] and ethane[13] (Table VI), and CH_3F and CH_2F^+ [14] (Table VII). For methylenimmonium, protonated formaldehyde, and CH_2F^+, the SCF calculations were also carried out forcing the $C(2p_\pi)$ orbital to be empty in order to examine the energetic importance of resonance stabilization of these ions; also the rotational barrier of methylenimmonium was examined by calculating the total energy for the CH_2–NH_2 staggered conformations. All the *ab initio* computations were carried out using the MOLE quantum chemistry system[15] with Roothaan's SCF formalism.[16]

Table I. CNDO/2 Results on



methylenimmonium ion



methylenimine

Geometry Search on Methylenimmonium
Minimum energy = −21.3431 au at
R_{CN} = 2.45 au
$\theta(H_1CH_2)$ = 116°
$\theta(H_3NH_4)$ = 115°
$r_{CH_1} = r_{CH_2}$ = 2.10 au
$r_{NH_3} = r_{NH_4}$ = 2.06 au

Methylenimine at Geometry of Ref 10
Energy = −20.8480 au

Mulliken Atomic Populations

	Methylenimine	Methylenimmonium
C	5.910	5.746
N	7.159	7.010
H_1	1.013	0.875
H_2	0.994	0.875
H_3	0.924	0.747
H_4		0.747

Table II. STO-3G Results on Methylenimine and Methylenimmonium

Geometry Search (methylenimmonium)

R(C–N), au	*R*(N–H), au	*R*(C–H), au	E_T, au
2.45	2.06	2.10	−93.22952
2.45	2.06	2.20	−93.22465
2.45	2.06	2.00	−93.22523
2.45	2.16	2.10	−93.21601
2.45	1.96	2.10	−93.23433
2.35	2.06	2.10	−93.22586
2.55	2.06	2.10	−93.22430
2.45	1.86	2.10	−93.22810
2.45	1.96	2.10	−93.09481[a]

Methylenimine (geometry from ref 10)
$E = -92.81955$

Methylenimmonium		Methylenimine	
Atomic Populations at Minimum Energy Geometries			
C	5.797	C	6.008
N	7.283	N	7.293
H_1	0.793	H_1	0.942
H_2	0.793	H_2	0.921
H_3	0.666	H_3	0.835
H_4	0.666		
Overlap Populations			
C–N	1.021	C–N	1.052
C–H	0.760	C–H_1	0.771
N–H_3	0.683	C–H_2	0.781
		C–H_3	0.644

[a] HCH and HNH planes perpendicular.

Rotational Barrier in the Methylenimmonium Ion

One can compute the rotational barrier for the methylenimmonium ion by finding the total energy for the configuration in which the H_2N and CH_2 planes are perpendicular. This should be the maximum energy in the rotation of hydrogens about the central bond. The rotational barrier found with CNDO/2 is 76 kcal/mol; in the *ab initio* calculations, the barrier is found to be 87 (STO-3G) and 72 kcal/mol (double ζ). This high rotational barrier is consistent with the experiments of Olah and Kreienbühl.[17]

It is interesting to compare these computed rotational barriers with those found by Lehn[10] for methylenimine (57 kcal/mol) and Ros[18] for protonated formaldehyde (31 kcal/mol). Both these authors found the preferred motion for X–H (X = O or N) hydrogen motion to be in the molecular plane, with the inversion barrier (in plane hydrogen motion) found to be 26–28 and 17 kcal/mol for methylenimine and protonated formalde-

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(4) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966).

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(16) C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

(17) G. Olah and P. Kreienbühl, *J. Amer. Chem. Soc.*, **89**, 4756 (1967).

(18) P. Ros, *J. Chem. Phys.*, **49**, 4902 (1968).

Table III. Double Zeta Calculations on $CH_2NH_2^+$ and CH_2NH

	CH_2NH	$CH_2NH_2^+$	$CH_2NH_2^+$ (no C $2p_\pi$)	$CH_2NH_2^+$ (ϕ = 90°)
E_T, au	−93.98544	−94.34583	−94.23976	−94.23201
		Atomic Populations		
C	6.008	5.887	5.587	5.645
$C\sigma$	5.047	5.386	5.587	
$C\pi$	0.961	0.501	0.000	
N	7.293	7.563	7.903	7.822
$N\sigma$	6.254	6.064	5.903	
$N\pi$	1.039	1.499	2.000	
H_1	0.942	0.730	0.704	0.742
H_2	0.921	0.730	0.704	0.742
H_3	0.835	0.545	0.551	0.499
H_4		0.545	0.551	0.499
		Overlap Populations		
C–N	1.145	0.835	0.419	0.588
C–H_1	0.792	0.759	0.734	0.739
C–H_2	0.734	0.759	0.734	0.739
N–H_3	0.641	0.637	0.660	0.599
N–H_4	0.641	0.637	0.660	0.599
		Orbital Energies, au[a]		
	−15.5747	−15.9020	−15.8081	−15.8044
	−11.2953	−11.6111	−11.7123	−11.6829
	−1.2234	−1.5462	−1.5256	−1.5220
	−0.8541	−1.1714	−1.1861	−1.1718
	−0.6901	−1.0208 (A)	−1.0172 (A)	−0.9651
	−0.6164	−0.9675	−0.9712	−0.9570 (A)
	−0.4469 (π)	−0.8287 (A)	−0.8363 (A)	−0.9387 (A)
	−0.4174	−0.7755 (π)	−0.7058 (π)	−0.6471 (A)

[a] In this and subsequent tables, the orbitals which are antisymmetric with respect to the plane bisecting the hydrogens are labeled (A); those antisymmetric with respect to the molecular plane are labeled π.

Table IV. Double ζ Calculations on CH_2OH^+ and CH_2O

	CH_2O	CH_2OH^+	CH_2OH^+ (no $C\pi$)
E_T, au	−113.81835	−114.10442	−114.02880
		Atomic Populations	
C	5.981	5.721	5.523
$C\pi$	0.710	0.345	0.000
$C\sigma$	5.271	5.376	5.523
O	8.309	8.379	8.587
$O\pi$	1.290	1.655	2.000
$O\sigma$	7.019	6.724	6.587
H_1	0.855	0.731	0.720
H_2	0.855	0.697	0.684
H_3		0.472	0.486
		Overlap Populations	
C–O	1.044	0.732	0.465
C–H_1	0.733	0.723	0.695
C–H_2	0.733	0.716	0.694
O–H_3		0.529	0.552
		Orbital Energies (au)	
	−20.5816	−20.9327	−20.8577
	−11.3619	−11.7053	−11.7658
	−1.4312	−1.7835	−1.7518
	−0.8653	−1.2471	−1.2495
	−0.7042 (A)	−1.0737	−1.0742
	−0.6424	−0.9911	−0.9975
	−0.5364 (π)	−0.8866 (π)	−0.8389 (π)
	−0.4408 (A)	−0.8286	−0.8046

Table V. Double ζ Calculations on CH_3NH_2 and CH_3OH

CH_3OH E_T = −115.00410	CH_3NH_2 E_T = −95.17610
Atomic Populations	
C = 6.2694	C = 6.3873
O = 8.6276	N = 7.6819
H_1 = H_2 = 0.8395	H_1 = H_2 = 0.8189
H_3 = 0.8110	H_3 = 0.8496
H_4 = 0.6130	H_4 = H_5 = 0.7217
Overlap Populations	
C–O = 0.3887	C–N 0.4305
C–H_1 = 0.7760	C–H_1 = 0.7786
C–H_3 = 0.7697	C–H_3 = 0.7896
O–H_4 = 0.5502	N–H_4 = 0.6794
Orbital Energies (au)	
−20.5424	−15.5317
−11.2784	−11.2442
−1.3624	−1.1740
−0.9334	−0.9002
−0.6863	−0.6618 (A)
−0.6228 (A)	−0.6011
−0.5875	−0.5516
−0.4945	−0.5191 (A)
−0.4478 (A)	−0.3799

hyde, respectively. In the methylenimmonium ion, this inversion motion is not possible and rotation is the only pathway for "scrambling" the hydrogens. The fact that the rotational barrier for the methylenimmonium ion is computed to be higher than that for methylenimine is at first surprising, since one might expect that the C–N bond has less double bond character in the methylenimmonium ion than in methylenimine and that one is relieving two sets of H–H repulsions by rotating the NH_2 plane relative to the CH_2 plane. A possible way to rationalize this difference in barriers is to note that resonance stabilization of methylenimmonium (see later section) is greater than the strength of the C–N π bond broken in methylenimine. One can also rationalize this difference in rotational barriers by noting that the lone pair in methylenimine stabilizes the CH_2 fragment more effectively than the N–H bond does in methylenimmonium. The energy component changes[19] in this rotational barrier are as

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(19) L. C. Allen, *Chem. Phys. Lett.*, 2, 597 (1969).

Table VI. Double ζ Calculations on C_2H_6 and $C_2H_5^+$

C_2H_6 (staggered) E_T = −79.19503	$C_2H_5^+$ (with p_π) E = −78.27546	$C_2H_5^+$ (no p_π) E = −78.25811
	Atomic Populations	
C 6.484	C_M 6.545	C_M 6.663
H 0.839	C_+ 5.814 (0.120 = π)	C_+ 5.745
	H_M 0.705, 0.738 (2)	H_M 0.702, 0.740 (2)
	H^+ 0.730 (2)	H_+ 0.725 (2)
	Overlap Populations	
C–C 0.499	C_M–C 0.517	C–C 0.393
C–H 0.782	C_M–H 0.713, 0.752 (2)	C_M–H 0.759, 0.764 (2)
	C_+–H 0.725 (2)	C_+–H 0.716 (2)
	Orbital Energies	
−11.2138	−11.6418	−11.6610
−11.2133	−11.4796	−11.4701
−1.0146	−1.3213	−1.3251
−0.8347	−1.1143	−1.1198
−0.5945 (2)	−0.9367	−0.9485
−0.4930	−0.8372	−0.8409
−0.4813 (2)	−0.8190	−0.8054
	−0.7741	−0.7694

Table VII. Double ζ Calculations on CH_3F and CH_2F^+

CH_3F E_T = −139.01852	CH_2F^+ E = −138.04837	CH_2F^+ (no π) E = −137.99822
	Atomic Populations	
C 6.131	5.547	5.431
	0.211	0.000
	5.336	5.431
F 9.386	9.073	9.200
	1.789	2.000
	7.284	7.200
H 0.828	0.690	0.685
	Overlap Populations	
C–F 0.290	0.566	0.392
C–H 0.773	0.712	0.700
	Orbital Energies	
−26.2590	−26.6923	−26.6318
−11.3159	−11.7878	−11.8211
−1.5845	−2.0466	−2.0170
−0.9593	−1.3000	−1.3044
−0.6943	−1.1290	−1.1191
−0.6943	−1.0882	−1.0696
−0.6577	−1.0384 (π)	−1.0065 (π)
−0.5295	−0.9160	−0.9042
−0.5295		

follows; the hydrogen eclipsed (lower energy) conformation has 0.193 au less nuclear electronic attraction, 0.181 au less kinetic energy, 0.140 au less electron–electron repulsion; and 0.014 au more nuclear–nuclear repulsion than the H-staggered conformation. The energy component changes are compatible with our physical intuition; the electrons are more mobile, have lower kinetic energies and less electron–electron repulsion in the eclipsed (π bonded) conformation, and are more localized around the nuclei (more attractive V_{ne}) in the staggered conformation.

Proton Affinity of H_2CO and H_2CNH

From the total energies found for methylenimine, formaldehyde, and the two protonated species, we can compute the proton affinities of H_2CNH and H_2CO, which turn out to be 226 and 180 kcal/mol, respectively. There have been two previous studies of protonated formaldehyde, both using smaller basis sets than the "double zeta" used here. Ros[18] calculated a proton affinity of 220 kcal/mol and Hopkinson, *et al.*,[11] calculated a proton affinity of 172 kcal/mol for formaldehyde. The experimental proton affinity for H_2CO is 161 kcal/mol. Thus, our calculations, although of lower total energy than Hopkinson's, give a slightly poorer agreement with the experimental proton affinity of formaldehyde. Correction for zero point energy would bring our calculated proton affinities about 5 kcal/mol closer to experiment. If one assumes that our calculated proton affinity for methylenimine is roughly 20 kcal/mol higher than experiment (as in H_2CO), we see a striking similarity between the proton affinity of NH_3[11] (202 kcal/mol) and methylenimine (∼206 kcal/mol), as well as between the proton affinity of H_2O[11,20] (151 kcal/mol) and H_2CO (161 kcal/mol). However, this similarity in proton affinities is not found in sp bonded nitrogens (HCN, proton affinity 180;[21] N_2, proton affinity ∼100 kcal/mol)[21,22] and sp bonded oxygens (CO, proton affinity at the oxygen[22] 123 kcal/mol).

Not surprisingly,[11] the smaller basis set *ab initio* (STO-3G) and CNDO/2 calculations exaggerate the proton affinity of methylenimine, finding a protonation energy of 260 and 317 kcal/mol, respectively.

Resonance Stabilization and the Electronic Structure of Carbonium Ions

Methylenimmonium, protonated formaldehyde, and CH_2F^+ are carbonium ions stabilized by the contribution of resonance structures like $CH_2{=}NH_2^{(+)}$. For these ions we have computed the resonance stabilization in the following way. First, we have found the total energy after an SCF calculation with the complete atomic basis set and then carried out an SCF calculation without the C $2p_\pi$ atomic orbitals in the basis set. This difference in energies gives one the net resonance stabilization due to double-bonded structures; this stabilization turns out to be 31.4 kcal/mol for CH_2F^+, 47.5 kcal/mol for H_2COH^+, and 65.6 kcal/mol for $CH_2NH_2^+$. Not surprisingly, the methylenimmonium ion is more resonance stabilized than CH_2OH^+ and CH_2F^+; the lower electronegativity of the nitrogen causes the contribution of a resonance structure with a formal + charge on the nitrogen to be more favorable than one which involves a formal + charge on oxygen or fluorine. This greater resonance contribution of nitrogen is also reflected in the net orbital population in the carbon p_π orbitals; in the methylenimmonium ion, the C p_π population is 0.501 electron; in H_2COH^+, the π population is 0.345 electron; and in CH_2F^+, the π population is 0.211 electron. The loss of C p_π charge on protonation is the same in both $CH_2NH_2^+$ and CH_2OH^+; the carbons in H_2CO and H_2CNH lose 0.37 π electron on protonation.

Perhaps surprising is the fact that the rotational barrier of the methylenimmonium ion (72 kcal/mol) is greater than the resonance stabilization (66 kcal/mol)

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(20) There is some question whether the proton affinity of H_2O is ∼150 kcal/mol or nearer 180 kcal/mol; see, for example, M. DePaz, J. J. Leventhal, and L. Friedman, *J. Chem. Phys.*, **51**, 3748 (1969).

(21) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Droxl, and F. H. Field, "Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS 26, U. S. Government Printing Office, Washington, D. C., 1969.

(22) See S. Forsen and B. Roos, *Chem. Phys. Lett.*, **6**, 128 (1970), for a discussion of calculated and experimental proton affinities of N_2 and CO.

of this ion. This means that the π localized structure $H_2C^+{-}NH_2$ (planar) is more stable than $^+CH_2{-}NH_2$ with CH_2 and NH_2 planes perpendicular (Table III). The nuclear repulsion should be lower in the rotated structure, the bond lengths are the same, and one has 28 basis orbitals in the rotated structure (compared to 26 in the π localized structure). A reasonable explanation is found in the large and unfavorable (antibonding) overlap population (-0.112) between the nitrogen atom and the carbon hydrogens in the rotated structure; in the π localized structure, there are none such unfavorable overlap interactions.

It is also of interest to compare the electronic structure of these three carbonium ions with the simplest "resonance stabilized" carbonium ion, ethyl cation. The minimum energy geometry found for ethyl[2a] cation was used to study the resonance energy with the double ζ basis. The $-CH_2^+$ ethyl cation stabilization due to hyperconjugation interaction with the methyl group[2a] is found to be 10.9 kcal/mol, similar to that found by Williams, *et al.*[2a] (11.9 kcal/mol). One should also note that the C $2p_\pi$ populations and resonance energies are roughly proportional: the C $2p_\pi$ population in ethyl cation is 0.120 and the resonance stabilization 10.9 kcal/mol; the C $2p_\pi$ population in methylenimmonium is 0.501, and the resonance stabilization 66 kcal/mol.

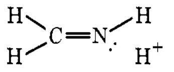
It is also interesting to compare the resonance stabilizations calculated with STO-3G and double ζ and this is done in Table VIII. As would be expected, the removal of a p_π orbital has a much larger energetic effect when one uses the more limited STO-3G basis and thus "resonance energies" calculated using this basis[14] should not be given any quantitative significance.

Table VIII

	$CH_2CH_3^+$	CH_2OH^+	$CH_2NH_2^+$
	STO-3G Results		
C_π population	0.112		0.571
Resonance energy (kcal/mol)	13.9		101
	Double ζ Results		
C_π population	0.120	0.345	0.501
Resonance energy (kcal/mol)	10.9	48	66

The electronic structure of the methylenimmonium ion has some surprising features; notice that the nitrogen appears to be partially negatively charged (Table III). This phenomenon is not unique; alkyl ammonium ions also appear to have negatively charged nitrogens.[23] As in the ammonium ions, in the methylenimmonium, the hydrogens bear most of the positive charge. This charge distribution seems to reflect the fact that electronegativity considerations are more important than valence bond double structures (with a formal + charge on the nitrogen) in determining the electron distribution. However, a more precise study of the charge distribution is needed since Mulliken atomic populations are often very basis set dependent.

If the Mulliken populations do reflect the true charge distribution of $CH_2NH_2^+$, one could rationalize this in valence bond language by saying these are surprisingly large contributions of



to the overall wave function.

It is also noteworthy that in the calculations with the most accurate double ζ basis, the charge on the nitrogen appears to actually increase on protonation (q_N = 7.29 for CH_2NH and q_N = 7.58 for $CH_2NH_2^+$). The same effect is found in the calculations on protonated formaldehyde (q_O = 8.31 for H_2CO; q_O = 8.38 for H_2COH^+). Nmr or nqr (^{14}N) might give insight into the actual charge distributions in these systems, but it is not clear how one could carry out these experiments on $CH_2NH_2^+$ or H_2COH^+, which would probably not be stable in a solution with a reasonably strong nucleophile. As noted before, nmr studies[6] have been carried out on $RCHNHR^+$ species, and it would be of interest to compare these nmr spectra with results for the neutral imines under similar conditions. Also, ^{15}N nmr studies on both neutral and ionic species might provide interesting information about the nitrogen charge distribution, although the paramagnetic "excited state" contribution[24] to the chemical shift would certainly outweigh direct electron density effects.

Role of Inductive and Resonance Stabilization in the Energetics of Carbonium Ions

Let us now determine the magnitude of the resonance and inductive stabilizations in these carbonium ions. The difference in the heats of formation of the carbonium ion and its neutral precursor (CH_3^+ and CH_4, $C_2H_5^+$ and C_2H_6, $CH_2NH_2^+$ and CH_3NH_2, CH_3OH and CH_2OH^+, CH_3F and CH_2F^+) are listed in Table IX. Also listed in the table is the total *stabilization* of the carbonium ion (the difference between $\Delta H(CH_3^+{-}CH_4)$ and $\Delta H(CH_2R^+{-}CH_3R)$ determined experimentally and the ΔE (stabilization) calculated using the energies found with the double ζ basis (the energies for CH_4 and CH_3^+ were computed using the geometries in ref 2a).

As one can see, the agreement between theory and experiment is quite good, given the uncertainty in the experimental data and the fact that no correction has been made for zero-point energy changes or correlation energy differences. In each case, the calculated stabilization appears to be somewhat small. The consistent underestimate of ΔE (stabilization) for $CH_2NH_2^+$ and CH_2F^+ allows us to say that the ΔH (stabilization) experimentally for $C_2H_5^+$ halfway between 31 and 42 kcal/mol and the ΔH (stabilization) for CH_2OH^+ is nearer 57 than 32 kcal/mol.

If one considers the resonance stabilization determined above for the carbonium ions, one can compute the inductive stabilization of the ions and this is also done in Table IX. Not surprisingly, the methyl group is inductively stabilizing, but what is surprising is the large inductive stabilizing effect of the NH_2 group and the inductive *neutrality* of OH. Fluorine is clearly inductively destabilizing. The NH_2 and OH groups are not destabilizing because their very acidic hydrogens

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(23) See, for example, J. M. George, L. B. Kier, and J. R. Hoyland, *Mol. Pharmacol.*, 7, 328 (1971).

(24) The theory of chemical shifts is discussed by J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press, Oxford, 1966.

Table IX

R	ΔH_{exptl} ($CH_2R^+ \rightarrow CH_3R$)[1,20]	ΔH_{stab} (exptl)[1,20]	ΔE_{stab} (calcd)	ΔE_{stab} (res)	ΔE_{stab} (ind)
H	280				
CH_3	238–249	31–42	27	11	16
NH_2	183.5	96.5	89	66	23
OH	223–248	32–57	45	48	−3
F	276	4	−5	31	−36

compensate for the electronegativity of the heteroatom and help to disperse the positive charge of the carbonium ion.

Conclusions and Future Issues

Let us compare the calculated results with CNDO/2 with those found in the *ab initio* calculations. The rotational barrier results are encouraging; the proton affinity results discouraging. Most of the trends in the population analysis are qualitatively similar in the three results although in the methylenimmonium ion CNDO/2 predicts a much less negative nitrogen (−0.01) than STO-3G (−0.28) or double ζ (−0.56).

We can predict from these results that the proton affinity of methylenimine should be ~200 kcal/mol and the rotational barrier of $CH_2NH_2^+$ 72 kcal/mol. $CH_2NH_2^+$ is significantly resonance stabilized and might be observable in solutions without strong nucleophiles.

There are three subjects of future interest: first, one would like to study substituent effects on the electronic structure of immonium ions by CNDO/2 or with small *ab initio* basis sets; secondly, a potential surface for nucleophilic attack on immonium ions will be of interest; finally, and most importantly, the development of an appropriate solvation model to estimate solvent stabilization of the various immonium ions and other possible intermediates in N-dealkylation reactions[3] would be very useful.

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Photoisomerization of 4*H*-Pyran-4-ones to 2*H*-Pyran-2-ones

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Abstract: Ultraviolet irradiation of 2,6-dimethyl-3,5-diphenyl-4*H*-pyran-4-one with a medium-pressure mercury lamp yielded 3,6-diphenyl-4,5-dimethyl-2*H*-pyran-2-one. Photolysis of 2,3,5,6-tetraphenyl-4*H*-pyran-4-one afforded 3,4,5,6-tetraphenyl-2*H*-pyran-2-one and 5,6,7,8-dibenzo-2,3-diphenyl-4-chromen-4-one. The photorearrangement of the hindered 4*H*-pyran-4-ones appears to proceed through two consecutive photoreactions; the first step is the light-induced rearrangement of the hindered 4*H*-pyran-4-ones to the 4,5-epoxycyclopent-2-en-1-one derivatives and the second is the photoisomerization of the latter to 2*H*-pyran-2-ones.

Under the influence of ultraviolet light, 2,6-disubstituted 4*H*-pyran-4-ones (Ia, Ib, and Ic) undergo dimerization to "head-to-tail" dimers (II).[1,2] When the photolysis of Ia was carried out under conditions chosen to retard dimerization, 4,5-dimethyl-2-furaldehyde (IIIa) was isolated in very low yield.[3] Yates and Still[3] suggested that this photoreaction proceeds by rearrangement to 3,4-dimethyl-4,5-epoxycyclopent-2-en-1-one (IVa), which is analogous to the photochemical transformation of cyclohexa-2,5-dienone derivatives.[4]

Studies on the photochemistry of 4,5-epoxycyclopent-2-en-1-one derivatives (IVb and IVc) have revealed that IV undergoes photoisomerization to the corresponding 2*H*-pyran-2-ones (Vb and Vc),[5–8] while furaldehyde derivatives (III) were actually formed *via* the acid-catalyzed rearrangement of IV.[5] Padwa and Hartman[5] have examined the photolysis of 2,6-diphenyl-4*H*-pyran-4-one (Ic) and could not detect the formation of either 3,4-diphenyl-4,5-epoxycyclopent-2-en-1-one (IVb) or 4,5-diphenyl-2*H*-pyran-2-one (Vb), but obtained only a "head-to-tail" cage dimer, IIc.[2,9]

It was anticipated that introduction of the phenyl group into the C-3 and C-5 positions of 4*H*-pyran-4-one

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(1) P. Yates and M. J. Jorgenson, *J. Amer. Chem. Soc.*, **85**, 2956 (1963); P. Yates, E. S. Hand, P. Singh, S. K. Roy, and I. W. J. Still, *J. Org. Chem.*, **34**, 4046 (1969).

(2) N. Sugiyama, Y. Sato, and C. Kashima, *Bull. Chem. Soc. Jap.*, 43, 3205 (1970).

(3) P. Yates and I. W. J. Still, *J. Amer. Chem. Soc.*, **85**, 1208 (1963).

(4) For reviews, see P. J. Kropp, "Organic Photochemistry," Vol. 1, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1967, p 1; H. E. Zimmerman, *Angew. Chem., Int. Ed. Engl.*, **8**, 1 (1969).

(5) A. Padwa and R. Hartman, *J. Amer. Chem. Soc.*, **88**, 1518 (1966).

(6) J. M. Duston and P. Yates, *Tetrahedron Lett.*, 505 (1964).

(7) For reviews of the photochemistry of small-ring carbonyl compounds, see A. Padwa, "Organic Photochemistry," Vol. 1, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1967, p 92; A. Padwa, *Accounts Chem. Res.*, 4, 48 (1971).

(8) In the case of IVc,[6] a pyrylium-3-oxide was formed by a photochemical valence isomerization. For a review, see E. F. Ullman, *ibid.*, 1, 353 (1968).

(9) The structure of IIc was deduced from the spectral data of the photoproduct only,[2] while the structures of IIa and IIb were confirmed not only by their spectral data but also some chemical reactions[1] (Scheme I).