

struct DC symbols for the  $(Q, Q)$  DC's in  $S_6$ . Again an extra specifying label is required in order to label uniquely each  $(Q, Q)$  DC. In the octahedral case permutation and point group parity are not in correspondence. However,

$$Q_h = (S_2 \times S_2 \times S_2)S_3^* = Q + \sigma Q \quad (D.3)$$

where the  $S_2$  symmetric groups permute indices within the blocks of (D.2) and the  $S_3^*$  symmetric group permutes the blocks among themselves. Then the  $(Q_h, Q_h)$  DC's which are uniquely labeled by DC symbols each decompose into 1, 2, or 4  $(Q, Q)$  DC's; for a particular DC, say  $Q_h G_q Q_h$ , this decomposition would depend on which, if any, of the sets

$$Q G_q Q, Q G_q \sigma Q, Q \sigma G_q Q, \text{ and } Q \sigma G_q \sigma Q \quad (D.4)$$

are distinct. Thus if all these four sets were equal, no extra specifying label would be appended; if all of these sets were distinct, the labels ++, +-, -+, and -- would be appended; and, if there were just two distinct sets

$$Q G_q Q = Q \sigma G_q \sigma Q \text{ and } Q G_q \sigma Q = Q \sigma G_q Q \quad (D.5)$$

then the labels + and - would be appended. The various DC symbols and DC representatives are indicated in Table III.

It is to be noted that the DC's  $m = 2++$  and  $m = 2--$  are reflections, and inverses too, of one another; they thus form a single mode, denoted  $m = 2+$ . Also the DC's  $m = 2+-$  and  $m = 2-+$  are reflections of one another, so that they too form a single mode, denoted  $m = 2-$ . Thus although there are seven  $(Q, Q)$  DC's there are only five modes.

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## The NH<sub>2</sub> Substituent Effect on the Properties of Ionic Compounds

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**Abstract:** Electronic structure calculations on NH<sub>2</sub> carbonium ions, their neutral precursors, and related amines have been carried out in order to analyze more closely the unusual stabilizing property of NH<sub>2</sub> groups on the electronic structure of ions. The rotational barriers in guanidinium, amidinium, and immonium are predicted as well as proton affinities of the imines from which these carbonium ions are formed by protonation. The substituent stabilizing effects for carbonium ions are compared with those expected for carbanions and it is found that the BH<sub>2</sub> group is the most effective at stabilizing a neighboring carbanion center, with an NH<sub>2</sub> group relatively ineffective.

The electronic structure of single substituted carbonium ions CH<sub>2</sub>R<sup>+</sup> has been previously studied by one of us<sup>1</sup> and it has been determined that the NH<sub>2</sub> group is unusually effective at stabilizing the carbonium ion center. In this work, we extend our studies to examine multiply substituted carbonium ions, amidinium and guanidinium, in order to com-

pare their electronic structure stability and properties with immonium CH<sub>2</sub>NH<sub>2</sub><sup>+</sup>.

This large stabilizing effect of an NH<sub>2</sub> group on carbonium ions has important conformational consequences and so the rotational barriers in immonium, amidinium, and guanidinium are of interest.

Table I. Rotational Barriers,<sup>a</sup> C–N Distances, and C  $\pi$  Population in Amino Carbonium Ions

	STO-3G	431G
Immonium CH <sub>2</sub> NH <sub>2</sub> <sup>+</sup>		
Rotational barrier, kcal/mol	81.6 (87.2)	70.5 (77.9)
Minimum energy R(C=N <sup>+</sup> ) planar species, Å	1.29	1.26
Minimum energy R(C=N <sup>+</sup> ) $\perp$ species, Å	1.38	1.33
C $\pi$ planar	0.57	0.53
C $\pi$ $\perp$	0.12	0.10
Amidinium CH(NH <sub>2</sub> ) <sub>2</sub> <sup>+</sup>		
Rotational barrier, kcal/mol	34.5 (39.1)	28.2 (31.7)
Minimum energy R(C=N <sup>+</sup> ) planar, Å	1.33	1.31
Minimum energy R(C=N <sup>+</sup> ) $\perp$ , Å	1.31	1.28
Minimum energy R(C–N) $\perp$ , Å	1.42	1.38
C $\pi$ planar	0.70	0.63
C $\pi$ $\perp$	0.60	0.54
Guanidinium (C(NH <sub>2</sub> ) <sub>3</sub> ) <sup>+</sup>		
Rotational barrier, kcal/mol	20.1 (22.6)	14.1 (15.5)
Minimum energy R(C=N <sup>+</sup> ) planar, Å	1.37	1.33
Minimum energy R(C=N <sup>+</sup> ) $\perp$ , Å	1.35	1.30
Minimum energy R(C–N) $\perp$ , Å	1.42	1.38
C $\pi$ planar	0.73	0.68
C $\pi$ $\perp$	0.71	0.65

<sup>a</sup> In parentheses, barriers computed assuming R(C–N) was the same for planar and  $\perp$  ions.

Although there is definitive work on the theoretical study of single bond rotational barriers in the literature, relatively little attention has been given to barriers in double bonded and partially double bonded species. Bunker<sup>2</sup> has studied the rotational barriers of allene and ethylene and concluded that configuration interaction was important in understanding the rotational barrier in this system. Similar conclusions were reached by Radom and Pople<sup>3</sup> and Radom, *et al.*,<sup>4</sup> in their studies of ethylene, propene, butadiene, and allyl cation. On the other hand, studies of rotational barriers in a wide variety of single bonded species<sup>5</sup> and partially double bonded species such as formamide<sup>6</sup> seem to be well represented within the single determinant framework. It is thus of some interest to study the barriers in this series of ions, since immonium has a very high rotational barrier, similar to "double bonds," and guanidinium has a barrier smaller than formamide.

Guanidinium C(NH<sub>2</sub>)<sub>3</sub><sup>+</sup> has a pK<sub>a</sub> of 13.7, greater than that for trimethyl ammonium (9.8). In view of the fact that one expects base strength to correlate with the "p character" of the lone pair, it is of some interest to compare the gas phase proton affinities of guanidine and trimethyl amine.

In view of the considerable "stabilizing" effect of NH<sub>2</sub> substitution on the basic carbonium ion CH<sub>3</sub><sup>+</sup>, it is of interest to see whether this same effect occurs in the basic carbanion CH<sub>3</sub><sup>-</sup>. We thus compare the NH<sub>2</sub> substituent effect with closely related substituents (BH<sub>2</sub>, CH<sub>3</sub>, OH, and F) with respect to the relative stabilizing effects on cationic and anionic centers.

In this work we address ourselves to the following questions. First, what is the rotational barrier calculated for immonium, amidinium, and guanidinium ions and how well do these results correspond with available experimental data? Second, what makes the NH<sub>2</sub> group so effective at stabilizing a carbonium ion center, *i.e.*, why are amidinium and guanidinium ions so "stable" relative to their neutral precursors (the corresponding *amines*). Third, why is guanidine such a strong base? Finally, in view of the relative ordering and magnitudes of stabilization of carbonium ions discussed here and in a previous paper, on what basis can one rationalize and understand the effectiveness of substituents on carbanion stabilities? Can one get a general overview of the effect of substituents on ionic centers?

### Computational Details

These calculations were carried out using STO-3G<sup>7</sup> and 413G<sup>8</sup> basis sets and the CDC 7600 version of the program GAUSSIAN 70.<sup>9</sup> For the immonium ion, CH<sub>2</sub>NH<sub>2</sub><sup>+</sup>, we used the geometry previously determined,<sup>1</sup> except for our optimization of the C–N distance for parallel and perpendicular forms of the ion. For amidinium and guanidinium, the C–H and N–H distances were kept as previously determined for CH<sub>2</sub>NH<sub>2</sub><sup>+</sup> but all angles were held at 120°; in these two molecules, all C–N distances were optimized at parallel and perpendicular geometries. For methylene imine, the geometry used was that found by Lehn,<sup>10</sup> with the exception of the fact that the C=N bond length was optimized. For amidine CH(NH<sub>2</sub>)NH and guanidine C(NH<sub>2</sub>)<sub>2</sub>NH, the C=N bond was fixed at the optimum value for imine (R = 1.26 Å) and the C–N bond at R = 1.3 Å, the C–H and N–H distances were kept at the values found for CH<sub>2</sub>NH<sub>2</sub><sup>+</sup>, and the angles were all 120°. In methylamine, trimethylamine, diaminomethane, and triaminomethane, the C–N distance was kept at 1.47 Å, the C–H length 1.09 Å, the N–H length 1.00 Å, and the bond angles tetrahedral. In triaminomethane, a C<sub>3</sub> symmetry element was retained, with the N lone pairs in a propeller arrangement, each one eclipsing a nearby N–H bond. This type of geometry was also employed for diaminomethane. Geometrical structures for CH<sub>3</sub>NH<sub>2</sub>, CH<sub>2</sub>NH, and CH<sub>2</sub>NH<sub>2</sub><sup>+</sup> (STO-3G optimized) have been previously reported.<sup>11</sup>

### Results and Discussion

(a) **Structure and Rotational Barriers of NH<sub>2</sub>-Substituted Carbonium Ions.** Table I summarizes the C–N bond distances and rotational barriers predicted for immonium, amidinium, and guanidinium at both the STO-3G and 431G level. As one can see, geometrical optimization and the use of the more flexible (431G) basis set have significant lowering effects on the predicted rotational barriers. As expected, the double bond character decreases (bond length increases) as one goes from immonium to guanidinium.

The barrier to rotation in immonium (CH<sub>2</sub>NH<sub>2</sub><sup>+</sup>) is similar to that found in the previous study, which used a somewhat larger basis set, but did not optimize the C–N distance for planar and perpendicular forms of the ion ( $\Delta E = 72$  kcal/mol).

The calculated amidinium rotational barrier (28 kcal/

Table II. Total Energies, Orbital Energies, and Mulliken Populations of Amino Carbonium Ions

		Immonium (CH <sub>2</sub> NH <sub>2</sub> <sup>+</sup> )	Amidinium (CH(NH <sub>2</sub> ) <sub>2</sub> <sup>+</sup> )	Guanidinium (C(NH <sub>2</sub> ) <sub>3</sub> <sup>+</sup> )
$E_T$ , au		-94.24510	-149.24484	-204.22345
Orbital energies, au		-15.8846	-15.8101	-15.7830 (2)
		-11.5886	-15.8100	-15.7828
		-1.5554	-11.5870	-11.6124
		-1.1687	-1.5578	-1.5475
		-1.0242	-1.4238	-1.3942 (2)
		-0.9712	-1.1073	-1.0653
		-0.8230	-1.0176	-0.9767 (2)
		-0.7812 ( $\pi$ )	-0.9698	-0.8643
		-0.1406 ( $\pi^*$ )	-0.8836	-0.8587 (2)
		-0.0159 ( $\sigma^*$ )	-0.8327	-0.8148 ( $\pi$ )
			-0.8069 ( $\pi$ )	-0.6286 (2 $\pi$ )
			-0.6417 ( $\pi$ )	-0.0117 ( $\pi^*$ )
			-0.0613 ( $\pi^*$ )	-0.0099 ( $\sigma^*$ )
			-0.0008 ( $\sigma^*$ )	
Atomic populations	N <sup>a</sup>	7.73 (1.48)	7.87 (1.685)	7.92 (1.78)
	C <sup>a</sup>	5.87 (0.52)	5.40 (0.63)	4.87 (0.66)
	H <sub>N</sub>	0.52	0.54-0.56	0.56
	H <sub>C</sub>	0.68	0.66	
Overlap population	C-N	0.66	0.68	0.66
	C-H	0.74	0.74	
	N-H	0.61	0.64	0.64

<sup>a</sup> $\pi$  population in parentheses.

mol) should be compared with that found by Neumann, *et al.*<sup>12</sup> ( $7 \pm 2$  kcal/mol), for substituted amidinium ions. The nmr spectrum showed a marked change at temperatures in the range 30-115°, similar to that found in the nmr spectrum of formamide and *N,N*-dimethylformamide. However, the early determinations of the energy barriers of amides have been shown to be too small by a factor of  $\sim 2$ , and the currently accepted rotational barrier of formamide is 19 kcal/mol.<sup>13</sup> It should be noted that *ab initio* calculations<sup>6</sup> of the rotational barrier of formamide indicate an energy barrier of  $\sim 17$ -24 kcal/mol. Thus we have some evidence that the rotational barrier in the amidinium ion is significantly larger than previously determined. Since Neumann, *et al.*,<sup>12</sup> studied the rotational barrier in methyl amidinium (C(CH<sub>3</sub>)(NH<sub>2</sub>)<sub>2</sub><sup>+</sup> and *N*-substituted species) we calculated the barrier in the methyl amidinium ion in perpendicular and planar amidinium geometries previously optimized with the 431G basis, replacing the hydrogen with a methyl group. The methyl group lowered the barrier from 28.2 to 26.8 kcal/mol. STO-3G calculations on *N,N*-dimethyl immonium find a very small barrier increase on *N,N*-dimethyl substitution<sup>14</sup> (from 87 to 92 kcal/mol without optimizing the C-N distance), so the effect of *N*-Me substitution should have a small effect on the barrier of amidinium.

For the guanidinium ion, we predict a barrier in the range of 14 kcal/mol, and a change in the nmr spectrum as the temperature is lowered. Studies on creatine<sup>15</sup> find that the nmr spectrum changes significantly in the temperature range -70 to -80°, indicating that  $\Delta H^\ddagger$  is near 13 kcal/mol.

How reliable are these calculated barriers? We have some evidence that they are somewhat high, based on the experimental results on creatine and the fact that amidinium should have a barrier near that of formamide (19.0 kcal/mol). The immonium barrier would be expected to be too high, since Buenker<sup>2</sup> has calculated a barrier of 126 kcal/mol for C<sub>2</sub>H<sub>4</sub> at the SCF level and 83 kcal/mol for the same barrier including configuration interaction. He used a somewhat inflexible basis set and did not optimize the C-C distance in planar and perpendicular forms, so we have repeated his calculations at the SCF level using the 431G basis and optimizing the C-C distance for planar and perpendicular forms of C<sub>2</sub>H<sub>4</sub>. We find a barrier of 110 kcal/mol, much higher than the experimental value of 65 kcal/mol.<sup>16</sup> Buenker's calculations do show the importance of an

inclusion of configuration interaction to get a quantitative representation of the barrier in C<sub>2</sub>H<sub>4</sub> and, by analogy, CNH<sub>4</sub><sup>+</sup>.

We do not feel that the configuration interaction contribution to the barrier will be as large for CNH<sub>4</sub><sup>+</sup> as C<sub>2</sub>H<sub>4</sub> because the two singlet states are not degenerate for CNH<sub>4</sub><sup>+</sup> (at long C-N distances) as they are for C<sub>2</sub>H<sub>4</sub>, but this contribution is certain to be significant.

We cannot tell at this point how close the barriers in the three ions are to the 6:3:2 ratio expected from simple "bond order" arguments. The considerable success that SCF level calculations have had in reproducing single bond rotational barriers makes it worthwhile to examine how much "CI" contributes to the barrier in the compounds discussed above. We expect that CI will lower the immonium barriers, but not as greatly (percentage-wise) as Buenker found for ethylene. Thus we can predict with some confidence that the barrier in CNH<sub>4</sub><sup>+</sup> is  $\geq 70.5(65/110) = 42$  kcal/mol, the barrier in amidinium is  $\geq 17$  kcal/mol, and the barrier in guanidinium is  $\geq 8$  kcal/mol.

(b) **The Electronic Structure of CNH<sub>4</sub><sup>+</sup>, CN<sub>2</sub>H<sub>5</sub><sup>+</sup>, and CN<sub>3</sub>H<sub>6</sub><sup>+</sup> and the Neutral Imines.** Tables II and III contain the results of 431G calculations on the neutral and protonated imines. Comparing the neutral and protonated compounds one finds the following. The orbital energies are all decreased on protonation, which one would expect for any neutral-positively charged species comparison. The imine HOMO is a  $\sigma$  orbital (the nitrogen lone pair), whereas the HOMO in amidine and guanidine is a  $\pi$  orbital. The orbital energy differences are small enough and the calculations not sufficiently accurate to be sure if this difference is real. The protonated compounds each have their  $\pi$  orbitals higher in energy than their  $\sigma$ . Comparing the 1s orbital energies, one can predict the relative shift in the ESCA levels for C1s and N1s and one sees that all three compounds should experience  $\sim 0.3$  au C1s and N1s shifts on protonation. In the neutral compounds, there should be detectable shift between the imino and amino nitrogens, the latter having less tightly bound 1s electrons. It would also be very interesting to see if the nonmonotonic trend in the C1s energies predicted for the ions was real (CH<sub>2</sub>NH<sub>2</sub><sup>+</sup>,  $\epsilon_{C1s} = -11.5886$ ; CH(NH<sub>2</sub>)<sub>2</sub><sup>+</sup>,  $\epsilon_{C1s} = -11.5870$ ; C(NH<sub>2</sub>)<sub>3</sub><sup>+</sup>,  $\epsilon_{C1s} = -11.6124$ ).

The computed Mulliken populations are not particularly surprising, but two things should be pointed out in this con-

Table III. Total Energies, Orbital Energies, and Mulliken Populations of Imines

		Imine (CH <sub>2</sub> NH)	Amidine (CH(NH <sub>2</sub> )NH)	Guanidine (C(NH <sub>2</sub> ) <sub>2</sub> NH)
$E_T$ , au		-93.88092	-148.84920	-203.80359
Orbital energies, au		-15.5377	-15.5404	-15.5451
		-11.2622	-15.4800	-15.5359
		-1.2383	-11.2895	-15.4396
		-0.8449	-1.2787	-11.3122
		-0.6938	-1.1430	-1.3339
		-0.6140	-0.8299	-1.1877
		-0.4546 ( $\pi$ )	-0.7562	-1.1226
		-0.4113	-0.6488	-0.8331
		0.1688 ( $\pi^*$ )	-0.6111	-0.7537
		0.2367 ( $\sigma^*$ )	-0.5385 ( $\pi$ )	-0.7324
			-0.3924	-0.6536
			-0.3430 ( $\pi$ )	-0.6022
			0.2210 ( $\pi^*$ )	-0.5935 ( $\pi$ )
			0.2254 ( $\sigma^*$ )	-0.4222 ( $\pi$ )
				-0.3765
	Atomic populations	C <sup>a</sup>	6.09 (.89)	5.64 (.83)
--N <sup>a</sup>			7.89 (1.35)	7.94 (1.86)
=N <sup>a</sup>		7.54 (1.11)	7.68 (1.82)	7.73 (1.49)
H <sub>N</sub>		0.70	0.61-0.64 (=NH: 0.72)	0.60-0.65 (=NH: 0.76)
H <sub>C</sub>		0.82-0.85	0.82	
C=N		0.99	1.15	1.29
CN			0.24	0.27
CH		0.76-0.79	0.81	
NH		0.66	0.66-0.68	0.66-0.69
				0.1984 ( $\sigma^*$ )
			0.2848 ( $\pi^*$ )	

<sup>a</sup> $\pi$  population in parentheses.

text. The total nitrogen population *increases* on protonation in each of these species, which goes against one's chemical intuition; on the other hand, the ESCA shift, which has often been correlated with valence Mulliken population, indicates that the nitrogen is becoming more "positive" in the protonated species than the neutral. These findings can be made compatible when one realizes that, as Schwartz<sup>17</sup> has pointed out, it is the electrostatic potential at the atom rather than Mulliken population which should be correlated with ESCA shift and the positive charge at other atoms in contributing to how tightly bound the N1s electrons are.

There is one feature of the overlap populations in these compounds which deserves comment. The C-N overlap populations for the imine C=N, the immonium C=N<sup>+</sup>, and the imine C-N are 1.0-1.2, 0.7 and 0.2-0.3, respectively, despite the fact that the C-N distances in these three types of bonds are very similar. Even though these populations have no quantitative significance they imply that the immonium C<sup>+</sup>=N has a fraction of double bond character intermediate between imine C=N and amine C-N bonds. Since the optimum C-N bond length in methylene imine is very close to that in methylene immonium, the overlap population cannot be used to compare bond *lengths*, and since C=N ir stretching frequencies for imines and immonium salts are so similar, it is not clear that these overlap populations reflect bond strengths.

(c) **Proton Affinity of Amines vs. Imines and the "Stabilization" of NH<sub>2</sub>-Substituted Carbonium Ions.** Table IV contains information about two other interesting properties of these imines and carbonium ions. First, the proton affinity of the imines is quite high. We expect (from a comparison of the experimental and calculated proton affinities of small molecules carried out with similarly accurate calculations) that these proton affinities are on the average 12 kcal/mol too high;<sup>18-20</sup> however, the relative affinities should be reasonably correct.

Guanidine is truly unusual in its basicity, having a calculated proton affinity of 264 kcal/mol compared to that calculated for trimethylamine of 243 kcal/mol. This is the

Table IV. Proton Affinities and Stabilization Energies and Rotational Barriers of Amino-Substituted Compounds (kcal/mol)

R	PA	Stabilization of RH <sup>+</sup>	Rotational Barrier in RH <sup>+</sup>
CH <sub>2</sub> NH	228	89 <sup>a</sup>	70.5
CH(NH <sub>2</sub> )NH	249	128	28.2
C(NH <sub>2</sub> ) <sub>2</sub> NH	264	147	14.1

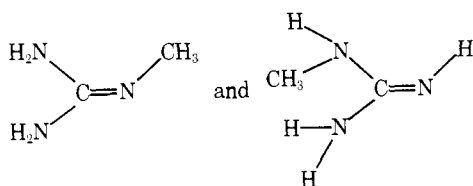
<sup>a</sup> Reference 1 and this study (431G) both predict the same stabilization.

same trend as their relative pK<sub>a</sub>'s in water; TMA has a pK<sub>a</sub> of 9.8, guanidine's pK<sub>a</sub> is 13.7, although the similarity in the trend may be partially fortuitous because of hydration differences. The pK<sub>a</sub> for TMA is less than that of methylamine (10.5) but calculated and experimental proton affinities are greater for TMA. This is easy to rationalize when one considers that methyl ammonium can form three strong N<sup>+</sup>-H...O hydrogen bonds in water and trimethyl ammonium only one. In fact, the difference between gas phase proton affinities and water pK<sub>a</sub>'s for the methyl-substituted amines was clearly demonstrated by Munson.<sup>21</sup>

We have previously<sup>1</sup> analyzed the stability of carbonium ions RCH<sub>2</sub><sup>+</sup> with R = H, CH<sub>3</sub>, NH<sub>2</sub>, OH, and F and have noted that the difference in the heat of formation of the carbonium ion and its neutral precursor RCH<sub>3</sub> gives a measure of carbonium ion stability. Using R = H as a reference, we found R = NH<sub>2</sub> to be the most highly stabilized carbonium ion in the above series, with an experimental "stabilization" compared to methyl cation of 96 kcal/mol and a calculated stabilization of 89 kcal/mol. This study, with the 431G basis, finds the same stabilization energy for immonium but significantly greater stabilization in amidinium (128 kcal/mol) and guanidinium (147 kcal/mol). If we consider the energy loss on rotation of the NH<sub>2</sub> group to a perpendicular orientation to be the resonance stabilization, we find the resonance stabilization of guanidinium to be ~102 kcal/mol and the inductive stabilization to be 45 kcal/mol (for immonium ion, resonance = 70, inductive = 19, for amidinium resonance = 98, inductive = 29). Thus our calcula-

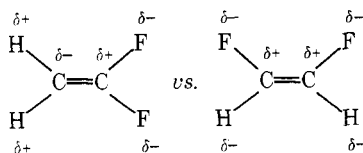
tions find the guanidinium ion an unusually stable entity and allow us to rationalize the well known stability of guanidinium and substituted analogs.

What simple qualitative picture emerges from these studies on guanidinium to explain its stability analogous to the valence bond explanation put forward by Pauling?<sup>22</sup> The Mulliken population indicates that the carbon in guanidinium is unusually positive (+1.13), although less of its positive charge resides in the  $\pi$  (+0.34) than the  $\sigma$  (+0.79). The positive charge in the  $\pi$  framework is shared by all (each nitrogen is +0.22 in its  $\pi$  electron distribution) and the  $\pi$  LUMO is less tightly bound than that for immonium and amidinium, supporting its greater stability to nucleophilic attack. One might speculate that the large inductive stabilizations observed in these carbonium ions are due to the  $\text{NH}_2$  groups spreading much of the positive charge on the hydrogens far from the positive  $\pi$  center carbon. Pauling<sup>22</sup> has predicted on the basis of resonance theory that  $=\text{NCH}_3$  and  $-\text{NCH}_3$  guanidines should be weaker bases than guanidine itself so we carried out a single calculation on these two methyl-substituted guanidines and methyl guanidinium  $\text{C}(\text{NH}_2)_2\text{NHCH}_3^+$ .<sup>23</sup> Our calculations predict proton affinities of 268 and 272 kcal/mol for



compared to 264 kcal/mol for guanidine. A similar calculation on the proton affinity of  $\text{CH}_2\text{NCH}_3$  finds a proton affinity of 232 kcal/mol. Thus, we predict that the presence of a methyl substitution on the imino nitrogen raises the proton affinity by 4 kcal/mol in  $\text{CH}_2\text{NH}$  and  $\text{C}(\text{NH}_2)_2\text{NH}$ , and we expect that the presence of three equivalent resonance structures in guanidinium is not the cause of the unusual basicity of guanidine, but rather its ability to disperse its positive charge to its peripheral hydrogens.

What is the physical force behind this "dispersal" stabilization? One might speculate that an inductive effect  $\text{C}^{\delta+}-\text{N}^{\delta-}-\text{H}^{\delta+}$  is energetically favorable because it is consistent with the relative electronegativities of the atoms and relative ionicities of the bonds. Thus the "stabilization" occurs through an increase in  $\sigma$  bonding strength (more ionic character).<sup>24</sup> This interpretation is consistent with the greater stability of 1,1- than 1,2-difluoroethylenes, e.g., with the charge effects<sup>25</sup>



(relative to  $\text{C}_2\text{H}_4$ ). One must be careful to add as a caveat that in  $\text{CF}_3^+$ , there is a possibility for great  $\text{C}^{\delta+}-\text{F}^{\delta-}$  stabilization, but probably far too great a localization of the positive charge. The implications of the above are hard to quantify, but they lead to some interesting qualitative deductions. For example, in the difluoropropanes, 1,1- and 1,3-difluoro isomers would be expected to be more stable than the 1,2 isomer. In cases where there are electron-withdrawing and electron-donating substituents on propane the 1,2 isomer would be expected to be more stable than the 1,1 and 1,3 isomers.

#### (d) Energetic Consequences of Substituents on Ionic Cen-

Table V. Calculated Stabilization Energies for Carbanions and Carbonium Ions

R	$\Delta E^f$	R	$\Delta E^g$
H	0	H	0
$\text{BH}_2^e$	$23^b$ ( $0^d$ )	$\text{BH}_2$	$67^{b,c}$
$\text{CH}_3$	$27^a$	$\text{CH}_3$	$1^b$
$\text{NH}_2$	$89^a$ ( $89^b$ )	$\text{NH}_2$	$1^b$
OH	$45^a$	OH	$12^b$
F	$-5^a$	F	$19^b$

<sup>a</sup> Reference 4. <sup>b</sup> This work. <sup>c</sup> In this case, unlike the other carbanions, geometrical optimization was carried out. In the non-optimized species, the stabilization energy was 50 kcal/mol. In the optimized geometry (only the BCH angle and B-C distance were optimized), the molecule was planar, with a B-C distance of 1.45 Å. <sup>d</sup> Hydrogens in same plane as  $\text{CH}_2$  group. <sup>e</sup> Optimized C-B bond length for neutral  $(\text{CH}_3\text{BH}_2)$  ( $R = 1.575$  Å) and positive ion ( $R = 1.53$  Å). <sup>f</sup>  $\Delta E(\text{CHR}^+ + \text{CH}_4 \rightarrow \text{CH}_3\text{R} + \text{CH}_3^+)$ . <sup>g</sup>  $\Delta E(\text{CH}_2\text{R}^- + \text{CH}_4 \rightarrow \text{CH}_3\text{R} + \text{CH}_3^-)$ .

ters. We next ask whether our results on the resonance and inductive effects in carbonium ions can be extended to carbanions; i.e., what is the energetic effect of a  $\text{CH}_3$ ,  $\text{NH}_2$ , OH, and F substituent on the basic  $\text{CH}_2\text{R}^-$  fragment, relative to  $\text{R} = \text{H}$  (the methyl anion)? To determine this, we repeated our previous calculations<sup>1</sup> on  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{NH}_2$ ,  $\text{CH}_3\text{F}$ ,  $\text{C}_2\text{H}_6$ , and  $\text{CH}_4$  with the 431G basis (we have already determined the  $\text{CH}_3\text{NH}_2$  energy to construct Table IV), and also determined the energy of  $\text{CH}_3^-$ ,  $\text{CH}_3\text{CH}_2^-$ ,  $\text{NH}_2\text{CH}_2^-$ ,  $\text{HOCH}_2^-$ ,  $\text{FCH}_2^-$ ,  $\text{CH}_3\text{BH}_2$ ,  $\text{CH}_2\text{BH}_2^+$ , and  $\text{CH}_2\text{BH}_2^-$ .<sup>26</sup> The relative energies calculated for the reactions  $\text{CH}_2\text{R} \rightarrow \text{CH}_2\text{R}^- + \text{H}^+$  and  $\text{CH}_2\text{R} \rightarrow \text{CH}_2\text{R}^+ + \text{H}^-$  are presented in Table V.

We have already considered carbonium ion stabilization<sup>4</sup> for  $\text{CH}_3$ ,  $\text{NH}_2$ , OH, and F, so only the results for  $\text{BH}_2$  carbonium ion stabilization are new. When the hydrogens are all in the planar form, a  $\text{BH}_2$  group has no inductive stabilizing effect on the carbonium ion center; with hydrogens in the perpendicular form, the hyperconjugative interaction between the B-H bonds and the  $\text{C}^+$  center is significant (23 kcal/mol stabilization) and twice that found for the methyl group. It is interesting that there is no inductive stabilization of the carbonium ion due to the  $\text{BH}_2$  group; this is consistent with the previous conclusion<sup>1</sup> that acidic ( $\delta^+$ ) hydrogens are crucial for neighboring inductive stabilization of carbonium ions.

Carbanion stabilization involves very different substituent effects than carbonium ion stabilization. Interestingly,  $\text{CH}_3$  and  $\text{NH}_2$  groups are not effective at withdrawing charge from the carbanion center; only OH and F show significant inductive stabilization of carbanions. We have found the rotational barrier in planar  $\text{CH}_2\text{BH}_2^-$  to be 64 kcal/mol, indicating that the  $\text{BH}_2$  group has a resonance stabilizing effect (64 kcal/mol) and inductive stabilizing effect (3 kcal/mol) on the carbanion center. We postulate that, just as positive ( $\delta^+$ ) hydrogens can inductively stabilize carbonium ions, negative ( $\delta^-$ ) hydrogens can play a small role in the inductive stabilization of carbanions. The electronegativities of boron and hydrogen are so similar that polarity  $\text{B}(\delta^+)-\text{H}(\delta^-)$  could be energetically favorable.

#### Conclusion

In this study, we have examined the properties of carbonium ions and carbanions, concentrating mainly on multiple substituted  $\text{NH}_2$  carbonium ions because of their unusual properties and high stability. We have predicted the rotational barriers in a number of the  $\text{NH}_2$  substituted carbonium ions; our results indicate that SCF level calculations are not adequate to quantitatively describe the rotational barrier in immonium ( $\text{CH}_2\text{NH}_2^+$ ), but do much better in the

barriers for guanidinium and amidinium. We have provided a rationale for the unusual basicity and stability of guanidine and a working model to understand the effects of substituents ( $\text{BH}_2$ ,  $\text{CH}_3\text{NH}_2$ ,  $\text{OH}$ , and  $\text{F}$ ) on ionic centers.

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- (25) See P. Kollman, *J. Amer. Chem. Soc.*, **96**, 4362 (1974), for a discussion of the relative stabilities of the difluoroethylenes.
- (26) To be consistent, we used the experimental geometry for each molecule, keeping the rest of the molecule fixed when we removed a proton. That this is not too bad an approximation is evident when one compares the geometry of  $\text{CH}_4$  ( $r = 1.09 \text{ \AA}$ ,  $\theta = 109.5^\circ$ ) with that predicted for  $\text{CH}_3^-$  by R. Kari and I. Czimadia, *J. Chem. Phys.*, **50**, 1443 (1969) ( $r = 1.12 \text{ \AA}$ ,  $\theta = 105^\circ$ ). In any case, the relative energies should probably be more accurate than their absolute value. We did not examine the relative energies of isomeric species; for example,  $\text{CH}_3\text{O}^-$  is likely to be comparable in stability to  $^-\text{CH}_2\text{OH}$ .

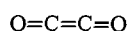
## An *ab Initio* Molecular Orbital Study of Ethylenedione ( $\text{O}=\text{C}=\text{C}=\text{O}$ )

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Contribution from the Research School of Chemistry, Australian National University, Canberra, ACT 2600, Australia. Received September 30, 1974

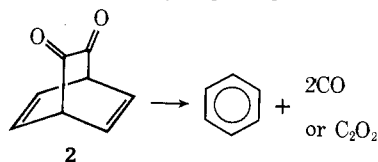
**Abstract:** *Ab initio* molecular orbital theory with minimal (STO-3G) and split-valence (4-31G) basis sets has been used to study ethylenedione ( $\text{O}=\text{C}=\text{C}=\text{O}$ ) at the real and complex single determinant and configuration interaction levels. The linear (forbidden) and trans (allowed) dissociative pathways leading to two molecules of carbon monoxide have been examined in detail, their differences clearly delineated and found to be in accord with orbital symmetry requirements. It is shown that ethylenedione is kinetically (singlet) and thermodynamically (singlet and triplet) unstable with respect to two molecules of carbon monoxide. This result is consistent with experimental evidence but contrasts with the findings of previous theoretical studies.

Recently, ethylenedione (**1**) has become the subject of much experimental<sup>2</sup> and theoretical<sup>3,2c</sup> interest.

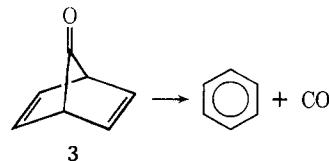


**1**

Experimentally, attention has focussed on the possibility of generating ethylenedione by thermal decomposition of molecules such as the bicyclo[2.2.2]octadienones (**2**).<sup>2</sup> It



now appears that this reaction, which proceeds with difficulty, in contrast to the decomposition of bicyclo[2.2.1]heptadienones<sup>4</sup> (**3**), occurs by stepwise loss of CO, rather than



by the concerted elimination of ethylenedione. That the involvement of **1** in this reaction is likely to be transitory at best is supported by a number of observations. All attempts to trap **1** have been unsuccessful (although CO has been de-