The contents of the magnetically stirred reaction flask were heated to 70 °C. After $\sim$3 h, nitrogen was carefully bled in to relieve the slight vacuum within the system, and an aliquot of AIBN (100 mg in 2 mL of benzene) was added. This procedure was repeated eight times. Periodically a sample was drawn for GLC or ^{31}P NMR analysis to determine the ratio of phosphite to phosphate. (No other products were detected.) After 12 h the phosphite had consumed 60% of the available oxygen. After approximately 2 days, the consumption was nearly 95%.

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Registry No. *cis*-**1**, 23201-70-9; *trans*-**1**, 23201-71-0; *cis*-**2**, 26344-07-0; *trans*-**2**, 26344-06-9; *cis*-**3**, 66386-45-6; *trans*-**3**, 66386-46-7; *cis*-**4**, 120056-30-6; *trans*-**4**, 120056-31-7; **5**, 119998-99-1; **6**, 119999-00-7; dimethylamino 3′,5′-cyclic thymidine phosphoramidite, 40652-74-2.

Energetics of the Singlet and Triplet States of Alkylnitrenium Ions: Ab Initio Molecular Orbital Calculations

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Abstract: The structures and energies of the nitrenium ions NH_2^+, CH_3NH^+, $(CH_3)_2N^+$, $\overline{CH_2(CH_2)_3N}^+$, and $\overline{CH_2(CH_2)_4N}^+$ were studied by using ab initio molecular orbital calculations with various basis sets and corrections for electron correlation up to the MP4(SDTQ) level. On the singlet energy surface, CH_3NH^+ and $(CH_3)_2N^+$ are predicted to be transition states for degenerate hydrogen migration in the isomeric immonium ions. CH_3NH^+ was predicted to have a triplet, and $\overline{CH_2(CH_2)_3N}^+$, a singlet ground state. The singlet–triplet energy difference in the remaining secondary ions was small, and an unambiguous determination of their ground-state multiplicities was not possible. For CH_3NH^+ and $(CH_3)_2N^+$, the calculated energies of both states are too high to be consistent with their supposed formation in the EI mass spectra of amines, even as transient intermediates. The most detailed calculations were carried out on NH_2^+. At the MP4(SDTQ)/6-311+G(3d2f,2p)//MP2/6-311+G(3d,2p) level including vibrational corrections, the singlet–triplet energy difference was calculated to be 32.4 kcal mol^{-1}, 2.3 kcal mol^{-1} greater than the experimental value.

The nitrenium ion, NH_2^+ (**1**), is an electron-deficient species isoelectronic with methylene. However, in contrast to the latter, the nitrenium ion and its simple alkyl derivatives have received relatively little attention.[1] The relative energetics of the lowest electronic states are known only for the parent. Indeed, only in this case is even the ground-state multiplicity known with certainty. Here, a recent photoionization study[2] of the corresponding neutral radical showed the lowest singlet to lie 30.1 ± 0.2 kcal mol^{-1} above the triplet ground state. Several alkyl- and dialkylnitrenium ions have been prepared in the gas phase by charge reversal collisional activation (CR CA) of the corresponding negative ions.[3] However, other evidence[4-9] for the existence of these ions in the gas phase is tentative. From the CA spectra of the $C_2H_6N^+$ and $C_3H_8N^+$ ions derived from a wide variety of compounds, Levsen and McLafferty[7] concluded that only the isomeric immonium ions had lifetimes $>10^{-5}$ s.

The pioneering work of the Gassman group clearly indicates that in solution electron-deficient divalent nitrogen species are involved in a wide variety of reactions including ring cleavages and rearrangements.[1b,11,12] However, whether these species correspond to true reaction intermediates, or simply to transitory points on the reaction pathway, remains an open question. The initially convincing evidence for the existence of certain bicyclic nitrenium ions as discrete intermediates, based on what appeared to be a heavy-atom-catalyzed conversion to the triplet,[11] now seems less clear-cut.[13-15]

In contrast to the situation for the simple aliphatic, and alicyclic nitrenium ions, the aryl derivatives have been the subject of numerous investigations,[1a,16,17] many of them stimulated by the suggestion[18] that these species are involved in aromatic amine carcinogenesis.

Quantitatively reliable ab initio molecular orbital calculations for the singlet–triplet energy differences in nitrenium ions have been reported only for the parent (**1**).[19-23] Other ab initio cal-

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Table I. Calculated Energies Obtained from Optimized HF/6-31G(d) Geometries

structure	point group	electronic state	total energy[a]	vibrational energy[b]	Hessian index[c]
NH_2^+ (**1**)	C_{2v}	$^1A_1$	−55.127 29[d]	11.0	0
		$^3B_1$	−55.208 52[d]	10.2	0
CH_3NH^+ (anti) (**2**)	C_s	$^1A'$	−94.220 92	28.2	1
		$^3A''$	−94.284 72	28.9	0
CH_3NH^+(syn) (**3**)	C_s	$^1A'$	−94.223 44	28.2	1
		$^3A''$	−94.284 62	28.3	1
$CH_2NH_2^+$ (planar[e]) (**4**)	C_{2v}	$^1A_1$	−94.383 18[f]	32.8	0
		$^3A_1$	−94.236 31	27.6	2
$CH_2NH_2^+$ (perp) (**5**)	C_s	$^1A'$	−94.276 08	29.4	1
$CH_2NH_2^+$ (perp) (**6**)	C_{2v}	$^1A_1$	−94.267 83	28.6	2
		$^1A_2$	−94.290 05[g]	27.3	2[h]
		$^3A_2$	−94.286 07	28.5	1
CH_3NH^+ (**7**)	C_{3v}	$^3A''$	−94.283 20		2
$CH_2NH_2^+$ (perp[d]) (**8**)	C_s	$^3A''$	−94.286 37	29.2	0
CH_3NH^+ (ts) (**9**)	C_s	$^3A''$	−94.185 69	25.6	1
$CH_2NH_2^+$ (planar) (**10**)	C_s	$^3A'$	−94.264 85	28.6	1
$H_2N^+{=}CHCH_3$ (syn) (**11**)	C_s	$^1A_1$	−133.442 90	50.3	0
$H_2C{=}NH^+CH_3$ (syn) (**12**)	C_s	$^1A_1$	−133.427 27	50.6	0
$H_2N^+{=}CHCH_3$ (anti) (**13**)	C_s	$^1A_1$	−133.440 52	49.7	1
$H_2C{=}NH^+CH_3$ (anti) (**14**)	C_s	$^1A_1$	−133.425 15	50.0	1
$(CH_3)_2N^+$ (staggered) (**15**)	C_2	^1A	−133.300 41	46.6	0
$(CH_3)_2N^+$ (anti, syn) (**16**)	C_s	$^1A'$	−133.296 32	46.1	1
	C_s	$^3A''$	−133.351 98	46.9	1
$(CH_3)_2N^+$ (anti, anti) (**17**)	C_{2v}	$^1A_1$	−133.290 37	45.5	2
		$^3B_1$	−133.352 17	47.5	0
$(CH_3)_2N^+$ (syn, syn) (**18**)	C_{2v}	$^1A_1$	−133.299 41	45.5	2
	C_{2v}	$^3B_1$	−133.351 84	46.3	2
$H_2C^+NHCH_3$ (perp) (**19**)	C_1	*i*	−133.341 64	47.2	0
$H_2NCH^+CH_3$ (perp) (**20**)	C_1	*i*	−133.335 86	47.3	0
$C_4H_8N^+$ (twist) (**24**)	C_2	^1A	−210.225 37	69.7[j]	0[j]
	C_2	^3B	−210.258 91	71.1[j]	0[j]
C_4H_8N (planar) (**25**)	C_{2v}	$^1A_1$	−210.220 59	69.1[j]	1[j]
	C_{2v}	$^3B_1$	−210.225 89	70.7[j]	1[j]
$C_5H_{10}N^+$ (chair) (**26**)	C_s	$^1A'$	−249.262 75	88.1[j]	0[j]
	C_s	$^3A''$	−249.310 79	89.4[j]	0[j]
$C_5H_{10}N^+$ (twist boat) (**27**)	C_2	^1A	−249.259 41	87.6[j]	1[j]
	C_2	^3B	−249.303 87	89.5[j]	0[j]

[a] Hartrees. [b] Kilocalories per mole. [c] The number of negative eigenvalues of the force constant matrix. [d] Reference 29. [e] Terms *perpendicular* and *planar* are used to describe the approximate conformation and do not necessarily imply a particular point group. A more complete description of geometry can be obtained by referring to the structures in the text. [f] Data from ref 42a. [g] Singlet UHF calculation. [h] This structure was only 0.006 kcal mol^{-1} higher than the almost identical C_s structure with a Hessian index of 1. [i] Triplet UHF calculation. Unique state symmetry could not be assigned. [j] HF/3-21G force constant calculation.

culations on both states have been reported in the alkyl[24] and aryl[25] series. However, these have used small basis sets, with no allowance for electron correlation, and undoubtedly grossly overestimate the stabilities of the triplets. Other calculations have mainly focused on singlet nitrenium ions and their isomers.[24,26-28] But, with the exception of the entries in the Carnegie Mellon Quantum Chemistry Archive[29] for CH_3NH^+, most have used rather small basis sets, and again, none have included the effects of electron correlation.

In our earlier study using MNDO semiempirical molecular orbital theory,[30] the aryl derivatives, unlike the parent, were predicted to be ground-state singlets. Indeed, the same calculations revealed a quantitative parallel between the singlet–triplet energy differences and the electron-donating abilities of the substituents directly bound to nitrogen across the entire series.[31]

While there is no a priori reason to doubt the validity of the previous MNDO calculations,[30] they nevertheless represent an extension of the semiempirical procedure into a very different realm than that represented by the molecules in its parameterization set. In view of the importance of this class of molecules generally, as well as the almost complete lack of firm experimental data relating to the simpler members, we felt that a comprehensive reexamination of these species using the considerably more sophisticated computational techniques now available to us was warranted. Ab initio molecular orbital calculations at a series of carefully chosen levels of sophistication on a representative series of alkyl- and cycloalkylnitrenium ions and some of their isomers are presented below. Similar calculations on the acyl- and on the arylnitrenium ions will be reported in due course.

Methods and Results

All ab initio calculations were carried out using the GAUSSIAN 82 program system.[32] Geometries were completely optimized within the specified point groups at the Hartree–Fock level (RHF for singlets, UHF

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Table II. Total Energies[a] Calculated from HF/6-31G(d) Geometries

molecule	symmetry	state	basis	HF	MP2	MP3	MP4
NH_2^+ (**1**)	C_{2v}	$^1A_1$	6-31G(d)	−55.127 29[b]	−55.240 82	−55.259 97	−55.265 26
			6-31G(d,p)	−55.135 07[b]	−55.257 88[b]	−55.277 55[b]	−55.282 99[b]
			6-311G(d,p)	−55.149 35	−55.278 74	−55.298 05	−55.303 93
			6-311+G(d,p)	−55.149 48	−55.279 01	−55.298 34	−55.304 25
			6-311+G(3d,2p)	−55.152 95	−55.292 06	−55.311 18	−55.317 53
	C_{2v}	$^3B_1$	6-31G(d)	−55.208 52[b]	−55.303 55	−55.318 76	−55.322 30
			6-31G(d,p)	−55.217 03[b]	−55.319 84[b]	−55.335 45[b]	−55.339 08[b]
			6-311G(d,p)	−55.230 66	−55.340 25	−55.355 65	−55.359 55
			6-311+G(d,p)	−55.230 83	−55.340 45	−55.355 86	−55.359 78
			6-311+G(3d,2p)	−55.232 64	−55.350 82	−55.366 17	−55.370 50
CH_3NH^+ (**2**)	C_s	$^1A'$	6-31G(d)	−94.220 92	−94.480 14	−94.505 18	−94.521 47
			6-31G(d,p)	−94.230 50	−94.511 18	−94.537 51	−94.553 46
			6-311G(d,p)	−94.250 80	−94.543 52	−94.569 68	−94.587 51
		$^3A''$	6-31G(d)	−94.284 72	−94.508 53	−94.535 02	−94.545 44
			6-31G(d,p)	−94.294 02	−94.539 22	−94.567 28	−94.577 51
			6-311G(d,p)	−94.313 74	−94.570 19	−94.598 54	−94.609 94
CH_3NH^+ (**3**)	C_s	$^1A'$	6-31G(d)	−94.223 44	−94.485 79	−94.510 10	−94.526 66
		$^3A''$	6-31G(d)	−94.284 62	−94.508 35	−94.534 87	−94.545 28
$CH_2NH_2^+$ (**4**)	C_{2v}	$^1A_1$	6-31G(d)	−94.383 18[b]	−94.658 38[b]	−94.676 32[b]	−94.689 40[b]
			6-31G(d,p)	−94.394 70	−94.690 87	−94.710 39	−94.723 58
			6-311G(d,p)	−94.413 26	−94.720 76	−94.739 49	−94.755 04
		$^3A_1$	6-31G(d)	−94.236 31	−94.487 81	−94.515 11	−94.523 55
$CH_2NH_2^+$ (**5**)	C_s	$^1A'$	6-31G(d)	−94.276 08	−94.535 06	−94.555 87	−94.566 86
$CH_2NH_2^+$ (**6**)	C_{2v}	$^1A_1$	6-31G(d)	−94.267 83	−94.525 00	−94.545 90	−94.556 03
		$^1A_2$	6-31G(d)	−94.290 05	−94.518 95	−94.544 77	−94.554 12
		$^3A_2$	6-31G(d)	−94.286 07	−94.517 29	−94.543 36	−94.552 81
$CH_2NH_2^+$ (**8**)	C_s	$^3A''$	6-31G(d)	−94.286 37	−94.517 35	−94.543 33	−94.552 80
CH_3NH^+ (**9**)	C_s	$^3A''$	6-31G(d)	−94.185 69	−94.430 67	−94.454 94	−94.467 04
$CH_2NH_2^+$ (**10**)	C_s	$^3A'$	6-31G(d)	−94.264 85	−94.489 02	−94.516 10	−94.524 52
$H_2N^+{=}CHCH_3$ (**11**)	C_s	$^1A_1$	6-31G(d)	−133.442 90	−133.847 67	−133.875 29	−133.894 21
$H_2C{=}NH^+CH_3$ (**12**)	C_s	$^1A_1$	6-31G(d)	−133.427 27	−133.832 73	−133.859 73	−133.879 84
$(CH_3)_2N^+$ (**15**)	C_2	^1A	6-31G(d)	−133.300 41	−133.694 34	−133.727 14	−133.750 10
			6-31G(d,p)	−133.311 25	−133.739 41	−133.774 52	−133.796 88
			6-311G(d,p)	−133.337 28	−133.782 45	−133.817 73	
$(CH_3)_2N^+$ (**17**)	C_{2v}	$^3B_1$	6-31G(d)	−133.352 17	−133.705 29	−133.742 28	−133.759 55
			6-31G(d,p)	−133.362 43	−133.750 34	−133.790 11	−133.806 92
			6-311G(d,p)	−133.388 34	−133.792 07	−133.832 61	
$H_2C^+NHCH_3$ (**19**)	C_1	*c*	6-31G(d)	−133.341 64	−133.701 95	−133.737 87	−133.754 19
$H_2NCH^+CH_3$ (**20**)	C_1	*c*	6-31G(d)	−133.335 86	−133.697 59	−133.733 49	−133.749 21
$C_4H_8N^+$ (**24**)	C_2	^1A	6-31G(d)	−210.225 37	−210.877 07		
	C_2	^3B	6-31G(d)	−210.258 91	−210.868 05		
$C_5H_{10}N^+$ (**26**)	C_s	$^1A'$	6-31G(d)	−249.262 75	−250.044 23		
	C_s	$^3A''$	6-31G(d)	−249.310 79	−250.052 48		

[a] Hartrees. MP calculations restricted to valence-shell electrons. MP4 includes all single, double, and quadruple excitations. [b] Reference 29. [c] Triplet UHF calculation. Unique state symmetry could not be assigned.

for triplets) with gradient-based algorithms[33] included as standard program options. Optimizations were performed by using the split valence 6-31G(d) basis, which includes a single set of d-type polarization functions on non-hydrogen atoms.[34] Force constant calculations were carried out on the optimized geometries at the same level and the species classified as local minima, saddle points, or hilltops on the basis of the number of negative force constants (Hessian index[35]). One exception concerns the force constant calculations for the five- and six-membered cyclic nitrenium ions. For economic reasons, the Hessian indexes and vibrational energies here refer to calculations on the analogous geometries optimized by using the more economical split-valence 3-21G basis set.[36] Vibrational energies at 298 K were computed from standard formulas[37a] after uniformly scaling the vibrational frequencies by 0.90 or 0.89 for calculations at the HF/3-21G and HF/6-31G(d) levels, respectively.[38] These data are collected in Table I.

Single-point calculations using the HF/6-31G(d) geometries with allowance for valence electron correlation at the Moller–Plesset second[39] (MP2), and in some cases third[40] (MP3) and fourth,[41] [MP4(SDTQ)] orders are collected in Table II. The fourth-order Moller-Plesset calculations were carried out with inclusion of all single, double, and triple excitations. For convenience, calculated data for the methylene immonium ion (**4**) reported by Del Bene[42a] are also included in Tables I and II. After our calculations were complete, it was evident that the singlet structure **3** was identical with one reported by Frisch,[43] while a singlet structure reported by Del Bene[42b] to have C_1 symmetry appears to be identical with **2**.

For the nitrenium ions themselves, specific basis set effects on the singlet–triplet energy separation were investigated by systematically elaborating the 6-31G(d) basis. These results are also included in Table II together with the standard basis set designation devised by Pople and co-workers. Thus, the 6-31G(d,p) basis set is derived from the 6-31G(d) basis by the addition of a set of p functions on hydrogen.[34] The 6-311G(d,p) basis set[44] incorporates an additional set of valence sp functions. Unlike those in the simpler basis sets, the Gaussian orbital exponents here were specifically chosen for optimal results in calculations at the Moller–Plesset level.[44] The 6-311+G(d,p) includes a set of diffuse sp-type functions[45] on non-hydrogen atoms, while the rather large 6-

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(42) Del Bene, J. E. (a) entry no. 8675 in ref 24. (b) entry no. 9705 in ref 24.

(43) Frisch, M. J. entry no. 10512 in ref 24.

(44) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650–654.

(45) Spitznagel, G. W.; Clark, T.; Chandrassekhar, J.; Schleyer, P. v. R. *J. Comput. Chem.* **1982**, *3*, 363–371.

Table III. Total Energies[a] Calculated from MP2(Full)/6-311+G(3d,2p) Geometries

molecule	structure	basis set	HF	MP2	MP3	MP4
NH_2^+	**1** ($^1A_1$), C_{2v}	6-311+G(3d,2p)	−55.15268	−55.29251[b]	−55.31175	−55.31823
		6-311+G(3df,2p)	−55.15287	−55.30450	−55.32459	−55.33117
		6-311+G(3d2f,2p)	−55.15301	−55.30629	−55.32599	−55.33260
	1 ($^3B_1$), C_{2v}	6-311+G(3d,2p)	−55.23260	−55.35088[c]	−55.36624	−55.37059
		6-311+G(3df,2p)	−55.23308	−55.36158	−55.37768	−55.38220
		6-311+G(3d2f,2p)	−55.23304	−55.36293	−55.37873	−55.38330

[a] Hartrees. Single-point MP calculations restricted to valence-shell electrons. [b] MP2 (full) energy, −55.31350. [c] MP2 (full) energy, −55.37216.

Table IV. Calculated Singlet–Triplet Energy Difference (kcal mol^{-1}) Obtained from HF/6-31G(d) Geometries[a]

molecule	structure	basis	HF	MP2	MP3	MP4
NH_2^+	**1**	6-31G(d)	51.0	39.4	36.9	35.8
		6-31G(d,p)	51.4	38.9	36.3	35.2
		6-311G(d,p)	51.0	38.6	36.1	34.9
		6-311+G(d,p)	51.0	38.6	36.1	34.8
		6-311+G(3d,2p)	50.0	36.9	34.5	33.2
CH_3NH^+	**2**	6-31G(d)	40.0	17.8	18.7	15.0
		6-31G(d,p)	39.9	17.6	18.7	15.1
		6-311G(d,p)	39.5	16.7	18.1	14.1
$(CH_3)_2N^+$	**15**,[b] **17**[c]	6-31G(d)	32.5	6.9	9.5	5.9
		6-31G(d,p)	32.1	6.9	9.8	6.3
		6-311G(d,p)	32.0	6.0	9.3	
$C_4H_8N^+$	**24**	6-31G(d)	24.0	−5.7		
$C_5H_{10}N^+$	**26**	6-31G(d)	30.1	5.2		

[a] S–T calculated from data in Table II. [b] Singlet state. [c] Triplet state.

Table V. Singlet–Triplet Energy Differences[a] (kcal mol^{-1}) Calculated from the MP2(full)/6-311+G(3d,2p) Geometries

molecule	structure	basis set	HF	MP2	MP3	MP4
NH_2^+	**1**	6-311+G(3d,2p)	50.1	36.6[b]	34.2	32.9
		6-31+G(3df,2p)	50.3	35.8	33.3	32.0
		6-311+G(3d2f,2p)	50.2	35.5	33.1	31.8

[a] Single-point MP calculations restricted to valence-shell electrons. [b] MP2(full) value, 36.8 kcal mol^{-1}.

Table VI. Comparison of Present and Previous Calculations on NH_2^+

singlet		triplet		ΔE, kcal mol^{-1}	
r_{NH}	θ	r_{NH}	θ	($^1A_1$ − $^3B_1$)	ref
1.033	108.2	1.018	143.3	29.1	Bender et al. 1977[a]
1.027[b]	107.6	1.027	149.6	29.9	Peyerimhoff et al. 1979[c]
1.058	106.2	1.037	149.7	31.2	Pope et al. 1984[d]
1.029	110.0	1.021	150.9	33.6	Pople et al. 1986[e]
1.043	107.1	1.025	149.4	32.4	present work[f]

[a] Reference 19. RHF calculations using a contracted Gaussian basis set: N(13s8p3d/9s6p3d), H(6s2p/4s2p), and two-configuration treatment for the singlet state. [b] r_{NH} for the triplet state. [c] Reference 20. MRD-CI treatment using contracted Gaussian basis set: N(9s5p2d/5s3p2d), H(5s1p/2s1p), with additional s- and p-type bond functions. [d] Reference 21. MRD-CI treatment using contracted Gaussian basis set: N(11s6p2d/6s3p2d), H(5s1p/3s1p). Geometries from CASSCF calculations using the same basis set. [e] Reference 22. "Projected" MP4/6-311+G(2df,p) calculations on HR/6-31G(d) geometries. Includes a thermal correction (0.83 kcal mol^{-1}) calculated from the scaled HF/6-31G(d) vibrational frequencies. [f] MP4(SDTQ)/6-311+-G(3d2f,2p)//MP2/6-311+G(3d,2p) calculation. Includes a thermal correction (0.55 kcal mol^{-1}) calculated from the scaled MP2/6-31(d,p) frequencies.

311+(3d,2p) basis includes two further sets of d-type functions on non-hydrogen and an additional set of p functions on hydrogen. The latter was constructed in an attempt to duplicate the valence and polarization characteristics of the very large basis sets used by Schaefer and co-workers in their calculations on NH_2^+,[19] and CH_2.[46]

In addition to the calculations described so far, the geometries of the singlet and triplet states of NH_2^+ were optimized with the inclusion of electron correlation at the MP2 level by using the 6-311+(3d,2p) basis set. Finally, following Pople and co-workers,[22] the effects of supplementing this basis set with nitrogen f functions was investigated. These data are summarized in Table III. The resulting singlet–triplet energy differences at all levels are summarized in Tables IV and V.

Discussion

Nitrenium Ion, NH_2^+. This molecule has already been studied extensively by others.[19-22] It was reexamined in detail here for the insight into the likely performance of the necessarily lower levels of theory applicable to its more computationally burdensome derivatives it was expected to provide.

Recent calculations on the ground ($^3B_1$), and lowest singlet ($^1A_1$) states, of NH_2^+ are summarized in Table VI together with the results of the highest level calculations carried out here. The basis sets, and contraction schemes used by each group, are provided in footnotes to the table. The results obtained by Bender et al.[19] are from restricted Hartree–Fock open-shell calculations using a large polarized basis set (65 contracted Gaussians) estimated to lead to total energies within 0.005 hartree (~3 kcal) of the Hartree–Fock limit for the triplet state. The singlet calculations were carried out by using a two-configuration wave function. The multireference determinant (MRD) CI calculations of Peyerimhoff and Buenker[20] and Pope, Hillier, and Guest[21] used extensively polarized, although somewhat smaller, basis sets (52 and 39 contracted Gaussians, respectively) built on extensions to the Dunning[47] triple ζ valence bases. The singlet–triplet separations predicted by all three groups agree remarkably well with one another and with the experimentally determined value[2] of 30.1 ± 0.2 kcal mol^{-1}.

In a philosophically different approach, Pople and co-workers[22] used single-configuration spin-restricted (RHF) and spin-unrestricted Hartree–Fock (UHF) wave functions for the singlet and triplet states, respectively. Corrections for electron correlation were introduced at the level of fourth-order Moller–Plesset perturbation theory including all single, double, and triple excitations. Single-point calculations using the 6-311G(d,p) basis and three extensions of it including diffuse functions, extra d functions, and f functions were carried out on the HF/6-31G(d) geometries. The resulting energies were combined to afford a single "projected" MP4/6-311+G(2df,p) energy for each state. This yielded a singlet–triplet energy separation (32.7 kcal mol^{-1}) some 2.6 kcal mol^{-1} larger than the experimentally determined value. Correction for zero-point energies increased this discrepancy slightly further (cf. Table VI).

The present calculations again used a large polarized extension to the 6-311G(d,p) basis but were carried out directly rather than by additive projections from lower levels of theory. However, apart from the use of more refined geometries, our calculations followed the methodology of the Pople group exactly. Like theirs (and like their previous calculations[48] on CH_2) the predicted singlet–triplet energy difference was slightly overestimated. Although small,[49]

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(46) Meadows, J. H.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1976**, *98*, 4383–4386.

(47) Dunning, T. H., Jr.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; Vol. 3, pp 1–27.

(48) Cf.: Pople, J. A.; Luke, B. T.; Frisch, M. J.; Binkley, J. S. *J. Phys. Chem.* **1985**, *89*, 2198–2203.

(49) Radom and co-workers[50] obtained a singlet–triplet separation of 36.3 kcal mol^{-1} at the MP3/6-31G(d,p)//HF/6-31(d) level (excluding vibrational corrections). This is identical with the value obtained in analogous calculations here (Table IV), but 4.5 kcal mol^{-1} larger than that obtained in our most elaborate calculations (Table V).

(50) Yates, B. F.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1986**, *108*, 6545–6554.

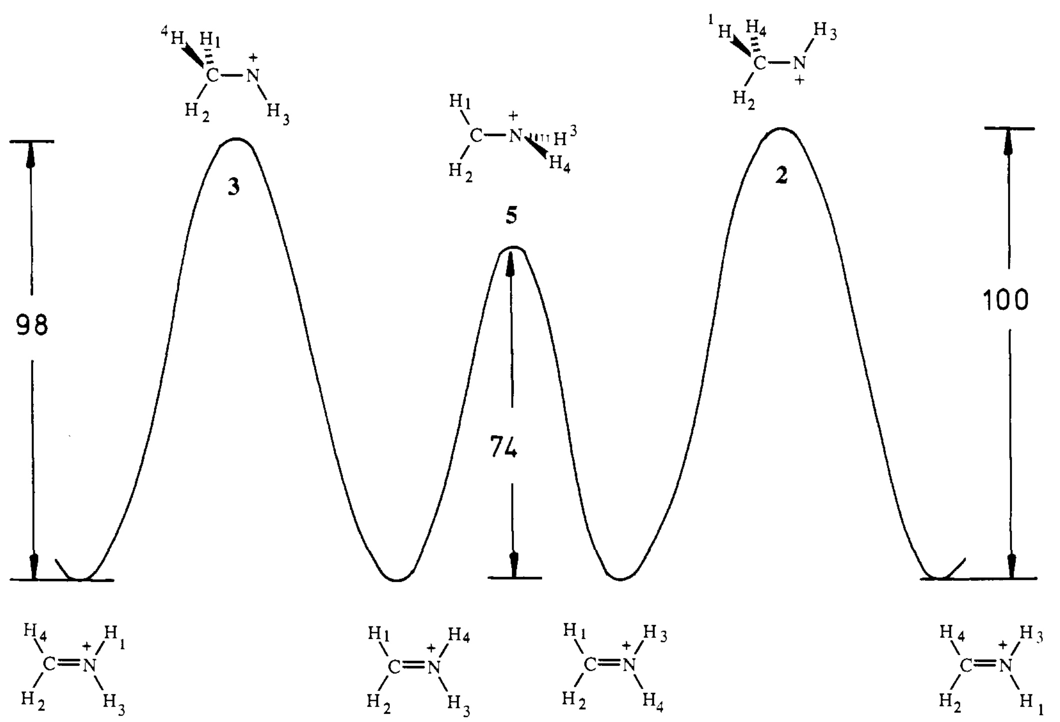

Figure 1. Singlet CH_4N^+ potential surface. Relative energies are from MP4/6-31G(d) calculations including vibrational corrections. Units, kilocalories per mole.

the discrepancy appears to be inherent in the approach and seems to be, at least partly, associated with the use of the triplet UHF wave function. As is well-known, the UHF wave function does not correspond to a pure spin state, but is "contaminated" with states of higher multiplicity. This was apparent in the present calculations where, for the basis sets used, the expectation value of the S^2 operator, $\langle S^2 \rangle$ was around 2.022 rather than the 2.000 anticipated for pure triplet. The UHF wave function also allows a degree of correlation in the triplet absent in the RHF treatment of the singlet. At the SCF level, these factors combine to exaggerate the singlet–triplet energy difference by ~6 kcal mol^{-1}. Thus, computation of the triplet energy using the 6-311+G(3d,2p) basis set and open-shell spin-restricted,[51] rather than the UHF, procedure reduced the calculated singlet–triplet energy separation from 50.0 to 44.0 kcal mol^{-1}. This value, which includes no corrections for electron correlation, is very close to the analogous single configuration SCF results of Bender et al.[19] (44.7 kcal mol^{-1}) and Peyerimhoff and Buenker[20] (44.3 kcal mol^{-1}). The Moller–Plesset treatment appears to correct some of the problems inherent in the use of the unrestricted wave function. While systematic improvements in the basis set had little effect at the SCF level, the predicted energy difference at the MP4 level fell monotonically, albeit slowly, to within a few kilocalories per mole of the MCSCF values (Tables IV and V).

The use of the single-configuration wave function in calculations of this kind was criticized by Shavitt,[52] who cited the dramatic narrowing of the energy difference between the $^1A_1$ and $^3B_1$ states of CH_2 found by Meadows and Schaefer[46] on going from a one- to a two-configuration wave function. However, since the two-configuration treatment itself allows for significant electron correlation in the singlet, this observation may not bear directly on the adequacy of the single determinantal treatment in procedures where electron correlation is recovered in another way. Certainly, the residual error for the most elaborate calculations reported here seems quite small. Single-point MP4(SDTQ)/6-311+G(3d2f,2p) calculations on the MP2/6-311+G(3d,2p) geometries, with thermal corrections at the MP2/6-31G(d,p) level, predict the $^3B_1$ state to lie 32.4 kcal mol^{-1} below the $^1A_1$ state; an error of 2.3 ± 0.2 kcal mol^{-1}. At the same time it is clear that calculations at the lower levels of theory applicable to the larger ions systematically underestimate the relative stability of the triplet. We return to this problem below following a survey of the nitrenium ion structures and the nature of the potential surfaces on which they reside.

Table VII. Relative Energies[a] of Singlet CH_4N^+ Structures Calculated from HF/6-31G(d) Geometries and the 6-31G(d) Basis Set

structure	HF	MP4	MP4 + vib
2	101.8	105.4	100.0
3	100.2	102.1	97.5
5	67.2	76.9	73.6
4	0.0	0.0	0.0

[a] Kilocalories per mole. Calculated from data in Table I and II.

Table VIII. Relative Energies[a] of Triplet CH_4N^+ Structures Calculated from HF/6-31G(d) Geometries and the 6-31G(d) Basis Set

structure	HF	MP4	MP4 + vib
9	63.0	53.8	51.0
10	13.4	17.8	18.0
3	0.9	4.7	4.5
2	0.9	4.6	5.0
6	0.0	0.0	0.0

[a] Kilocalories per mole. Calculated from data in Table I and II.

Methylnitrenium Ion, CH_3NH^+. The relative energies of the singlet and triplet methylnitrenium ion and related isomers found with the 6-31G(d) basis set are summarized in Tables VII and VIII. The MP4(SDTQ)/6-31G(d) results, including vibrational corrections, are presented schematically in Figures 1 and 2. Despite the rather modest basis set used, the relative energies of species of the *same spin multiplicity* should not be drastically altered at higher levels of theory. For example, on the singlet surface the relative energies of **2** and **4** at the MP4 level are changed by only 0.3 kcal mol^{-1} on going from the 6-31G(d) to the 6-311G(d,p) basis set (data from Table II).

Perhaps the most striking aspect of the potential surface shown in Figure 1 is that neither conformation of the singlet methylnitrenium ion is predicted to be a local minimum. Instead, both were predicted to be transition structures, **2** for interchange of

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(51) $^3B_1(NH_2^+)$: ROHF/6-311+G(3d,2p)//UHF/6-31G(d,p) energy = −55.223078 au. We are grateful to Professor M. L. McKee, Auburn University, for this calculation.

(52) Shavitt, I. *Tetrahedron* **1985**, *41*, 1531–1542.

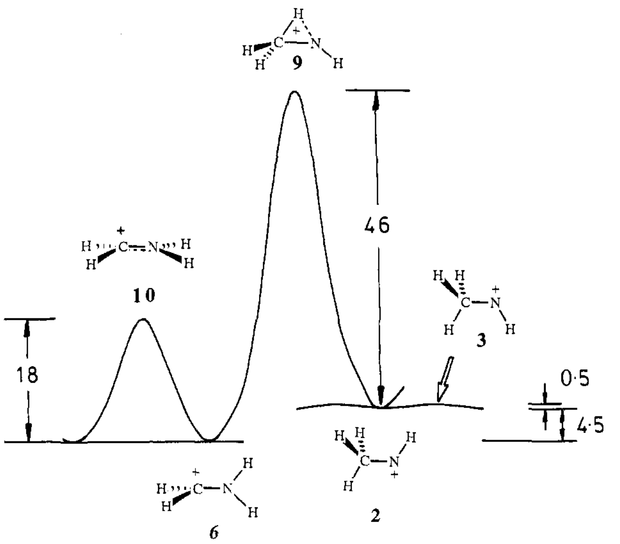


Figure 2. Triplet CH_4N^+ potential surface. Relative energies are from MP4/6-31G(d) calculations including vibrational corrections. Units, kilocalories per mole.

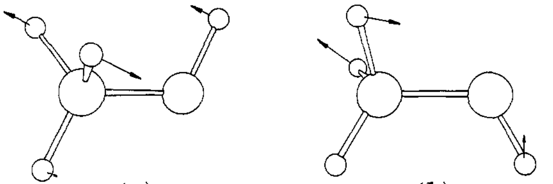
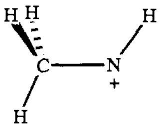

(a) (b)

Figure 3. HF/6-31G(d) transition vectors for saddle points corresponding to the singlet methylnitrenium ion. (a) anti conformation, **2**. (b) syn conformation, **3**.

the trans and **3** for interchange of the cis hydrogens in **4** (cf. Figure 1). The forms of the transition vector for each process are shown in Figure 3. Despite considerable effort, we were unable to locate a local minimum corresponding to the singlet methyl nitrenium ion on the HF/6-31G(d) surface.[53] This is consistent with previous results for the related carbenium ions which, in the absence of resonance stabilization, also represent transition states rather than energy minima.[54-56]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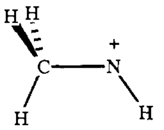
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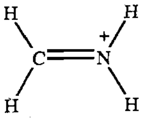
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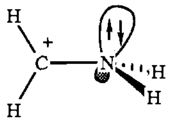
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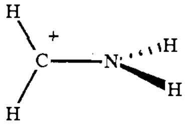
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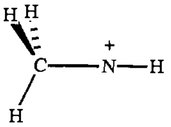
The only[57] minimum energy structure on the singlet surface appears to be the planar C_{2v} immonium ion **4**. The maximum on the CN rotational pathway was calculated to be the amino-substituted carbenium ion **5**, 73.6 kcal mol^{-1} above **4**. The C_{2v} "perpendicular" immonium ion **6** corresponded to an almost degenerate biradical state. An open-shell singlet UMP4 calculation here led to an energy only 1.2 kcal mol^{-1} higher than **5** and just 0.8 kcal mol^{-1} below the corresponding triplet biradical. The near coincidence of the S_0, S_1, and T_1 states in this system has been discussed in detail by Michl and co-workers.[58]

The role of the nitrenium ion on the triplet surface (Figure 2) was completely different. Here **2** and **3** corresponded to two points on an essentially flat rotational manifold. At the HF level, **2** was calculated to be a local minimum and **3** a saddle point for the methyl rotation. However, their relative stabilities were reversed when vibration corrections were included. Although the CNH bond angle in **2** was distinctly "bent" (151.1°), distortion to the C_{3v} structure **7**, a "hilltop", required only 1.0 kcal mol^{-1} at the HF/6-31G(d) level. The global minimum on this surface corresponded to the "perpendicular" methylene immonium ion. The optimized geometry of the latter had the C_s structure **8** in which the plane of the methylene group was tilted slightly (23.9°) from the CN bond axis. However, the C_{2v} structure **6**, although higher in energy at the HF level, appears to be preferred when allowance for electron correlation is included.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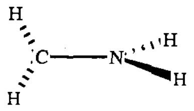
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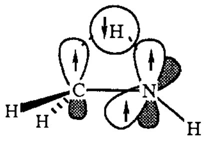
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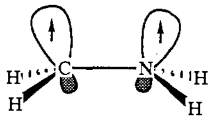
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In contrast to the situation on the singlet surface, hydrogen migration in the nitrenium ion was hindered by a substantial barrier of 46 kcal mol^{-1}. Unlike the corresponding process on the singlet surface, the reacting system here (**9**) involves three electrons, one of which is forced to occupy an antibonding level.[59]

The saddle point for rotation about the CN bond corresponded to the triplet biradical **10** in which both termini were slightly pyramidized,[60] presumably allowing maximum localization of the unpaired electrons. Here the more symmetrical C_{2v} structure **4**

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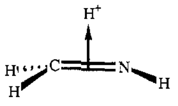
(53) A C_1 structure of this kind was found at the HF/3-21G level. However, this was predicted to be only marginally stable, its conversion to **4** being hindered by a barrier of only 0.17 kcal mol^{-1}. We assume this structure is an artifact of the lower level calculation.

(54) Raghavachari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5649–5657.

(55) Ford, G. P.; Smith, C. T. *J. Am. Chem. Soc.* **1987**, *109*, 1325–1331.

(56) Ford, G. P.; Raghuveer, K. S. *Tetrahedron* **1988**, *44*, 7489–7498.

(57) In the search for other minima on this surface we traced the reaction pathway **2** → **9** using the H^4CN angle as a reaction coordinate performing MP2/6-31G(d) on the HF/3-21G geometries. Again, no evidence for either a transition state or a π-complex-like ion (i) analogous to the "nonclassical"


(*i*)

$C_2H_5^{+\,47}$ was found. At both the HF/6-31G(d) and MP2(full)/6-31G(d) levels we did locate local minima corresponding to C_1 structures of the carbene H_3N^+CH: (E = −94.240889, −94.50755 au). Pople and co-workers[35] concluded that the analogous ethylidene, also a minimum at the HF/6-31G(d) level, collapses without activation to ethylene at higher levels. We assume a similar situation holds here, especially since the corresponding rearrangement is even more exothermic.

(58) Bonacic-Koutecky, V.; Schoffel, K.; Michl, J. *Theor. Chim. Acta* **1987**, *72*, 459–474.

(59) Dewar, M. J. S.; Dougherty, R. C. *The PMO Theory of Organic Chemistry*; Plenum: New York, 1975; p 449.

(60) The inclination of the methylene plane to the CN bond axis was 35.6°. The NH_2 group was tilted in the same direction by 4.0°.

Table IX. Relative Energies[a] of Singlet $C_2H_6N^+$ Structures Calculated from HF/6-31G(d) Geometries and the 6-31G(d) Basis Set

structure	HF	MP4	MP4 + vib	exp
15	89.4	90.4	86.7	
12	9.8	9.0	8.7	9[b]
11	0.0	0.0	0.0	0

[a] Kilocalories per mole. [b] Reference 62.

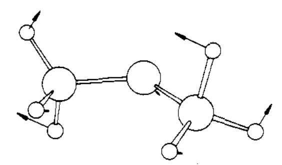


Figure 4. MP2(full)/6-31G(d) transition vectors for the saddle point corresponding to the singlet dimethylnitrenium ion **15**.

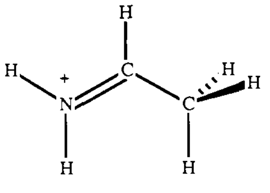
was calculated to be less stable at all levels of theory.

The formation of **4** in the mass spectral fragmentation of amines is well-known.[7] While somewhat higher values are given in some of the older literature,[61] recent appearance potential measurements[62] have firmly established a heat of formation close to 178 kcal mol^{-1} for this ion. Combining this value with the relative energy of **2** in Table VII yields a theoretical estimate of 278 kcal mol^{-1} for the heat of formation of the singlet nitrenium ion. Using reasoning explained below, our best estimate of the singlet–triplet energy separation in the nitrenium ion is 10.6 ± 2.8 kcal mol^{-1}. The theoretical estimate of the heat of formation of the triplet is then 267 ± 3 kcal mol^{-1}. These values are in excellent agreement with the corresponding MNDO ones (277.9 and 271.7 kcal mol^{-1}, respectively[30]) but very different from the 206.9 kcal mol^{-1} suggested by Collin and Franskin.[5] The latter was deduced from the appearance potential of the m/z 31 ion in the mass spectrum of CH_3ND_2 assumed to be CH_3ND^+. In view of this discrepancy, it now seems most likely that the ion observed by Collin and Franskin was $CH_2{=}NHD^+$, formed in an alternative reaction channel involving simultaneous $D^\bullet$ loss and $H^\bullet$ migration. The heat of formation deduced from the appearance potential would then apply to the energy of the activated complex for this rather unusual process. In an ion cyclotron resonance study of vibrationally excited $CD_3NH_3^+$ formed by condensation of CD_3^+ and ammonia, Huntress and Elleman[4] observed two distinct unimolecular decomposition pathways. One involved loss of HD and rather clearly[4] led to an electronically excited state of **4**. The other involved loss of H_2 and was assumed to lead to CD_3NH^+. However, even if all the energy of the condensation reaction were retained, this would be insufficient[61] to produce the nitrenium ion if our estimate of its heat of formation is correct. Thus, a concerted process, in this case involving simultaneous H_2 loss and $D^\bullet$ migration, again seems likely. This essentially amounts to entry to the $CD_3NH^+ \rightarrow CD_2{=}NH_2^+$ reaction surface below its maximum (cf. Figure 1).

The methylnitrenium ion itself has been generated in the gas phase by charge reversal collisional activation (CRCA) mass spectrometry from CH_3NH^-.[3] Here, the experimental conditions apparently permit formation of the nitrenium ion in its triplet ground state in which it is expected to have a finite lifetime. The resulting fragmentation pattern included the expected CH_3^+ peak at m/z 15 and was quite different from the corresponding pattern for the immonium ion.

In the condensed phase the situation appears to be different altogether. Thus, photolysis of *N*-(methylamino)pyridinium precursors of CH_3NH^+ in either benzene/trifluoroacetic acid or toluene/trifluoroacetic acid mixtures led to significant amounts of the arylamines expected on the basis of an electrophilic substitution involving the singlet nitrenium ion.[10] Thus, it appears that the trifluoroacetate gegen ion preferentially stabilizes the singlet state of the nitrenium ion[63] and at the same time reduces its propensity to rearrange.

Dimethylnitrenium Ion, Me_2N^+. In agreement with previous calculations,[27,28,64] the lowest energy isomer on the singlet $C_2H_6N^+$ surface was calculated to be the immonium ion **11**. The isomeric



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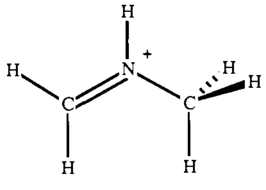

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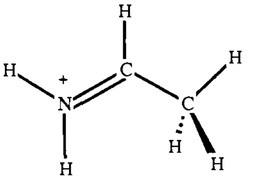

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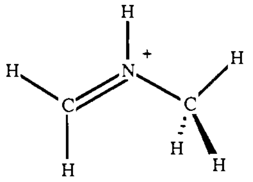
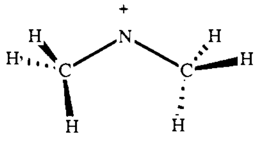


14

ion **12** was calculated to be 8.7 kcal mol^{-1} higher in energy, in excellent agreement with the 9 kcal mol^{-1} determined experimentally by Lossing et al.[62] The alternative conformers **13** and **14** corresponded to transition states for methyl rotation in **11** and **12**, respectively. The relative energetics on the singlet structures are summarized in Table IX. At the HF/6-31G(d) level the singlet dimethylnitrenium ion, $(CH_3)_2N^+$, was predicted to exist in a local minimum corresponding to the C_2 structure **15**. Here,



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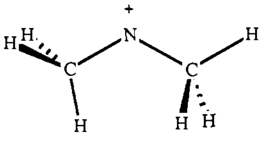

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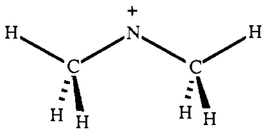

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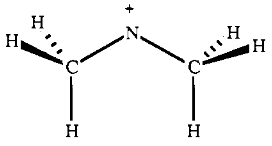

18

both methyl groups are staggered relative to the adjacent CN. The C_s structure **16** was 2.9 kcal mol^{-1} less stable and was a transition state for internal rotation of one of the methyl groups. The C_{2v} structure **17** was 6.1 kcal mol^{-1} higher than **15** and corresponded to a hilltop for simultaneous rotation of both methyl groups. The relative instability of the latter is noteworthy since this is usually the preferred conformation in compounds of the type $(CH_3)_2X$.[65] This preference has been discussed by Cremer et al.,[65] who suggested that long-range overlap of methyl hydrogens close a pseudo cyclic π system which typically (X = O, NH, etc.) contains six electrons and is, therefore, at least partially aromatic. In the singlet nitrenium ion, these orbitals are occupied by only 4π electrons. Analogous reasoning[65] therefore suggests that this species should be partially antiaromatic and therefore destabilized relative to the alternative conformations.

The HF/6-31G(d) transition structure for the rearrangement of the nitrenium ion, **15** → **14**, had C_1 symmetry. However, the calculated barrier at this level was only 4.5 kcal mol^{-1} and dis-

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(61) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* **1977**, *6* (*Suppl 1*).

(62) Lossing, F. P.; Lam, Y.-T.; Maccoll, A. *Can. J. Chem.* **1981**, *59*, 2228–2231.

(63) Takeuchi, H.; Hayakawa, S.; Murai, H. *J. Chem. Soc.* **1988**, 1287–1289.

(64) Barone, V.; Lelj, F.; Grande, P.; Russo, N.; Toscano, M. *Chem. Phys. Lett.* **1987**, *133*, 548–552.

(65) Cremer, D.; Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1974**, *96*, 6900–6903.

Table X. Relative Energies[a] of Triplet $C_2H_6N^+$ Structures Calculated from HF/6-31G(d) Geometries and the 6-31G(d) Basis Set

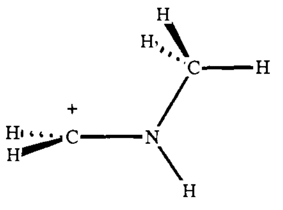
structure	HF	MP4	MP4 + vib
20	10.3	6.5	8.3
19	6.6	3.4	5.1
17	0.0	0.0	0.0

[a] Kilocalories per mole.

appeared altogether when correlation corrections were added. This suggests that, like CH_3NH^+, the dimethylnitrenium ion does not correspond to a local minimum on the singlet surface, but to a transition state for H migration in the immonium ion. This was confirmed in an MP2/6-31G(d) optimization and force constant calculation on **15** [MP2(full)/6-31G(d) energy, −133.71000]. The MP2 transition vector is shown in Figure 4.

The minimum energy structure corresponding to the triplet dimethylnitrenium ion was calculated to be **17**. However, like CH_3NH^+, rotation of the methyl group was essentially unhindered. The energies of structures **16–18** all fell within 0.2 kcal mol^{-1} of one another.

The relative energies of the triplet isomers are summarized in Table X. On the triplet surface the nitrenium ion is slightly more stable than the related immonium ions **19** and **20**, which have the expected "perpendicular" structures.



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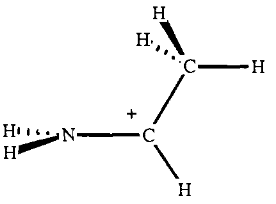
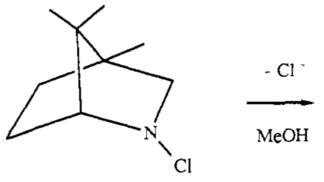


20

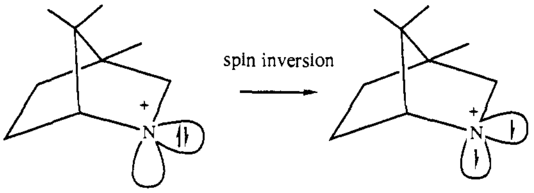
Evidence for the dimethylnitrenium ion in the gas phase was obtained by Parker and her associates,[3] who observed a fragmentation pattern quite distinct from that of the immonium ion in the CA spectrum of $C_2H_6N^+$ generated by charge reversal of $(CH_3)_2N^-$. The dimethylnitrenium ion has also been postulated as an intermediate in the electron impact (EI) mass spectra of various amines of general type $(CH_3)_2NX$.[6-9] The loss of $CH_3^\bullet$ in the EI spectrum of trimethylamine was studied in detail by Levsen and McLafferty.[7] Here, the CA spectrum of the resulting $C_2H_6N^+$ ions revealed only the immonium ion: $CH_3N^+{=}CH_2$. These authors therefore concluded[7] that rapid rearrangement of the initially formed dimethylnitrenium ion had occurred. Unfortunately, attempts to determine the appearance potential for this process,[6,8,9,66] and therefore the heat of formation of the intermediate ion, have led to widely divergent values. Most recently Solka and Russell[8] and Loudon and Webb[66] gave 10.68 ± 0.09 and 11.25 eV, respectively. These lead[67] to 206 and 219 kcal mol^{-1} for $\Delta H_f[(CH_3)_2N^+]$. While the level of agreement is still poor, both values seem too small to be consistent with the formation of $(CH_3)_2N^+$ as a discrete intermediate. Using the well-established[62] value of 157 kcal mol^{-1} for the heat of formation of $H_2N^+{=}CHCH_3$, the present calculations (Table X and below) suggest heats of formation of 244 and 242 ± 3 kcal mol^{-1} for the singlet and triplet ions, respectively. The latter values are consistent with the MNDO[30,68] ones of 253.2 and 252.2 kcal mol^{-1}, especially when it is remembered that this method tends to underestimate the stabilizing effect of alkyl groups directly bound to electron-deficient centers.[69,70] Thus, if the appearance potential measurements are correct, fragmentation of the precursor radical cation must take place on the singlet manifold with concurrent $CH_3^\bullet$ loss and $H^\bullet$ migration at energies well below those necessary for the discrete existence of the nitrenium ion itself. In this case, the CN bond cleavage and H migration must follow ionization of electrons from a high-lying σ(CN) orbital[71] without unpairing the nonbonding electrons on nitrogen. On the other hand, direct ionization of the $(CH_3)_2N$ radical might be expected to produce the nitrenium ion either as a triplet or as a transient singlet species geometrically similar to the radical. Unfortunately, the experimental data for both the ionization potential[6] and the heat of formation of the radical[72] are rather uncertain. Nevertheless, it is tempting to note that together they do indeed lead to a heat of formation for the dimethylnitrenium ion (247 kcal mol^{-1}) that is very similar to our theoretical estimates of 244 for the singlet and 242 ± 3 for the triplet.

Alicyclic Nitrenium Ions $C_4H_8N^+$ and $C_5H_{10}N^+$. The work of Gassman and colleagues on the heterolysis of bicyclic *N*-chloroamines has played a central role in the development of solution-phase nitrenium ion chemistry.[1b] They found that **21a** reacted in methanol via two distinct mechanistic pathways.[11] One led to skeletal rearrangement and solvent incorporation typical of onium ion reactivity. The other led to amine formation. Thus **21a** was assumed to lead initially to the singlet nitrenium ion **22**, which subsequently underwent spin inversion to the triplet **23** which, as a 1,1-biradical, then abstracted hydrogen from the solvent. This was apparently confirmed by the observed increase in the relative yield of amine in the presence of halogenated solvents known to promote spin inversion. This rationalization for the formation of amine products was subsequently challenged by a number of authors.[13-15] Convincing evidence against the intervention of the triplet state was provided by Hoffman and co-workers, who found that heterolysis of various *N*-sulfonyloxyamines, including **21b**, gave only rearrangement, and none of the H-abstraction product even in the presence of heavy-atom solvents.[13] Further, from a survey of the known solvolysis reactions of various amine derivatives, they found the proportions of H-abstraction products increased as the efficiency of the leaving group decreased. Since these solvolyses are frequently anchimerically assisted by the migrating group,[13] this result is exactly the reverse of that expected if intersystem crossing to the triplet is important. Thus, for the poorest leaving groups, bond formation to the migrating group



21

a, X = Cl
b, X = $OSO_2C_6H_4NO_2$



22 **23**

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(66) Loudon, A. G.; Webb, K. S. *Org. Mass Spectrom.* **1977**, *12*, 283–287.

(67) $\Delta H_f[(CH_3)_3N]$ = −5.7 kcal mol^{-1}: Pedley, J. B.; Rylance, J. *Sussex—N.P.L. computer analysed thermochemical data: organic and organometallic compounds*; University of Sussex: Brighton, U.K., 1977. $\Delta H_f[CH_3]$ = 34.4 kcal mol^{-1}: Traeger, J. C.; McLoughlin, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 3647–3652.

(68) The MNDO heat of formation for singlet $(CH_3)_2N^+$ referred to structure **18**. A more complete search of the MNDO surface showed **15**, ΔH_f = 253.2 kcal mol^{-1}, to be the lowest energy structure.

(69) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4907–4917.

(70) Ford, G. P.; Scribner, J. D. *J. Comput. Chem.* **1983**, *4*, 594–604.

(71) The onset of the peak corresponding to ionization from the highest σ(CN) molecular orbital in the photoelectron spectrum of trimethylamine occurs around 11.6 eV: Al-Joboury, M. I.; Turner, D. W. *J. Chem. Soc.* **1964**, 4434–4441. See also: Kimura, K.; Katsumata, S.; Achiba, Y.; Yamazaki, T.; Iwata, S. *Handbook of HeI photoelectron spectra of fundamental organic molecules*; Japan Scientific Societies Press: Tokyo, 1981; p 121.

(72) Kerr, J. A. *Chem. Rev.* **1966**, *66*, 465–500.

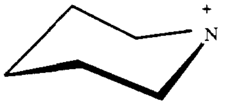
should be most advanced and therefore the formation of the "free" divalent nitrogen species necessary for such intersystem crossing least likely.[13]

The bicyclo compounds **22** and **23** themselves are too large to study at meaningful levels of ab initio theory. However, we did carry out MP2/6-31(d)//HF/6-31G(d) calculations on the structures and energies of both the singlet and triplet states of the constituent five- and six-membered nitrenium ions.

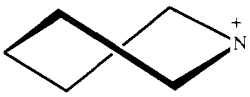
In both states the lower energy conformers of the pyrrolidine nitrenium ion had the twist, or half-chair, structure **24** with C_2 symmetry. Initial geometries having C_s symmetry (with nitrogen out the plane) optimized to the less stable C_{2v} planar conformers (**25**).

24

25



26



27

For the piperidine nitrenium ions the lowest energy structures in both states were calculated to have the familiar C_s chair form **26** with the twist boats **27** being somewhat less stable. Force constant calculations were carried out only on the corresponding HF/3-21G geometries. Here, **24** and **26** were predicted to be local minima, and **25** and **27** saddle points.

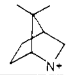
Singlet–Triplet Separation in Nitrenium Ions. In the previous sections the relative energies of the alkylnitrenium ions and their isomers were discussed by using the fairly modest 6-31G(d) basis set in the expectation that, for comparisons among species of the same spin multiplicity, residual basis set and correlation errors should largely cancel. For species of different spin multiplicities correlation effects are quite different and the same cancellation cannot be relied upon. This behavior is very clear on inspection of the calculated data for NH_2^+. At the Hartree–Fock level, the calculated singlet–triplet splitting is rather insensitive to the quality of the basis set. However, at the MP level, the calculated energy difference falls monotonically as the basis set is elaborated, reflecting the inherently larger correlation error in the singlet where all electrons are paired. Elaboration of the basis set allows progressively higher proportions of the correlation energy to be recovered. The energy of the singlet is therefore lowered relative to the triplet, closing the gap between them. Although fewer calculations were performed on the methyl- and dimethylnitrenium ions, the same qualitative behavior was evident for both. Thus, the calculated singlet–triplet energy differences can apparently be rather confidently regarded as upper limits of the actual values.

We had originally hoped to make more precise estimates of the singlet–triplet splittings in the larger species by combining the calculated energies of eq 1 with the experimental data for NH_2^+

$$RR'N^+ (s) + R''R'''N^+ (t) \rightarrow RR'N^+ (t) + R''R'''N^+ (s) \qquad (1)$$

(R, R′ = H). Since the calculation of only relative energies is required, it might be anticipated that good results could be obtained at rather modest levels of theory (cf. ref 37b). In the present case, the success of this strategy requires that correlation errors on the singlet–triplet splitting be independent of the level of the calculation and the nature of the groups bound to nitrogen. The data in Table IV show that neither condition is fulfilled. As the nitrenium ion becomes more complex, the absolute magnitude of the correlation effect on the singlet–triplet splitting at the MP2 level increases substantially. At the same time the magnitudes of the correlation corrections beyond this level become progressively smaller. Both effects are simply explained if it is assumed that as the complexity of the ion increases, a greater proportion of the correlation energy is recovered at the MP2 level due simply to the larger number of basis functions involved. Estimation of the singlet–triplet splitting in the alkylnitrenium ions via eq 1 would then be expected to exaggerate the stabilities of the singlets. Such a procedure would then lead to a probable lower limit of the true singlet–triplet splitting. Data of this kind were calculated at the highest level available by using eq 1 except that each ion was referenced to the previous ion in Table IV rather than **1**. The resulting lower bounds to the singlet–triplet energy differences were combined with the corresponding upper bounds calculated directly from the data in Table IV and presented together in Table XI as deviations about the central values. Also included in Table XI are the corresponding MNDO values.[30,68]

Table XI. Singlet–Triplet Energy Differences (S–T) in Alkylnitrenium Ions

structure	ab initio[a]	MNDO[b]
CH_3NH^+	10.6 ± 2.8[c]	6.2
$(CH_3)_2N^+$	2.1 ± 3.3[d]	2.1[e]
	0.3 ± 3.6[f]	−4.5
	−10.7 ± 3.6[g]	−10.5
		−14.5[h]

[a] Calculated from data in Table IV together with vibrational corrections at 298 K from Table I. The higher value in each case was obtained directly from the data in Tables I and IV without modification. The lower values were obtained from the data in Tables I and IV by using eq 1. The identities of the R groups in each case are given in the relevant footnotes. E(S–T) for the reference molecule in eq 1 is the lower bound from the present table except for NH_2^+ where the experimental value[2] 30.1 kcal mol^{-1} is used. [b] Data from ref 30. [c] MP4/6-311G(d,p) calculation. R, R′, R″ = H; R‴ = CH_3. [d] MP4/6-31G(d,p) calculation. R = H; R′, R‴ = CH_3. [e] Singlet data from this work, cf. ref 68. [f] MP2/6-31G(d) calculations. R, R′ = CH_3; R″–R‴ = $-(CH_2)_5-$. [g] MP2/6-31G(d) calculation. R, R′ = CH_3; R″–R‴ = $-(CH_2)_4-$. [h] This work.

The overall agreement between the two series of calculations is very good. The progressively greater stability of the singlet state with increasing substitution at nitrogen has been discussed before.[30] Both methods predict the methylnitrenium ion to be a ground-state triplet. In the dimethyl and piperidine nitrenium ions the singlet–triplet separation is rather small and unambiguous assignments of the ground-state multiplicities at the ab initio level is not possible. On the other hand, the pyrrolidine nitrenium ion is rather unambiguously predicted to be a ground-state singlet. The apparent stabilization of the singlet state in the cyclic systems, especially the latter, is associated with distortions of the C–N–C angles in the triplets imposed by the constraints of the cyclic geometries as discussed by Koser.[73] Thus the CNC angle in unstrained triplet nitrenium ions is around 150°. In the HF/6-31G(d) structure of the triplet **17**, for example, this angle is calculated to be 150.3°. In the five- and six-membered cyclic ions (**24** and **26**) it is forced to adopt much smaller values of 121.4 and 135.6° corresponding to distortions of ca. 29 and 15°, respectively. In the singlets, where the nitrogen is approximately trigonal, the distortions are much smaller. The CNC angle in singlet **17** is 120.8° while those in **24** and **26** are 109.4 and 121.7°.

MNDO calculations on the bicyclic ions **22** and **23**, suggest even greater distortions of the CNC angles and a further lowering of the singlet, relative to the triplet state. Thus, together the present calculations support the growing opinion[13-15] that the H-abstraction products observed in the heterolysis of **21a** observed by Gassman[12] and others (for summaries, see ref 13) cannot be attributed to the intermediacy of the triplet nitrenium ion **23**.

Comparison of Nitrenium and Carbenium Ion Stabilities. Given the clear analogy between the reactivities of carbenium and singlet nitrenium ions, it is of interest to inquire into their relative inherent stabilities. Although such quantities cannot of course be unam-

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(73) Koser, G. F. *J. Chem. Soc., Chem. Commun.* **1973**, 461–462.

biguously defined, the energies of the following processes are illuminating:

$$\underset{261.3}{CH_3^+} + \underset{-11.0}{NH_3} \rightarrow \underset{-17.9}{CH_4} + \underset{332}{NH_2^+} \quad \Delta H = 64 \text{ kcal mol}^{-1}$$

$$\underset{221.8}{CH_3CH_2^+} + \underset{-5.5}{CH_3NH_2} \rightarrow \underset{-20.2}{CH_3CH_3} + \underset{278}{CH_3NH^+} \quad \Delta H = 42 \text{ kcal mol}^{-1}$$

$$\underset{191.8}{(CH_3)_2CH^+} + \underset{-4.4}{(CH_3)_2NH} \rightarrow \underset{-24.8}{(CH_3)_2CH_2} + \underset{244}{(CH_3)_2N^+} \quad \Delta H = 32 \text{ kcal mol}^{-1}$$

The experimental heats of formation from standard sources[61,67] are given below the individual species. The data for $CH_3CH_2^+$ are from Beauchamp and co-workers[74] and refer to the classical ion. The data for CH_3NH^+ and $(CH_3)_2N^+$ are theoretical estimates from this work. On this basis, the nitrenium ion (**1**) itself is significantly less stable than CH_3^+ presumably as a result of the required placement of the formal positive charge on the electronegative nitrogen. This difference is lowered considerably in the presence of electron-donating alkyl groups.

Conclusion

Ab initio molecular orbital calculations using RHF and UHF wave functions for the singlet and triplet states, respectively, and allowing for electron correlation using Moller–Plesset perturbation theory tend to overestimate the stabilities of the triplet states in nitrenium ions relative to the singlets. The error becomes progressively smaller at the MP4 level as the quality of the basis set is improved. For NH_2^+, a ground-state triplet, MP4/6-311+G-(3d2f,2p)//MP2/6-311+G(3d,2p) calculations with vibrational corrections at the MP2/6-31G(d,p) level gave a singlet–triplet energy difference just 2.3 kcal mol^{-1} greater than the experimental value.

Calculations using smaller basis sets, and in some instances electron correlation corrections only at the MP2 level, should therefore give an upper bound to the true singlet–triplet energy difference. Lower bounds to the true singlet–triplet energy separations were obtained by using the known value for NH_2^+ and the calculated energies of the appropriate isodesmic relationships.

On this basis the methylnitrenium (**2**) and pyrrolidine nitrenium ions (**24**) are predicted to have triplet and singlet ground states, respectively. The singlet–triplet separations in the piperidine nitrenium (**26**) and dimethylnitrenium ions (**15**) were predicted to be small and their ground-state multiplicities could not be unambiguously determined.

The heats of formation of both the singlet and triplet states of the methyl- and dimethylnitrenium ions were calculated to be substantially more positive than values derived from appearance potential measurements. Further, on the singlet surfaces neither was predicted to be a local minimum. Instead both were predicted to be transition states involving degenerate hydrogen migrations in the much more stable immonium ions. Thus, if the appearance potential measurements are correct, the nitrenium ions themselves cannot be involved in the corresponding fragmentation processes even as transient intermediates.

The reported generation of both nitrenium ions by charge reversal of the gaseous anions must lead to the ions in their triplet states, which are expected to have finite lifetimes. Thus, the triplet methylnitrenium ion is separated from the corresponding immonium structure by a substantial (46 kcal mol^{-1}) barrier, while the dimethylnitrenium ion is itself lower in energy than the related immonium structures.

The nitrenium ions are inherently less stable than the analogous carbenium ions. This difference is markedly reduced by alkyl substituents, which reduce the positive charge on the electron-deficient nitrogen atom. The overall energetics deduced at the ab initio level are remarkably similar to those obtained previously by use of MNDO semiempirical molecular orbital theory.

Acknowledgment. This work was supported by the Robert A. Welch Foundation (Grant N-1080). Many of the larger calculations were carried out on IBM 3081 and 3090 computers at the Los Angeles Scientific Center. We thank the IBM Corp. for access to these facilities under Grant RSP 1044. We are grateful to SMU for a generous allocation of computer time on the IBM 3081 at the Bradfield Computer Center where the remainder of the calculations were performed.

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(74) Schultz, J. C.; Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 3917–3927.