The Singlet–Triplet Gap of the Halonitrenium Ions NHX+, NX2+ and the Halocarbenes CHX, CX2 (X = F, Cl, Br, I)

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Ab initio studies at the MP4/6-311G(2df)//MP2/6-31G(d) level of theory using effective core potentials for Br and I predict, that halonitrenium ions NX_2^+ and NHX^+ (X = F, Cl, Br, I) have a ($^1A_1$) singlet ground state and a singlet–triplet gap between 57–12 for NX_2^+ and 8–4 kcal mol^{-1} (1 cal = 4.184 J) for NHX^+; a comparison of experimental and theoretical results of the isoelectronic carbenes shows that the theoretical level is quite reliable.

The singlet–triplet gap of methylene has extensively been studied, both theoretically[1] and experimentally.[2] Also the $^3B_1 < -^1A_1$ excitation energy of halogen substituted methylenes CF_2,[3–7] CCl_2,[3,6,7] CBr_2,[6,7] CHF,[3,4,7,8] $CHCl$,[3,4,7,8] $CHBr^{4,7,8}$ and CHI^4 was the subject of numerous studies. Much less is known about the isoelectronic nitrenium ions NX_2^+ and NHX^+ (X = F, Cl, Br, I). The only theoretical investigation of the singlet–triplet gap of halonitrenium ions is an earlier theoretical study of NF_2^+ and NHF^+.[9] NF_2^+ has been experimentally observed,[10] but the excitation energy has not been measured yet. There are no experimental studies of other halonitrenium ions known to us.

We now report theoretically predicted equilibrium geometries and the relative energy for the energetically lowest $^1A_1$ and $^3B_1$ states of the halonitrenium ions NX_2^+ and NHX^+ and the halocarbenes CX_2 and CHX (X = F, Cl, Br, I). The geometries were optimized using Møller–Plesset perturbation theory[11] terminated at second order (MP2) using the ECP by Hay and Wadt[12] for Br and I and the 6-31G(d)[13] all electron basis set for the other atoms. The minimal valence basis sets for Br and I are uncontracted and augmented by a set of d-type polarisation functions[14] *i.e.* the valence basis set is [21/21/1]. The energy second derivatives were calculated at this level of theory to predict the contribution of zero point vibrational energy (ZPE), which is scaled by 0.9.[15] Improved total energies are predicted at the MP4(SDTQ) level using uncontracted ECP valence basis sets augmented by two sets of d functions[14] and one set of f functions[16] for Br and I [111/111/11/1] in conjunction with a 6-311G(2d, f)[17] basis set for the other atoms. We will discuss the energies at this level of theory including the ZPE correction. All calculations were done using the Convex version of the GAUSSIAN 92 program series.[18]

The theoretically predicted energy differences between the ($^1A_1$) singlet state and the ($^3B_1$) triplet state for the carbenes and nitrenium ions in comparison with available experimental data and previously calculated results are shown in Table 1. The geometries are given in Table 2.

The nitrenium cation NH_2^+ is theoretically predicted to have a $^3B_1$ ground state, which is 33.5 kcal mol^{-1} lower in energy than the $^1A_1$ excited state. The experimentally

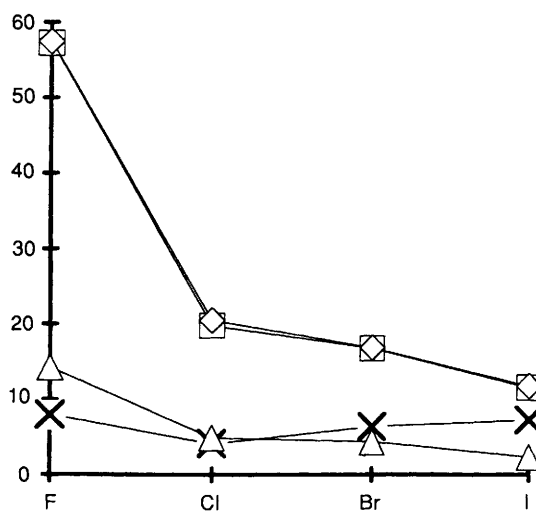Fig. 1 Theoretically predicted energy differences (kcal mol^{-1}) between the lowest lying $^1A_1$ and $^3B_1$ states: $\square$ = NX_2^+, × = NHX^+, $\lozenge$ = CX_2 and $\triangle$ = CHX

Table 1 Theoretically predicted and experimentally observed energy differences (kcal mol^{-1}) between the lowest lying $^1A_1$ and $^3B_1$ states; (negative values indicate, that the $^3B_1$ state is the ground state)

	MP2/6-31G(d)	MP4/6-311G(2df)	MP4/6-311G(2df)+ZPE	Exp.	Calc.[a] CCCI/DCCI	Calc.[b] TCSCF + CI	Calc.[c] DFT LDA, LDA/NL	Calc. (other)
CH_2	−14.1	−13.4	−12.9	−8.998, −9.023[d]	−9.0, −10.0		−12.22, −7.2	−9.1[e]
CF_2	53.1	57.6	57.6	56.7[f], >50[g]	57.5, 57.1,		55.8, 55.6	
CCl_2	15.6	20.2	20.5		25.9, 20.5		21.91, 23.75	
CBr_2	10.2	16.7	16.5				20.89, 22.41	7.7[h]
CI_2	2.6	11.5	11.2				15.73, 16.49	
CHF	11.3	14.3	14.3	14.7; 11.4; 8.1[g]	17.7, 14.5	13.2		
CHCl	2.0	4.8	4.8	<11.4[g]	9.3, 6.0	5.4		
CHBr	1.0	4.3	4.4	<9[g]		4.1		
CHI	−1.7	2.6	2.6	<9[g]				
NH_2^+	−34.1	−32.9	−33.5	−30.1[i], −22.8[j]				−33.2[k], −29.9[l], −45[m]
NF_2^+	46.6	57.8	57.3					33[m]
NCl_2^+	11.5	20.1	19.8					
NBr_2^+	4.9	17.1	16.3					
NI_2^+	−2.3	12.0	11.3					
NHF^+	1.9	8.7	8.1					−4[m]
$NHCl^+$	−1.0	4.6	4.1					
$NHBr^+$	−0.5	7.0	6.4					
NHI^+	−1.2	8.0	7.5					

[a] Ref. 3. [b] Ref. 8. [c] Ref. 6. [d] Ref. 2,26. [e] Ref. 20. [f] Ref. 5. [g] Ref. 4. [h] Ref. 7. [i] Ref. 19. [j] Ref. 27. [k] Ref. 28. [l] Ref. 29. [m] Ref. 9.

Table 2 Theoretically calculated and experimentally observed geometries; interatomic distances AB (Å) angles ω (°)

	Calc. MP2/6-31G(d)						Exp.					
	$^1A_1$			$^3B_1$			$^1A_1$			$^3B_1$		
	C/N-X	C/N-H	ω	C/N-X	XH	ω	C/N-X	C/N-H	ω	C/N-X	C/N-H	ω
CH_2		1.109	102.1		1.078	131.5		1.11[a]	102.4[a]		1.0748[b]	133.84[b]
CF_2	1.315		104.2	1.329		119.8	1.3035[c]		104.8[c]			
CCl_2	1.718		109.9	1.679		127.6	1.7157[d]		109.2[d]			
CBr_2	1.893		111.0	1.840		129.9	1.74[e]		114[e]	1.74[e]		150[e]
CI_2	2.105		112.6	2.034		132.3						
CHF	1.320	1.121	101.9	1.329	1.086	121.2	1.305[f]	1.138[f]	104.1[f]			
CHCl	1.697	1.110	102.9	1.670	1.082	125.8	1.696[g]	1.112[g]	101.4[g]			
CHBr	1.862	1.110	101.9	1.827	1.082	126.5						
CHI	2.068	1.111	101.3	2.018	1.084	128.2						
NH_2^+		1.049	108.3		1.034	151.1						
NF_2^+	1.258		107.6	1.270		124.8						
NCl_2^+	1.608		117.3	1.582		137.0						
NBr_2^+	1.771		118.9	1.734		140.4						
NI_2^+	1.946		122.1	1.902		147.5						
NHF^+	1.246	1.055	104.2	1.245	1.055	125.4						
$NHCl^+$	1.549	1.045	109.1	1.524	1.037	134.1						
$NHBr^+$	1.704	1.042	107.9	1.669	1.033	134.5						
NHI^+	1.877	1.040	108.0	1.830	1.029	136.1						

[a] Ref. 30. [b] ref. 31. [c] Ref. 32. [d] Ref. 33. [e] Ref. 34. [f] Ref. 35. [g] Ref. 36.

determined $^1A_1 \leftarrow {}^3B_1$ excitation energy is 30.1 kcal mol^{-1},[19] 3.4 kcal mol^{-1} less than the calculated value. The singlet–triplet gap of NH_2^+ is larger than that of CH_2. The $^1A_1 \leftarrow {}^3B_1$ excitation energy of methylene is 9.0 kcal mol^{-1},[2,20–22] the calculated value is 12.9 kcal mol^{-1}. The difference between the calculated and experimental values is due to the one-configurational treatment of the singlet state.[7,23]

A ground state with $^1A_1$ symmetry is theoretically predicted for NF_2^+, 57.3 kcal mol^{-1} lower in energy than the $^3B_1$ excited state. This is nearly the same value for the $^3B_1 \leftarrow {}^1A_1$ excitation energy as calculated for CF_2 (57.6 kcal mol^{-1}). Since the latter result is in good agreement with the experimentally determined singlet–triplet gap (56.7 kcal mol^{-1}),[5] we think that the theoretical value for NF_2^+ is quite reliable. Also for the other dihalonitrenium ions NX_2^+ are the calculated $^3B_1 \leftarrow {}^1A_1$ excitation energies very close to

the theoretical results for the corresponding dihalocarbenes CX_2 (Table 1). The singlet–triplet gap becomes smaller for NX_2^+ and CX_2 in the order X = F >> Cl > Br > I. All halogen substituted nitrenium ions and carbenes are predicted to have a ground state with $^1A_1$ symmetry.

The singlet–triplet gap of the monohalogen substituted nitrenium ions NHX^+ is calculated as slightly different to the corresponding CHX molecules (Table 1). While the $^3B_1 \leftarrow {}^1A_1$ excitation energy for CHX becomes smaller in the same order as predicted for CX_2, the nitrenium ions NHX^+ are calculated with higher excitation energies for NHI^+ (7.5 kcal mol^{-1}) > $NHBr^+$ (6.4 kcal mol^{-1}) > $NHCl^+$ (4.1 kcal mol^{-1}). No experimental data for the $^3B_1 \leftarrow {}^1A_1$ excitation energy of halonitrenium ions are known to us. Because the calculated values for the halocarbenes are in good agreement with experiment and previous high-level theoret-

ical studies (Table 1), we expect the calculated singlet–triplet gaps for the nitrenium ions to be rather accurate.

The calculated geometries for the nitrenium ions and the carbenes are shown in Table 2. Because the agreement of the theoretical and experimental values for the carbenes is generally quite good, we think that the results for the nitrenium ions are reliable. The bending angles X–N–H and X–N–X in the nitrenium ions are always larger than the corresponding X–C–H and X–C–X angles in the carbenes. For both molecule types holds that the $^3B_1$ state has a significantly larger bending angle than the $^1A_1$ state. These trends can be explained using Mulliken–Walsh[24] type diagrams.[25]

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