Heteroatom Chemistry
Volume 5, Number 2, 1994

Molecular and Electronic Structure of Bromamines

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Received 4 December 1993

ABSTRACT

Molecular and electronic structures and properties of NH_2Br, $NHBr_2$, and NBr_3 have been studied using ab initio calculations at the Hartree–Fock (HF) and MP2 levels with the aim of complementing very scarce experimental information available for the title molecules. The properties and molecular structures of bromamines are discussed in relationship to other haloamines (fluor- and chloramines).

INTRODUCTION

The bromamines NH_xBr_{3-x} ($x = 0$–2) are rather unstable molecules and have not yet been isolated in a pure form. They have been identified, however, in solution and in the gas phase and their electronic structures studied with photoelectron spectroscopy [1–3]. NBr_3 has not been isolated, although its existence was postulated. Semiempirical MO methods (AM1 and PM3) have suggested values for its enthalpy of formation (in the gas phase) and its geometry [4]. These molecules thus represent good candidates for theoretical analysis that can complement experimental investigations, which is the aim of the present work.

CALCULATIONS

A Gaussian 92 ab initio MO package [5] has been used to obtain molecular properties. The standard 6-31G(d, p) basis set was used for N and H atoms, while the Br atom was described by an effective core potential basis set (including d polarization functions) [6]. All molecular geometries were fully optimized at HF and MP2 levels and corresponded to local minima on potential surfaces, as indicated by the absence of imaginary values for harmonic vibrational frequencies. The optimized geometries of all molecules were found to be nonplanar. The vibrational zero-point energy (ZPE) corrections were included in calculations of inversion barriers and enthalpies of formation (ΔH_f°). Ionization energies (E_i) for the NBr_3 were estimated from the relationship $E_i = 0.799\epsilon_{SCF} + 2.004$ obtained as a linear fit of experimental E_i [1–3] vs. HF SCF eigenvalues for NH_2Br and $NHBr_2$. The NBr_3 values thus obtained are presented in Table 1.

The inversion barrier heights (E_{inv}) were obtained by subtracting total MP4(SDTQ) energies (corrected for ZPE) for the planar and nonplanar geometries optimized at the MP2 level (Table 2).

RESULTS AND DISCUSSION

The results of calculations are presented in Tables 1 and 2 and Figure 1. The assignment and interpretation of photoelectron spectra of NH_2Br and $NHBr_2$, reported previously [1–3], are fully consistent with our work and the only comment we wish to make is to emphasize the points made earlier by So [7]. The HOMO orbital in bromamines cannot, in our view, be described as a nitrogen lone pair with some π antibonding halogen interaction, but (if anything) rather the reverse. The N 2p AO characters in NH_2Br, $NHBr_2$, and NBr_3 HOMO orbitals amount to ca. 20, 25, and 30%, respectively, thus indicating only a small increase in "nitrogen lone pair character" upon bromination.

Another interesting result of this work is the study of the inversion process. The meaningful analysis of such a process must consider the effects of electron correlation. The barrier height (E_{inv}) in-

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1042-7163/94/$5.00 + .25

TABLE 1 Equilibrium Bond Lengths and Angles (r, ϑ), predicted ionization energies (for NBr_3; E_i), and Dipole Moments (μ) and ΔH_f° (g, 298.15 K)[a]

	r, ϑ/pm, deg				μ/D		
Molecule	r, ϑ	*HF*	*MP2*	E_i/eV	*HF*	*MP2*	ΔH_f°/kJ mol^{-1}
NH_2Br	NH	100.16	101.93		2.1	2.2	100.04(73.2)
	NBr	189.40	192.02				
	<HNH	107.44	105.20				
	<HNBr	105.06	103.05				
$NHBr_2$	NH	100.23	102.64		1.55	1.54	238.21(192.3)
	NBr	188.91	193.97				
	<HNBr	104.53	100.86				
	<BrNBr	113.08	110.94				
NBr_3	NBr	189.35	196.84	10.25(e)	1.02	1.15	374.51(311.4)
	<BrNBr	111.28	107.43	10.89(a_2)			
				11.26(e)			
				12.01(e)			
				14.78(a_1)			
				15.08(e)			

[a]numbers in parentheses correspond to values estimated via bond enthalpies of NF_3, NOF, NOBr, and NH_3 [9].
1D = 3.335×10^{-30} cm

TABLE 2 Normal Modes of Vibration and Inversion Barriers (E_{inv}) in Bromamines[a]

	Frequency (symmetry)/cm^{-1}				
Molecule	*HF*		*MP2*	*Mode*	E_{inv}/kJ mol^{-1}
NH_2Br	3424	a″	3639	ν_{NH}	45.4
	3328	a′	3522	ν_{NH}	
	1536	a′	1625	δ_{NH2}	
	1087	a″	1147	δ_{HNBr}	
	974	a′	1069	δ_{HNBr}	
	572	a′	605	ν_{NBr}	
$NHBr_2$	3371	a′	3490	ν_{NH}	67.8
	1266	a″	1280	δ_{HNBr}	
	860	a′	978	δ_{HNBr}	
	643	a″	614	ν_{NBr}	
	503	a′	509	ν_{NBr}	
	174	a′	175	δ_{NBr2}	
NBr_3	660	e	566	ν_{NBr}	88.5
	385	a_1	426	ν_{NBr}	
	214	a_1	217	δ_{NBr}	
	155	e	151	δ_{NBr}	

[a]The correction factor of 0.89 was applied to zero-point energies and vibrational frequencies calculated at HF level.

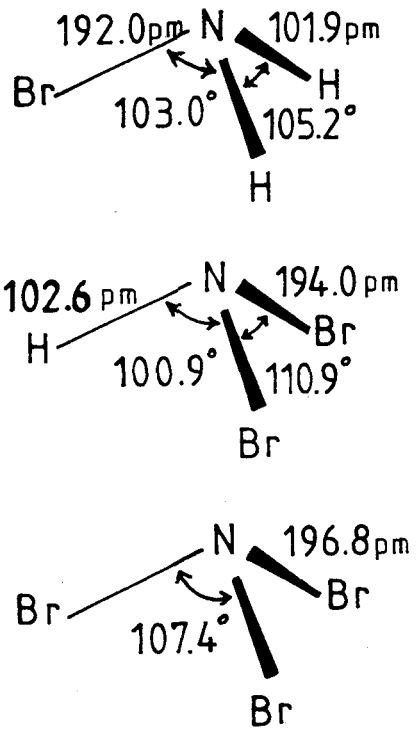

FIGURE 1 Molecular structures of bromamines optimized at MP2/6-31G (d, p) level.

creases upon bromination (Table 2). A study of pyramidal-planar transitions in the NH_3F_{3-n} and PH_3F_{3-n} (n = 0–2) series has been reported [8]. The general trends observed were similar to ours, especially the E_{inv} increase with halogenation. Schmiedekamp et al. [8] suggested that the increase in nitrogen atom 2s character in the HOMO with halogenation may be the source of barrier increase. Absolute values of barrier heights will of course depend on the level of theory employed in the calculations, but it seems that the inversion barrier heights increase in the sequence: $NH_3 < NH_xBr_{3-x} < NH_xF_{3-x} < PH_xF_{3-x}$; i.e., the more electronegative the ligands and the less electronegative the central atoms, the higher the barrier. Bromamines are unstable molecules, which makes

TABLE 3 HOMO Ionization Energies (E_i/eV) for Haloamines[a]

n	$NH_{3-n}F_n$	$NH_{3-n}Cl_n$	$NH_{3-n}Br_n$
0	10.82	10.82	10.82
1	11.62	10.52	10.18
2	12.38	10.56	10.1
3	13.83	10.69	10.25[a]

[a]Estimated value

measurement of basic thermodynamic parameters, such as ΔH_f°, difficult. We used a system of three hypothetical isodesmic reactions,

$$3NOBr + NH_3 \Rightarrow NBr_3 + 3HNO$$
$$NOBr + NH_3 \Rightarrow NH_2Br + HNO$$
$$2NOBr + NH_3 \Rightarrow NHBr_2 + 2HNO$$

to estimate the ΔH_f° values for bromamines (Table 1). The ΔH_f° values for HNO, NOBr, and NH_3 were taken from standard tables [9], and reaction enthalpies were calculated from molecular MP4 (SDTQ)/MP2 total energies corrected for ZPE. The results clearly indicate that NBr_3 is thermodynamically very unstable, which is a reason why it has not been isolated so far.

CONCLUSIONS

It is important to compare our results with those obtained for fluoramines and chloramines. Several molecular and electronic structure parameters may be compared: HOMO ionization energy, ΔH_f°, E_{inv}, and nitrogen–halogen bond lengths (N–X). Unfortunately, not all the values were measured experimentally owing to instability of some members of the haloamine series. The ionization energies obtained from photoelectron spectra [1–3,10,11] are summarized in Table 3. Only in fluoramines does an inductive shift toward higher binding energies occur with increasing fluorination. In chloramines and bromamines, the variations are very small, although it appears that, as expected, the monohaloamine has the lowest and the trihaloamine the highest HOMO ionization energy.

The ΔH_f° values and inversion barriers for $NH_{3-n}X_n$ (N = 0–3; X = F, Cl, Br) were mostly obtained via different quantum chemical methods [12–15]. Direct comparisons of absolute values would thus be misleading and are not tabulated. The trends show, however, that ΔH_f° and E_{inv} values increase in the sequence $NH_{3-n}F_n < NH_{3-n}Cl_n < NH_{3-n}Br_n$ (for the same n). Also, all haloamines seem to be "stiffer" molecules than ammonia; i.e., they have larger inversion barriers. Finally, let us compare the N–X bond lengths. The experimental values vary little (<0.002 nm) within each haloamine series. This is further evidence of the fact that the N–X bond is rather weak, as already indicated from large and positive bond enthalpies. HOMO character can also be expected not to vary much in chlor- and bromamines, since E_i's do not change significantly. In fluoramines, on the other hand, the HOMO changes from a slightly antibonding (in NH_2F and NHF_2) to a slightly bonding nature [10].

Haloamines, and chloramines in particular ($NH_{3-n}Cl_n$), are good oxidizing agents for both organic and inorganic species. Chloramines have been used in disinfection of drinking water supplies for some time, where their reactivity toward organic and microbiological contaminants has been found to be superior to chlorine [16]. Study of oxidation of hydrogen sulfite [17] provided a clear indication that the reactivity depends on the degree of halogenation, NCl_3 being the most and NH_2Cl the least effective oxidizing agent.

NOTE ADDED IN PROOF

After this article was accepted for publication, a review appeared:

I. C. Tornieporth-Oetting, T. M. Klapötke, *Comments Inorg. Chem., 15*, 1994, 137. The ab initio geometry data for NBr_3 reported in that review are in good agreement with ours, whereas the ΔH_f° values are not. The value reported (ca. +280 kJ mol^{-1}) seems to agree better with our estimate based on bond enthalpies (+311.4 kJ mol^{-1}).

ACKNOWLEDGMENT

This work was supported by the research grant RP900624 from The National University of Singapore.

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