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Ab initio calculations of the structure and inversion barriers of chloramide, H_2NCl, and N-chloro-N-methylmethanamine, $(CH_3)_2NCl$

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Abstract

The ab initio geometries of the equilibrium forms and transition states of the amino nitrogen inversion for H_2NCl and $(CH_3)_2NCl$ were calculated by the RHF and MP2 methods with the use of the 6-31G*, 6-31G**, and 6-311G** basis sets. The inclusion of electron correlation at the MP2 level increases the barrier height estimates and yields a somewhat better agreement between the calculated and experimental geometric parameters. The obtained data do not agree with the idea that a larger inversion barrier is associated with a more pyramidal configuration of the nitrogen atom. Methyl substituents flatten the nitrogen configuration in $(CH_3)_2NCl$. The barrier heights calculated by the MP2 method are 10.2 kcal mol^{-1} for H_2NCl and 12.6 kcal mol^{-1} for $(CH_3)_2NCl$, or 9.3(1.0) and 12.0 (1.0) kcal mol^{-1}, respectively, when zero-point corrections are made. © 1997 Elsevier Science B.V.

1. Introduction

It is generally recognized that electronegative ligands, like the chlorine atom, should increase the inversion barrier of the amino group in substituted ammonia and favour the larger pyramidality of the amine nitrogen bond configuration [1–3]. Up to now, however, this influence has not been studied sufficiently.

In the case of the simplest chloramines, the above is in the first place related to the problem of the amino group inversion barrier. For N-chloro-N-methylmethanamine (dimethylchloramine), $(CH_3)_2NCl$, both experimental and theoretical data of this kind

are lacking. As to chloramide, H_2NCl, the experimental values of the inversion barrier estimated from the analyses of its microwave and high-resolution infrared spectra (approx. 12.6 kcal mol^{-1} [4,5]) exceed the ab initio calculated barrier heights by 3–4 kcal mol^{-1} [6]. The largest deviation from the experimental estimate corresponds to the correlated MP2 level calculations employing the triple-zeta basis set augmented with d and f polarization functions (TZ2P + f), which is the most enlarged basis of all those used in Ref. [6].

In this paper, we report some new ab initio calculation results for H_2NCl and $(CH_3)_2NCl$ molecules. The structure of their equilibrium (ES) and transition (TS) states of nitrogen inversion and barrier heights have been obtained by the RHF and MP2 methods with the

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standard 6-31G*, 6-31G** and 6-311G** basis sets. The calculations were carried out using the GAUSSIAN 92 series of programs [7] on a VAX-VMS-6.1 computer at the Universidad Complutense de Madrid.

2. Results and discussion

2.1. Geometrical parameters of chloramide and N-*chloro*-N-*methylmethanamine* in the equilibrium and transition states

The comparison between the results of our calculations that were carried out using various standard basis sets, and some published data, shows that only the inclusion of electron correlation has a decisive influence upon the geometric parameter values obtained for H_2NCl and $(CH_3)_2NCl$ (Table 1, Table 2 and Table 3). This is characteristic of both equilibrium forms and transition states of inversion for these two molecules. However, the effect of electron correlation for transition states is less essential. It gives information only on the NCl, NH, and methyl CH bond lengths (they increase by approx. 0.018 Å) and practically does not change the values of the other parameters.

For the equilibrium states of the molecules under consideration, the MP2 level estimates of the CN and NH bond lengths, valence angles, and N atom pyramidality show good agreement with the experimental microwave data [8,9]. As to the equilibrium NCl bond length, the RHF and MP2 calculations give, on the whole, lower and upper limits, respectively. The optimum H_2NCl structure calculated at the MP2/TZ2P level [6] has the best conformity with the results of the microwave study [8]. At the same time, it should be noted that the MP2 calculation, in which the triple-zeta plus polarization (TZ2P) basis set was enlarged with *f*-functions having exponents of 1.0 and 0.7 for nitrogen and chlorine, respectively, leads to a sharp shortening (by approx. 0.02 Å) of the NCl bond distance, as well as to some flattening of the nitrogen bond configuration in H_2NCl (Table 1). The obtained estimate of the equilibrium NCl bond length (1.735 Å [6]) is considerably lower than the experimental value ($r_s = 1.7480(1)$ Å [8]). But the latter must be very close to the equilibrium r_e value, since a major part of the vibrational effects are cancelled in

the r_s-structure determination [10]. Therefore, the difference between the MP2/TZ2P + f and r_s values, equal to 0.013 Å, seems excessive. It is rather hard, if one does not know all the details, to define the true causes of this discrepancy, when a theoretically higher calculation level yields worse results. We assume that, in this case, the reason for the deterioration most likely lies in the inadequacy of the *f*-function inclusion in the basis set.

According to the experimental data [8,9], the NCl bond distance remains practically unchanged in both compounds. Durig et al. [9] emphasize that such insensitivity of the NCl bond concerning the substitution of the hydrogens with methyl groups is rather surprising, because the inductive effect produced by the methyl substituents upon the corresponding carbon compounds results in a significant elongation of the CCl bond (1.803(2) Å in $(CH_3)_3CCl$ [11] against 1.7812(1) Å in H_3CCl [12]). Our calculations show that the equilibrium NCl bond length in $(CH_3)_2NCl$ must also be approx. 0.01 Å greater than in H_2NCl.

The peculiarities of the molecular models chosen in Ref. [9] for geometry refinement are significant with respect to the experimental estimates of the NCl bond length in $(CH_3)_2NCl$ (Table 3). Both models used differ only in the restrictions introduced concerning the parameters of the methyl groups. In the case of Model I, their conformations were fixed, whereas in Model II, the methyl groups were assumed to have "local" C_{3v} symmetry, but the symmetry axes were allowed to deviate from the NC bond directions and rotate about these bonds. Our calculation testifies to the insufficiency of each of these approaches separately. The $(CH_3)_2NCl$ molecule has unsymmetrical methyl groups, in which the CH bond trans-arranged relative to the nitrogen lone pair of electrons is longer than the other two CH bonds. The NCH valence angle which corresponds to the longest CH bond is 4–6° larger than the other two NCH angles. Thus, each methyl group has an upward tilt towards the lone pair.

As we have already noted, for a series of mono- and dinitramines [13], the passage from primary (or secondary) to tertiary amine derivatives by way of introducing a methyl substituent, which is bulkier than a hydrogen atom, flattens the amine nitrogen configuration noticeably. An analogous trend also appears on going from H_2NCl to $(CH_3)_2NCl$ (Table 1 and Table 3).

Table 1
Comparison between ab initio computed equilibrium geometry and experimental data for chloramide

Parameter	Hartree–Fock calculations				MP2 calculations					Microwave experiment [8][a]	
	[4]	This work			This work			[6]	[6]	r_s	r_0
	4-31G*	6-31G*	6-31G**	6-311G**	6-31G*	6-31G**	6-311G**	TZ2P	TZ2P+f		
Bond lengths (Å)											
NCl	1.731	1.732	1.731	1.735	1.755	1.754	1.753	1.754	1.735	1.7480(1)	1.7522
NH	1.002	1.002	1.002	1.001	1.022	1.018	1.018	1.013	1.014	1.017(5)	1.019
Bond angles (°)											
ClNH	105.4	105.6	105.6	105.3	104.5	104.2	104.6	103.8	104.5	103.7(4)	103.6
HNH	107.3	107.4	107.7	107.3	105.7	105.4	105.1	105.9	106.5	107.2	107
Angle between bond and plane (°)											
NCl/HNH	63.4	63.1	62.8	63.5	65.6	66.1	65.6	66.7	65.2	66.5	66.7
Dipole moment (D)											
μ	2.20	2.30	2.28	2.29	2.36	2.34	2.35	–	–	–	–

[a] Experimental uncertainties are given in parentheses in units of the last digit.

Table 2
Calculated geometric parameters of chloramide in the planar transition state of nitrogen inversion

Parameter	Hartree–Fock calculations			MP2 calculations				
	This work			This work			[6]	[6]
	6-31G*	6-31G**	6-311G**	6-31G*	6-31G**	6-311G**	TZ2P	TZ2P + f
Bond lengths (Å)								
NCl	1.675	1.676	1.679	1.688	1.686	1.689	1.689	1.675
NH	0.989	0.987	0.987	1.002	0.997	0.998	0.993	0.996
Bond angles (°)								
ClNH	117.8	117.6	117.5	117.8	117.9	117.6	117.6	117.8
HNH	124.4	124.8	125.1	124.4	124.3	124.8	124.8	124.4
Dipole moment (D)								
μ	1.69	1.69	1.67	1.70	1.70	1.68	–	–

The pyramidal inversion in the considered chloramines is accompanied by a shortening of the N atom bonds (Tables 1–3). According to our calculations, the NCl bond is the most sensitive to the motion, its length decreasing by approx. 0.06 Å in the planar transition states of both molecules. It is also significant that the CNC or HNH angle widening, which accompanies the decrease in the nitrogen atom pyramidality, is 1.5–2 times greater than that for the ClNC or ClNH angles.

2.2. Inversion barriers in chloramide and N-chloro-N-methylmethanamine

The latest experimental estimate of the inversion barrier height for H_2NCl (12.6 kcal mol^{-1} [4]) was derived by fitting the observed NH_2 wagging-inversion vibrational levels to the model double-minimum potential function. This function uses only the NH_2 wagging vibration as a coordinate. However, as will be shown in our next publication [14], the NH_2 wagging vibration is to some extent mixed with the HNH bending one. Their interaction may be the origin of the above mentioned discrepancy between the experimental and calculated values. The recent ab initio study of the inversion–CNC bending interaction in dimethylamine [15] confirms this possibility. According to the calculation, a good description of the inversion frequencies requires the employment of a two-dimensional model, and the inclusion of the coupling terms in the Hamiltonian causes a 30 cm^{-1} shift of the transition band position.

Ab initio calculations can directly yield barrier heights as the energy difference between two stationary points of potential energy surface. The full optimization of the geometric parameters of a molecule makes it possible to consider the effects of structure relaxation. The principal issue is to establish which calculation methods provide reasonable reliability. In Table 4, a series of our calculations of increasing quality together with ab initio results from other sources and experimental data are presented to estimate the ability of the used theory levels to provide accurate inversion barriers for H_2NCl and $(CH_3)_2NCl$.

First of all, it must be noted that the inclusion of electron correlation via second-order Møller–Plesset perturbation theory is systematically revealed in the increase of the calculated inversion barrier height. This increase is especially noticeable in the case of $(CH_3)_2$ NCl, where it reaches 3 kcal mol^{-1}. Upon basis set expansion, the estimates of the barrier height in H_2NCl gradually decrease, whereas a fairly weak opposite trend is possible for $(CH_3)_2NCl$. In the case of the MP2 calculations of H_2NCl, the augmentation of the TZ2P basis set with polarization f-functions causes a relatively sharp lowering of the estimate of the inversion barrier height. Our scepticism concerning the results of the MP2/TZ2P + f optimization of geometric parameters for H_2NCl in Ref. [6] (see above, Section 2.1) confirms doubts about the adequacy of the barrier height calculation as well.

Experience in carrying out ab initio calculations shows that the simplest correlated calculations by the MP2 method appear to describe energy changes for various intra- and intermolecular reactions accurate within ± 1 kcal mol^{-1} compared with both higher

Table 3
Comparison between ab initio computed geometric parameters of $(CH_3)_2NCl$, in equilibrium conformation (C_s) and in the transition state of nitrogen inversion (C_{2v}), and experimental data

Parameter	RHF/6-31G**		RHF/6-311G**		MP2/6-31G*		MP2/6-31G**		MP2/6-311G**		Microwave experiment C_{2v}, r_0 [9]	
	C_s	C_{2v}	C_s	C_{2v}	C_s	C_{2v}	C_s	C_{2v}	C_s	C_{2v}	Model I	Model II
Bond lengths (Å)												
NCl	1.741	1.692	1.741	1.692	1.764	1.704	1.764	1.704	1.761	1.702	1.742(2)	1.749(1)
CN	1.453	1.435	1.453	1.436	1.465	1.438	1.463	1.436	1.462	1.436	1.473(1)	1.470(1)
CH	1.089	1.087	1.090	1.088	1.100	1.099	1.095	1.094	1.100	1.099	1.116(4)	1.094(2)
CH'	1.084	1.083	1.085	1.083	1.093	1.093	1.089	1.088	1.093	1.093	1.083(6)	
CH"	1.081	1.087	1.081	1.088	1.090	1.099	1.086	1.094	1.091	1.099	1.091(3)	
Bond angles (°)												
ClNC	109.2	116.4	109.1	116.3	107.7	116.2	107.6	116.3	107.6	116.3	108.4(1)	108.0(1)
CNC	113.0	127.3	112.9	127.3	110.9	127.6	110.7	127.4	110.3	127.4	110.7	111.0
NCH	113.0	111.9	112.9	111.9	113.2	112.2	113.1	112.3	112.9	112.3	108.8(16)	112.6
NCH'	107.3	107.9	107.4	107.9	106.8	107.4	106.8	107.3	107.0	107.3	108.4(6)	108.1
NCH"	109.5	111.9	109.5	111.9	109.0	112.2	109.1	112.3	109.3	112.3	109.7(9)	105.6
Dihedral angles (°)												
HCNCl	−62.8	−61.0	−62.6	−61.0	−61.2	−61.2	−60.9	−61.2	−60.7	−61.2	–	–
HCNC'	58.9	119.0	58.9	119.0	56.3	118.8	56.4	118.8	56.4	118.8	–	–
H'CNCl	176.9	180.0	177.1	180.0	178.4	180.0	178.8	180.0	178.9	180.0	–	–
H'CNC'	−61.4	0.0	−61.5	0.0	−64.1	0.0	−63.9	0.0	−64.0	0.0	–	–
H"CNCl	59.3	61.0	59.3	61.0	60.8	61.2	61.1	61.2	61.0	61.2	–	–
H"CNC'	−179.1	−119.0	−179.2	−119.0	−181.7	−118.8	−181.6	−188.8	−181.9	−118.8	–	–
Angle between bond and plane (°)												
NCl/CNC	53.5	0.0	53.7	0.0	57.7	0.0	57.9	0.0	58.1	0.0	56.3	56.9
Dipole moment (D)												
μ	2.26	1.98	2.33	2.06	2.36	1.98	2.38	1.99	2.43	2.06	–	–

Table 4
Calculated energies and inversion barriers for chloramide and N-chloro-N-methylmethanamine

Method	Calculated energies (a.u.)		Barrier height (kcal mol^{-1})	ΔZPE[a] (kcal mol^{-1})
	Equilibrium state	Transition state		
Chloramide				
RHF/4-31G*[b]	–	–	12.48	–
RHF/6-31G*	−515.041564	−515.025822	9.88	−1.31
RHF/6-31G**	−515.048748	−515.034518	8.93	−1.20
RHF/6-311G**	−515.086823	−515.072081	9.25	–
RHF/TZP[c]	−515.096215	−515.082861	8.38	–
CISD/TZP//RHF/TZP[c]	−515.477794	−515.463557	8.93	–
MP2/6-31G*	−515.337561	−515.320131	10.94	−0.98
MP2/6-31G**	−515.356378	−515.339682	10.48	−0.88
MP2/6-311G**	−515.411336	−515.395493	9.94	−0.78
MP2/TZ2P[c]	−515.538545	−515.522495	10.07	−0.93
MP2/TZ2P + f[c]	−515.597173	−515.582944	8.93	–
MP2/TZ2P + f(d)[c]	−515.731378	−515.717312	8.83	–
Experiment[b]	–	–	12.58	–
N-chloro-N-methylmethanamine				
RHF/6-31G**	−593.112194	−593.096895	9.60	−0.82
RHF/6-311G**	−593.162731	−593.147119	9.80	–
MP2/6-31G*	−593.662310	−593.642327	12.54	–
MP2/6-31G**	−593.710320	−593.690513	12.43	–
MP2/6-311G**	−593.790154	−593.769787	12.78	–

[a] Zero-point energy correction [14,16].
[b] See Ref. [4].
[c] See Ref. [6].

level computations and experimental data [17–19]. Therefore, without taking zero-point corrections into account, the inversion barriers of 10.2(1.0) and 12.6(1.0) kcal mol^{-1} for H_2NCl and $(CH_3)_2NCl$, respectively, may be estimated from the calculations performed.

The ab initio calculations of the harmonic frequencies for the equilibrium and transition structures of H_2NCl (at the RHF and MP2 levels [14]) and of $(CH_3)_2NCl$ (at the RHF level [16]) allow the theoretical zero-point energies and, consequently, corrections to the barriers (ΔZPE, Table 4) to be obtained. With the use of appropriate scale factors [14,16], the modified ΔZPE values of − 0.9 kcal mol^{-1} for H_2NCl and − 0.6 kcal mol^{-1} for $(CH_3)_2NCl$ have been found, which finally yield the inversion barriers of 9.3(1.0) and 12.0(1.0) kcal mol^{-1}, respectively. The value that we have obtained for chloramide is approx. 3 kcal mol^{-1} lower than the experimental barrier reported by Hamada et al. [4].

It is interesting that for H_2NCl, with its more pyramidal equilibrium structure, a smaller inversion barrier height was obtained in comparison with the one for $(CH_3)_2NCl$, which has a more flattened equilibrium geometry (Table 1, Table 3, and Table 4). It is widely accepted that the magnitude of inversion barriers in amines is, at least in part, a function of nitrogen atom bond angles [1]. Our data do not agree with this conclusion. On the other hand, they do corroborate that the influence of an electronegative Cl-substituent leads to a practically double increase in the barrier height of amino nitrogen inversion compared with ammonia (5.8 kcal mol^{-1}, according to the experimental data [20,21]). Unlike our ab initio data for chloramide, the RHF/6-31G* and MP2/6-31G* calculations for ammonia slightly overestimated its inversion barrier height (6.5 and 6.6 kcal mol^{-1}, respectively [22]).

Acknowledgements

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