Ab initio MO STUDY OF PROTONATION OF CARBAMIC ACID, METHYL CARBAMATE AND METHYL N-METHYLCARBAMATE

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Received October 5th, 1987
Accepted November 6th, 1987

The *ab initio* SCF method was applied to the protonation of the carbonyl group in carbamic acid and its methyl derivatives, viz. methyl carbamate and methyl N-methylcarbamate.Complete geometry optimization was accomplished for these compounds and their protonated species using the MINI-1, 3-21G, and 6-31G* bases and the proton affinities were calculated at the MINI-1, 3-21G, 6-31G*, and 6-31G** levels. 2nd and 3rd order Moller–Plesset perturbation calculations were also performed for examining the effect of the correlation energy on the calculated protonation energies. The carbonyl protonation energies were found to increase in order carbamic acid < methyl carbamate < methyl N-methylcarbamate. The absolute values of calculated gas phase proton affinities depend on the basis used and way of evaluating the correlation energy. The results are discussed with respect to the theoretical proton affinities of structurally related amides and to related available theoretical gas phase proton affinities.

Various physico-chemical parameters of small molecules can be calculated nowadays with an accuracy commensurable with the experiment[1]; so, structures and properties that, because of experimental problems, do not lend themselves to examination by contemporary experimental techniques, can be successfully studied by *ab initio* calculations[2]. In this relation, we have applied the ab initio SCF theory at various levels to the study of the geometry, rotational barriers and hydrogen bonds in carbamic acid and its alkyl and aryl derivatives[3,4].

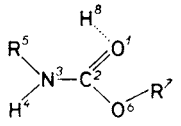
The present work is a theoretical study of the protonation of the carbonyl group in carbamic acid and of the effect of substitution consecutively to methyl carbamate and methyl N-methylcarbamate on the protonation energy. The effect of protonation on the optimized geometries of these molecules is also investigated.

Experimental X-ray geometries are only available for methyl carbamate[5] and ethyl carbamate[6], gas phase proton affinity has been determined[7] for ethyl N,N--dimethylcarbamate.

THEORETICAL

Geometries of carbamic acid, methyl carbamate, and methyl N-methylcarbamate and of their cations have been totally optimized by using the gradient optimization

method[8] and the MINI-1 (refs[9,10]), 3-21G (ref.[11]), and 6-31G* (ref.[12]) bases. In view of the fact that the X-ray structure of the carbamate >N—COO— group is practically planar[13], the C_s symmetry was considered during the optimization of the geometry of both the neutral and protonated forms of the compounds studied. Our calculations[3] revealed that the carbamic acid conformer with the intramolecular OH···O hydrogen bond and the metyl N-methylcarbamate conformer with the *trans* arrangement of the NH—C=O fragment (Scheme 1) are the energetically more stable ones; only these conformers are therefore treated in the present work. Since protonation of the carbonyl group can be both *cis* and *trans* with respect to the nitrogen atom, the structures of the two isomeric cations were determined at the MINI-1 level. For carbamic acid, protonation at the nitrogen atom was also studied for a comparison.



R = H, CH_3

SCHEME 1

The proton affinities of the bases B were calculated as the negative values of the differences E_p between the total energies of base B and its cation BH^+,

$$E_p = E_B - E_{BH^+}, \qquad (I)$$

for the exothermal reaction

$$B + H^+ \rightarrow BH^+. \qquad (A)$$

The MINI-1, 3-21G, 6-31G*, and 6-31G** bases[12] were employed, the 6-31G* optimized geometries being used for the 6-31G** calculations. The correlation energies were calculated by means of the second (MP2) and third (MP3) order Moller–Plesset perturbation theory[14–16]. The GAUSSIAN 80 program[17] was used for all calculations.

RESULTS AND DISCUSSION

Proton Affinities

The proton affinities for the carbonyl protonation, calculated with the four bases for three different geometries, along with the PM2/6-31G* proton affinities, are given in Table I. Since protonation of the C=O group can occur in the *cis* as well as *trans* position with respect to the nitrogen atom (Scheme 1), the structures of the

two isomers were first determined for the three compounds by using the MINI-1 basis; for carbamic acid and methyl carbamate, the *cis* isomers were found more stable (by 7·8 and 8·5 kJ mol^{-1}, respectively), whereas for methyl N-methylcarbamate the *trans* isomer emerged as the more stable, though by as little as 2·1 kJ mol^{-1}.

Table I demonstrates that the absolute values of the proton affinities depend on the basis employed. The highest values were obtained with the minimal MINI-1 basis set. The data derived from calculations with the higher-quality 6-31G* basis, containing polarization functions, were only 4–6% lower. The values from the MINI-1 calculations are anyway better than those from calculations with the minimal STO-3G basis in view of the fact that, e.g., the STO-3G data for the C=O protonation of the structurally related formamide are as much as 25% higher than the 6-31G* data[18]. Thus, even though the MINI-1 proton affinities are somewhat overestimated, this overestimation is of minor value and hence, the error associated with the use of this basis for the calculation of the preferred proton positions in the vairous complexes is reasonably low. For verifying this conclusion, the protonation at the nitrogen atom was also studied for carbamic acid. The protonation energies obtained using the MINI-1, 3-21G, and 6-31G* bases are 30–45% lower than the corresponding proton affinities calculated for the carbonyl oxygen. The same stability order has been found by Lee and coworkers during their MNDO study of the protonation of methyl carbamate[19].

Comparison of the proton affinities in carbamic acid, methyl carbamate and methyl N-methylcarbamate shows that the proton affinity of carbonyl protonation increases with the extent of methyl substitution, the effect of methyl substitution being higher in the case of the hydroxy group than the amine group. The absolute value of the calculated proton affinity decreases when passing from the MINI-1 minimal basis set to the extended 3-21G basis, which is consistent with the observation that the 3-21G data reproduce the absolute gas phase proton affinities somewhat better[20]. Inclusion of the polarization functions at the non-hydrogen atoms on passing

TABLE I

Ab initio proton affinities (kJ mol^{-1}) of compounds studied

Level	NH_2COOH	NH_2COOCH_3	$CH_3NHCOOCH_3$
MINI-1//MINI-1	882·8	921·3	944·5
3-21G//3-21G	864·1	894·5	905·2
6-31G*//6-31G*	844·3	877·8	889·5
6-31G**//6-31G*	854·8	881·5	890·9
MP2/6-31G*//6-31G*	820·2	851·9	866·4

from the 3-21G to the 6-31G* basis brings about additional lowering in the absolute values of the calculated proton affinities (Table I) while the 6-31G** calculations, including polarization functions also for the hydrogen and using the 6-31G* geometry, give slightly (0·2–1·2%) higher proton affinities than the 6-31G* basis.

The MP2/6-31G* protonation energies were also calculated for establishing the effect of the correlation energy on the absolute values of the proton affinities (Table I). The absolute values of the MP2 proton affinities were 2·6–3·0% lower than those derived from the 6-31G* calculations. For carbamic acid the MP3/6-31G*/6-31G* proton affinity was also calculated and the value of 838·5 kJ mol^{-1} was obtained. However, the MP3 contribution, 18·3 kJ mol^{-1}, is lower than the MP2 contribution (24·1 kJ mol^{-1}). If MP2 is positive, i.e., it lowers the proton affinity of the C=O group, MP3 is negative and increases the absolute value of the proton affinity of the C=O group in carbamic acid. The overall effect of the correlation energy, however, is lowering of the proton affinity as compared to the analogous calculations at the Hartree–Fock level. The MP2 contribution to the correlation energy of protonation of the carbonyl group in carbamic acid is higher with the 6-31G* basis (E_p = = 820·5 kJ mol^{-1}) than with the 6-31G** basis (E_p = 829·4 kJ mol^{-1}) and the 6-31G* geometry. Hence, inclusion of the polarization functions at the hydrogen atom of the cation brings about a better description of the cation in comparison to the neutral molecule and a lower correction of the correlation energy to the proton affinity.

Comparison of the MP3/6-31G*//6-31G* proton affinities for carbamic acid (838·5 kJ mol^{-1}) and the structurally related formamide (874·5 kJ mol^{-1}) and formic acid (771·1 kJ mol^{-1}) (ref.[18]) indicates that the proton affinity of the C=O group is higher in carbamic acid than in formic acid and lower than in formamide. In view of the facts that the gas phase proton affinities of the compounds studied are unavailable and that the E_p value in Eq. (*1*) represents the electronic contribution to the proton affinity only, the calculated and experimental data cannot be directly compared. The experimental gas phase proton affinity of ethyl N,N-dimethylcarbamate[7], 894 kJ mol^{-1}, represents the upper limit of proton affinity of a completely alkyl substituted carbamate. Our calculations show that the absolute value of the proton affinity approaches this value with increasing extent of methylation (Table I).

Geometry

The optimized geometries of carbamic acid, methyl carbamate, and methyl N-methylcarbamate along with those of their cations are given in Tables II–IV, respectively. Structures of the three neutral molecules have been studied[3] at various levels of theory, and the calculated structure parameters of the molecules are given in this paper only for a comparison with the optimized protonated forms. Since out of the MINI-1, 3-21G, and 6-31G* bases applied to the geometry optimization, the last

fitted the equilibrium structures of the substituted carbamates[3] best, only the results of the 6-31G* calculations are discussed.

Carbamic acid. The net effect of protonation of the C=O oxygen atom is a considerable (8·2 pm) lengthening of the C2—O1 bond and shortening of the C2—N3 and C2—O6 bonds (4·3 and 6·2 pm, respectively). As to the bond angles, the most marked changes are observed for the C2—N3—H5, N3—C2—O6, and C2—O6—H angles, increasing on the protonation (Table II).

TABLE II

6-31G* optimized geometry of carbamic acid B and its cation BH^+; atom labelling according to Scheme 1. Total energies E_{tot} are −243·70844 au for B and −244·02999 au for BH^+ (1 au = = 2 625·5 kJ mol^{-1})

Bond	Bond length, pm		Angle	Magnitude, deg	
	B	BH^+		B	BH^+
C2—O1	122·0	130·2	N3—C2—O1	126·3	125·6
C2—N3	134·0	129·7	C_2—N3—H4	120·7	119·1
N3—H4	98·9	99·9	C2—N3—H5	119·1	123·6
N3—H5	98·9	99·7	N3—C2—O6	111·2	117·9
C2—O6	135·5	129·3	C2—O6—H	112·8	118·9
O6—H	95·2	96·0	C2—O1—H8	—	123·4
O1—H8	—	95·8			

TABLE III

6-31G* optimized geometry of methyl carbamate B and its cation BH^+; atom labelling according to Scheme 1. Total energies E_{tot} are −282·71359 au for B and −283·04794 au for BH^+

Bond	Bond length, pm		Angle	Magnitude, deg	
	B	BH^+		B	BH^+
C2—O1	122·2	130·8	O1—C2—N3	125·5	123·9
C2—N3	134·4	130·5	C2—N3—H4	120·5	118·8
N3—H4	98·9	99·8	C2—N3—H5	119·1	123·6
N3—H5	98·9	99·5	N3—C2—O6	111·2	118·7
C2—O6	134·8	127·7	C2—O6—C7	118·9	125·4
O6—C7	144·5	150·1	O6—C7—H	108·4	106·4
C7—H	107·7	107·4	C2—O1—H8	—	122·5
O1—H8	—	95·6			

Methyl carbamate. Protonation brings about lengthening of the C2—O1 bond (from 122·2 to 130·8 pm) and shortening of the N3—C2 and C2—O6 bonds (by 3·9 and 7·1 pm, respectively) (Table III). The O6—C7 bond length increases 5·6 pm. As to the bond angles, the C2—N3—H5, N3—C2—O6, and C2—O6—C7 angles exhibit the highest changes (increase on protonation).

Methyl N-*methylcarbamate.* Similarly as with the two preceding compounds, protonation of this substance results in a lengthening of the C2—O1 and O6—C7 bonds and shortening of the C2—N3 (5·2 pm) and C2—O6 (5·2 pm) bonds (Table IV).

TABLE IV

6-31G* optimized geometry of methyl N-methylcarbamate B and its cation BH^+; atom labelling according to Scheme 1. Total energies E_{tot} are −321·72312 au for B and −322·06189 au for BH^+

Bond	Bond length, pm		Angle	Magnitude, deg	
	B	BH^+		B	BH^+
O1—C2	122·5	131·4	O1—C2—N3	126·1	118·3
C2—N3	134·2	129·0	C2—N3—H4	117·1	115·7
N3—H4	99·1	99·9	C2—N3—C5	123·2	126·4
N3—C5	145·1	147·8	N3—C2—O6	111·0	118·3
C2—O6	135·1	129·9	C2—O6—C7	118·9	127·5
O6—C7	144·5	148·1	O6—C7—H	108·5	107·3
C7—H	107·7	107·6	N3—C5—H	110·1	109·1
C5—H	108·1	107·7	C2—O1—H8	—	121·8
O1—H8	—	95·4			

TABLE V

6-31G* gross atomic charges of carbamate group in bases B and their cations BH^+; atom labelling according to Scheme 1

Atom	NH_2COOH		NH_2COOCH_3		$CH_3NHCOOCH_3$	
	B	BH^+	B	BH^+	B	BH^+
O1	−0·597	−0·664	−0·605	−0·682	−0·618	−0·688
C2	0·968	1·158	1·024	1·200	1·052	1·202
N3	−0·901	−0·828	−0·922	−0·860	−0·873	−0·811
O6	−0·732	−0·637	−0·734	−0·671	−0·742	−0·688
H8	—	0·512	—	0·503	—	0·502

The C2—N3—C5, N3—C2—O6, and C2—O6—C7 angles increase whereas the O1—C2—N3 angle decreases considerably (7·8°).

The C2—O1—H8 proton bond angle decreases gradually from 123·4° in carbamic acid to 121·8° in methyl N-methylcarbamate. Extending methyl substitution is also accompanied by shortening of the O1—H8 bond (Tables II – IV).

Mulliken Population Analysis

In relation to the study of the effect of protonation of the C=O group oxygen on the electronic charge distribution over the carbamate group, the gross atomic charges of the latter group were calculated for the most stable structures by using the 6-31G* basis (Table V). Protonation is accompanied by a considerable increase in the negative charge at the O1 carbonyl group oxygen; the positive charge at the C2 carbon atom of the C=O group increases appreciably. The N3 nitrogen and O6 hydroxy group oxygen atoms, on the other hand, possess considerably lower negative charges in the protonated species than in the bases. The H8 proton carries a high positive charge whose magnitude is little dependent on methyl substitution of the carbamate group.

Calculations in this paper were performed during the author's study stay at the Southern Illinois University, Carbondale, U.S.A. The author wishes to thank Prof. Steve Scheiner of that University for very good working conditions and for many stimulating discussions, and the Fulbright foundation for financial support.

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Translated by P. Adámek.