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# INDO-MO INVESTIGATION OF GAS-PHASE ACIDITIES OF CARBAMATES AND THIOCARBAMATES

R. HILAL, M.M. HAMED and H. MOUSTAFA

*Chemistry Department, Faculty of Science, Cairo University, Giza, Egypt*

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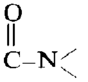
Gas-phase anion proton affinities of carbamic (I), thiol- (II), thio- (III) and dithiocarbamic (IV) acids are calculated by the INDO-MO method employing energy gradients for full geometry optimizations. The effect of d-type functions on sulphur on the calculated proton affinities has been examined. Detailed energy partitioning analysis enabled a much better understanding of the protonation process. Energetics of the isomerization II → III have been computed and discussed.

## 1. Introduction

The peptide linkage (I) is the structural backbone of polypeptides and proteins. The electronic properties of the side groups attached to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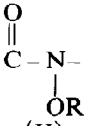
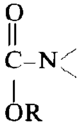
(I)


$\mathrm{O{=}C{-}N(OR){-}}$
(II)

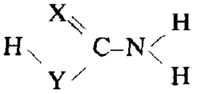

$\mathrm{O{=}C(OR){-}N\!<}$
(III)

it dominate in general the electronic behavior and dynamics of the peptide linkage. Thus, while the presence of the -OR group attached to the nitrogen atom of the peptide linkage (II) yields a medicinally important [1] class of compounds (hydroxamic acids), the presence of the same group attached to the carbon atom of the peptide linkage (III) yields a potentially carcinogenic [2] class of compounds, namely, carbamates (urethanes).

Previous publications in this series dealt with the electronic properties of the peptide linkage in simple amides, hydroxamic acids [3,4] and azolides [5]. In the present work, the investigation is extended to a structurally similar yet biologically different class of compounds, namely carbamates and thiocarbamates.

Biological activities of carbamic acids were reported [6] as early as 1950. However, recent research on the subject has been stimulated by the ability of this class of compounds to show a wide range of biological activities. Thus, the high activity of carbamic acids in inducing unscheduled DNA repair synthesis [7] and in the BHK-21 cell transformation test [8] have been extensively studied. The covalent binding index (DNA adduct) has been found to parallel the DNA repair index for carbamic acids, both showing the same level of correlation with carcinogenic potency [9]. Quite recently, it has been shown [10] that urethane (ethyl carbamate) alone is carcinogenic for mouse skin. On the other hand, the enzymatic action of transcarbamoylase, carbamoyl phosphate and the antimicrobial action of some carbamates were the subject of several investigations [11].

While the biological activity of carbamates has been subjected to extensive investigations, the literature does not seem to contain any systematic study of the electronic properties and bonding characteristics of this class of compounds. Although, it has been suggested [9] that proton abstraction and H-bonding underlie the high reactivity of carbamates in inducing unscheduled DNA repair synthesis, the proton affinity of carbamates has not been estimated either theoretically or experimentally. Furthermore, the enhanced acidity of thiocarbamates was only treated qualitatively on the basis of d-orbital conjugative effects. This model, although used extensively [15,16] for biological sulphur-containing compounds, has been shown to be inadequate [17,18]



I: X = Y = O
II: X = O; Y = S
III: X = S; Y = O
IV: X = Y = S

The present paper presents a comparative quantum-chemical study of the electronic structure, proton affinities and isomerization energies for carbamic (I), thiol carbamic (II), thiocarbamic (III) and dithiocarbamic (IV) acids. The principal objectives of the computations are: (1) to calculate reliable geometrical data for the parent carbamate structure, (2) to calculate proton affinities for the isomeric carbamates, (3) to determine whether the difference in proton affinities can be explained on the basis of bonding parameters and characteristics, and (4) to examine the effect of d-functions on the calculated proton affinities and isomerization energies. Each of the above objectives has now been reached. In addition, the large amount of data that have been generated have allowed a much better understanding of the C–N bond in the different environments studied.

## 2. Method of calculation

All calculations were performed within the INDO-MO framework. Details of the method have been given elsewhere [19]. The energy breakup scheme used in the present study has been detailed before [16,20]. However, its main outlines will be given here.

Within the INDO scheme, the total energy of a molecule may be partitioned into one- and two-atom energies [21], as

$$E = \sum_{A} E_A + \sum\sum_{A<B} E_{AB} \tag{1}$$

The two-atom energy, $E_{AB}$, may be further partitioned into

$$E_{AB}^{(1)} = -\tfrac{1}{2}\sum_{u}^{A}\sum_{v}^{B} P_{uv}^{2}\gamma_{AB} \tag{2}$$

$$E_{AB}^{(2)} = 2\sum_{u}^{A}\sum_{v}^{B} P_{uv}\beta_{uv}^{0}S_{uv} \tag{3}$$

$$E_{AB}^{(3)} = (P_A P_B - P_A Z_B - P_B Z_A)\gamma_{AB} \tag{4}$$

and

$$E_{AB}^{(4)} = Z_A Z_B / R_{AB} \tag{5}$$

where $Z_A$, $Z_B$ and $R_{AB}$ are the nuclear charges of atoms A and B and the internuclear distance. $S_{uv}$ is the overlap between two atomic orbitals, u and v, and $P_{uv}$ an element of the bond-order-charge density matrix.

$E_{AB}^{(1)}$ represents the exchange interaction energy, $E_{AB}^{(2)}$ is the overlap interaction energy and is a measure of the interference density [21], $E_{AB}^{(3)}$ an electrostatic attraction interaction, and $E_{AB}^{(4)}$ the nuclear repulsion interaction energy.

## 3. Results and discussion

### 3.1. Equilibrium geometries and charge distribution

The bond lengths and angles obtained with full geometry optimization for the four carbamates (I–IV) and their corresponding anions are listed in table 1.

Among the values given in table 1, there are small but significant trends, which may be pointed out as:

(a) The C–N bond length shortens upon going from a carbamate to the corresponding anion. This indicates a delocalization of the negative charge of the anion and hence increase of the extent of conjugation (increased resonance stabilization).

(b) The $<$XCY decrease on going from a carbamate to the corresponding anion. This is not expected in the sense that as the net negative charges on the two heteroatoms (X and Y) increase (in the case of the anions) one would expect the repulsive interaction to dominate and conse-

Table 1

Optimized geometries of carbamates I–IV and of the corresponding anions (IA–IVA)

Bond lengths given are in Å and bond angles in degrees. $f$, force constant in a.u.

| Parameter | Species | | | | | | |
|---|---|---|---|---|---|---|---|
| | I | IA | II | IIA | III | IV | IVA |
| C–N | 1.327 | 1.312 | 1.353 | 1.342 | 1.338 | 1.284 | 1.272 |
| C=O | 1.288 | 1.191 | 1.185 | 1.197 | | | |
| C–O | 1.398 | 1.191 | | | 1.290 | | |
| C=S | | | | | 1.60 | 1.59 | 1.611 |
| C–S | | | 1.716 | 1.643 | | 1.656 | 1.611 |
| $<$ OCO | 121.2 | 114.2 | | | | | |
| $<$ OCN | 121.0 | 122.9 | 111.7 | 122.3 | | | |
| $<$ SCS | | | | | | 128.3 | 123.9 |
| $<$ SCN | | | | | 116.6 | 111.0 | 118.05 |
| $<$ OCS | | | 126.1 | 121.9 | | | |
| $<$ SCO | | | | | 123.9 | | |
| $f$ ($\times 10^4$) C–N | 8.43 | 14.68 | 5.01 | 4.05 | 4.64 | 3.19 | 4.26 |

quently, an increase in $<$ XCY is expected. However, it seems that steric factors are very important in the present case. Thus, removal of the proton and further redistribution of the charge density release the strain originally responsible for large $<$ XCY.

The equilibrium geometrical parameters obtained in the present work are in good general agreement with the experimental geometries reported for carbamate and thiocarbamate esters [22].

Table 2 lists the net charges on each atom and the $\pi$-bond orders for all carbamates studied. Some general remarks ought to be made concerning these charge distributions:

(a) The tendency of oxygen to form p-p $\pi$-bonding is much greater than that of sulphur. Thus, the C–N $\pi$-bond order is very large in the

Table 2

Net charges on each atom and $\pi$-bond orders for all carbamates and anions studied

| | Species | | | | | | |
|---|---|---|---|---|---|---|---|
| | I | IA | II | IIA | III | IV | IVA |
| Atom | | | | | | | |
| –C | 0.3167 | 0.3383 | 0.2359 | 0.0712 | 0.1178 | −0.0731 | −0.0743 |
| –N | −0.1677 | −0.2472 | −0.1472 | −0.1929 | −0.1312 | −0.0689 | −0.1034 |
| =O | −0.3574 | −0.4813 | −0.3268 | | | | |
| –O | −0.1573 | −0.4813 | | −0.4261 | −0.0418 | | |
| =S | | | | | −0.3152 | −0.2366 | −0.4338 |
| –S | | | −0.0821 | −0.4261 | | −0.0388 | −0.4338 |
| Bond | | | | | | | |
| C–N | 0.5081 | 0.4004 | 0.5436 | 0.5041 | 0.6000 | 0.6951 | 0.6469 |
| C=O | 0.7386 | 0.6352 | 0.7725 | | | | |
| C–O | 0.3956 | 0.6352 | | 0.7629 | 0.4165 | | |
| C=S | | | | | 0.6211 | 0.5594 | 0.4876 |
| C–S | | | 0.2541 | 0.3252 | | 0.3519 | 0.4876 |

case of dithiocarbamic acid. In fact, it is even greater than that of the –C=S bond. This C–N $\pi$-bond order depends on the number and position of sulphur atoms and reaches a minimum in the case of carbamic acid.

(b) The presence of oxygen atoms directly bonded to carbon (of the C–N bond) enhances the ionic character of the C–N bond. This ionic character decreases and reaches a minimum in the case of dithiocarbamic acid, where both the carbon and nitrogen atoms carry almost the same negative charge. This increased covalency of the C–N bond reflects the much lower electron-withdrawing effect of the C=S as compared to the C=O group.

(c) More significant than the net charges on each atom are the $\sigma$- and $\pi$-components of these net charges. All carbamates studied are highly polarized, with the $\sigma$- and $\pi$-systems polarized in opposite directions.

(d) in carbamates there is cross-conjugation as a result of the competition between the two heteroatoms Y and N for conjugation with the C=X $\pi$-system. In the case of the two symmetric anions (X = Y) a delocalization of the $\pi$-system and the negative charge in the XCX region allows a linear conjugation with the nitrogen atom. Such stabilization is absent in the cross-conjugated asymmetric anions.

### 3.2. Proton affinities

The proton affinity (PA) of an anion, $A^-$, or the proton detachment energy (PDE) of an acid, AH, may be defined as $-\Delta H^0_{298}$ for the gas-phase reaction

$$A^- + H^+ \rightarrow AH$$

The PDE may be written as

$$\mathrm{PDE} = -\Delta E_0^{\mathrm{el}} - \Delta \mathrm{ZPE} - \int_0^{298} \Delta C_p \, \mathrm{d}T \qquad (6)$$

where $\Delta E_0^{\mathrm{el}}$ is the electronic energy difference $E(A^-) - E(AH)$, $\Delta$ZPE the zero-point energy difference ZPE(AH) – ZPE($A^-$), and $\Delta C_p$ the difference of constant-pressure molar heat capacities $C_p(H^+) + C_p(A^-) - C_p(AH)$. If $A^-$ and AH possess the same number of rotational degrees of freedom and if vibrational and electronic contributions to $C_p(A^-) - C_p(AH)$ are neglected, then the last term in eq. 6 reduces to the $H^+$ contribution of $(5/2)RT$ (6.2 kJ/mol at 298 K). This small contribution has been omitted from our tabulations.

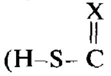
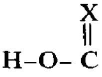
The computed energies of the seven species studied (four compounds and three anions) are given in table 3. In order to examine the effect of d-functions on the calculated proton affinities, the total energies of the thio- and dithiocarbamic acids and those of their corresponding anions, computed using an spd basis on sulphur, are also included in table 3. It is evident that the proton affinities of the two S-site acids IIA and IVA are much lower than that of the O-site acids IA and IIIA. That is, the gas-phase acidity of an H–S bond adjacent to a carbonyl or a thiocarbonyl group ( $\mathrm{H{-}S{-}\overset{\overset{X}{\|}}{C}}$ ; X = O or S) is greater than that of an H–O bond in the same environment ( $\mathrm{H{-}O{-}\overset{\overset{X}{\|}}{C}}$ ; X = O or S). This gas-phase acidity of the H–S bond is enhanced by a carbonyl group more than by a thiocarbonyl group.

Table 3

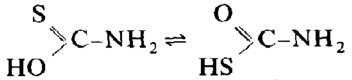
Theoretical proton affinities of carbamates and thiocarbamate anions studied

1 a.u. = 27.21 eV = 627.19 kcal/mol.

| Species | Basis set | Total energy (a.u.) | Theoretical proton affinity (kcal/mol) |
|---|---|---|---|
| I | sp | –51.2396 | |
| IA | sp | –50.7070 | 334.047 |
| II | sp | –44.7932 | |
| | spd | –44.8836 | |
| IIA | sp | –44.6034 | 119.035 |
| | spd | –44.6928 | 119.634 |
| III | sp | –45.1862 | |
| | spd | –45.2743 | |
| IIIA | sp | –44.6034 | 365.534 |
| | spd | –44.6928 | 364.665 |
| IV | sp | –38.7054 | |
| | spd | –38.9002 | |
| IVA | sp | –38.4546 | 170.443 |
| | spd | –38.6499 | 156.952 |

The inclusion of the d-functions in the basis set does not alter the conclusions drawn in the last paragraph. The d-functions did lower the energies in all cases, the extent of lowering amounting to 2.5 eV per sulphur atom. This behavior is expected. However, the energy lowering is almost exactly the same for each compound and its anion. This equality shows that the d-functions have the expected mathematical effect but without chemical significance, as far as the proton affinities are concerned. Therefore, the enhanced acidity of a proton attached to sulphur cannot be caused by d-orbital effects, a conclusion which elaborates upon the recent work of Wolfe et al. [18] on carbanions.

The isomerization process



$$\overset{S}{\underset{HO}{>}}C{-}NH_2 \rightleftharpoons \overset{O}{\underset{HS}{>}}C{-}NH_2$$

III II

is highly favorable in the direction II → III. The isomerization energy (246 kcal/mol) shows no significance for the d-functions. By means of CNDO/2 calculation, Whitehead [23] has shown that for a series of conformers, the ratio of the total energy of a conformer and its occupied orbital energy sum is a good indicator of its relative stability (the higher the value of this ratio, the higher the stability). For the two isomers II and III, these ratios are 4.85 and 4.71 (and 4.83 and 4.69) in the sp (and spd) calculations, respectively. That is, in contrast to CNDO/2, the INDO method predicts the most stable conformer to have a smaller ratio.

### 3.3. Energy partitioning analysis

In order to gain a much deeper insight into the origin of the calculated proton affinities and isomerization energies, let us analyse the total energy into one- and two-atom components. The results of this energy breakup are shown in table 4 for all species studied, with and without d-functions on sulphur. The main observations regarding table 4 are:

(a) The two-atom energy differences ($\Delta E_{AB}$) dominate the calculated proton affinities. With the exception of IIA, all anions show only a slight change in their one-atom energies ($\Delta E_A$) on protonation. In fact, the one-atom energy ($\Delta E_A$) of any anion is greater (more stable) than that of the corresponding compound. This indicates a greater stabilization of the anion via delocalization of the negative charge. Such a process involves considerable polarization of the atomic clouds.

(b) The role of the one-atom energy for the isomerization II → III is much more pronounced. In fact, the ratio $\Delta E_A/\Delta E_{AB}$ is approx. 2 for this isomerization process. Therefore, the stability of isomer III is largely due to the preferred polariza-

Table 4

One- and two-energy components and their bonded and non-bonded contributions to the protonation of carbamate anions

Values of energy components are given in eV. Values in parentheses correspond to the spd basis on sulphur.

| Energy component | IA–I | IIA–II | IIA–III | IVA–IV | II–III |
|---|---|---|---|---|---|
| $\Delta E_A$ | 1.65 | 8.19(8.20) | 1.19(1.11) | 2.79(2.81) | −7.00 |
| $\Delta E_{AB}$ | −16.15 | −13.36(−13.39) | −17.05(−16.93) | −9.62(−9.62) | −3.69 |
| $\Delta E_{AB}^{(1)}$ | −2.67 | −3.63 | −2.74 | −3.26 | 0.89 |
| $\Delta E_b^1$ | −2.96 | −3.60 | −2.79 | −3.30 | 0.81 |
| $\Delta E_n^1$ | 0.29 | −0.03 | 0.06 | 0.04 | 0.08 |
| $\Delta E_{AB}^{(2)}$ | −39.97 | −10.88 | −21.57 | −9.91 | −10.68 |
| $\Delta E_b^2$ | −39.86 | −11.73 | −21.58 | −10.12 | −0.85 |
| $\Delta E_n^2$ | −0.11 | 0.84 | 0.01 | 0.21 | 0.83 |
| $\Delta E_{AB}^{(3)}$ | −72.02 | −84.29 | −102.42 | −89.44 | −18.12 |
| $\Delta E_b^3$ | −26.05 | −35.05 | −40.85 | −36.81 | −5.79 |
| $\Delta E_n^3$ | −45.97 | −49.24 | −61.57 | −52.93 | −2.23 |
| $\Delta E_{AB}^{(4)}$ | 98.51 | 85.44 | 109.68 | 92.99 | 24.22 |

tion of atomic clouds and, to a lesser extent, due to tighter binding.

(c) Partitioning of the two-atom energies into components (table 4) shows clearly that protonation of all anions is enhanced by the increased binding (exchange, overlap and electrostatic attraction interactions) and is opposed by electrostatic repulsion interactions only. The former outweighs this latter interaction.

(d) The binding components of $E_{AB}$ are further partitioned into bonded and non-bonded contributions (table 4). The protonation process is dominated by the bonded overlap ($\Delta E_b^2$) and exchange ($\Delta E_b^1$) interaction energies, whereas both $\Delta E_b^3$ and $\Delta E_n^3$ are of equal importance.

The overlap interaction energy term $E_{AB}^{(2)}$ deserves further analysis. In Ruedenberg's original work [24], the concept of interference was introduced and was considered by him to be the 'primordial source for the positive or negative stabilization energy which leads to chemical binding and antibinding' [24]. Interference contributions were obtained through the partitioning of electronic density into quasi-classical and interference terms, so that

$$\rho_{(X)} = \rho_{(X)}^{CL} + \rho_{(X)}^{I}$$

where constructive interference ($\rho^I > 0$) leads to covalent bonding and destructive interference ($\rho^I < 0$) to anti-covalent bonding. The $E_{AB}^{(2)}$ term in the present treatment is directly related to this interference density ($E_{AB}^{(2)} \propto P_{uv}$). In fact, $E_{AB}^{(2)}$ is a measure of the interference energy and should be a characteristic of the AB bond.

Table 5 presents $E_{C-N}^{(2)}$ values for all molecules and anions studied in addition to their σ- and π-components. For the neutral molecules, $E_{C-N}^{(2)}$ shows an average value of $-36.85 \pm 1.5$ which is higher than that of the anions ($-34.48 \pm 3.5$). Variation from the mean $E_{C-N}^{(2)}$ value is such that replacement of oxygen by sulphur stabilizes the C–N bond. For the neutral molecules, it is interesting to note that while $E_{C-N}^{(2)}$ increases from I to IV systematically, the σ-components are more or less constant. It is the extent of delocalization of the π-density (note the regular increase of the π-component of $E_{C-N}^{(2)}$) that leads to increased binding in the C–N region.

Moffat and Tang [25] and Fischer and Kollmar [26] have stressed the importance of $E_{AB}^{(2)}$ and suggested that $E_{AB}^{(2)}$ correlates well with $E_{AB}$, the total two-centre energy for a given bond. To indicate such a correlation the final column of table 5 lists the ratio $E_{C-N}^{(2)}/E_{C-N}$. For the neutral molecules and anions studied the ratio is constant at 0.83, indicating that it is a characteristic of the bond under consideration.

It should be borne in mind that there is no

Table 5

Partitioned two-atom overlap interaction energies of C–N bonds in the carbamates studied

Values are expressed in eV.

| Species | | $E_{C-N}^2$ | | | $E_{C-N}^{total}$ | $E_{C-N}^{(2)}/E_{C-N}^{total}$ |
|---|---|---|---|---|---|---|
| | | σ- | π- | Total | | |
| I | sp | −29.34 | −6.41 | −35.75 | −43.29 | 0.83 |
| II | sp | −29.47 | −7.50 | −36.68 | −44.39 | 0.83 |
| | spd | −29.42 | −7.02 | −36.44 | −44.06 | 0.83 |
| III | sp | −29.49 | −7.03 | −36.52 | −44.16 | 0.83 |
| | spd | −29.12 | −7.49 | −36.61 | −44.31 | 0.83 |
| IV | sp | −29.54 | −9.91 | −38.46 | −46.60 | 0.83 |
| | spd | −29.46 | −8.88 | −38.34 | −46.46 | 0.83 |
| IA | sp | −25.59 | −5.33 | −30.93 | −37.86 | 0.83 |
| IIA | sp | −27.83 | −6.89 | −34.72 | −41.97 | 0.83 |
| | spd | −27.78 | −6.87 | −34.65 | −41.89 | 0.83 |
| IVA | sp | −28.93 | −8.88 | −37.80 | −45.68 | 0.83 |
| | spd | −28.83 | −8.83 | −37.65 | −54.52 | 0.83 |

significant difference between the energy components calculated with and without d-functions on sulphur. It is interesting to note that for the two isomeric thiocarbamates II and III, $\Delta E^{(2)}_{C-N}$ and $\Delta E^{\text{total}}_{C-N}$ is extremely small. The main effect of the isomerization process is localized in the S–C–O region.

## 4. Conclusion

The results of the present work indicate clearly the difference between the electronic features of carbamates and that of other simple amides. The origin of the high PA values calculated for the carbamates may be traced in the high residual electronegativities (as measured by net charges) and the increased polarizability upon protonation. These two parameters are dependent on atomic composition, molecular structure and the protonation site. These two parameters are markedly reduced when the protonation site is sulphur. Inclusion of d-orbitals does not have any significant effect in this respect, i.e., the enhanced acidity of $-SH$ compared to $-OH$ can best be rationalized by the inherent difference in the residual electronegativities and polarizabilities. This model seems general and has been suggested [27] to offer novel access to quantitative reactivity data.

The calculated two-atom energies for the C–N bond $E^{(2)}_{C-N}$ reflect the difference in electron density distribution upon replacement of oxygen by sulphur. The polarization decreases regularly as oxygen is replaced by sulphur, thus reducing the ionic character of the C–N bond (increasing the $\pi$-delocalization). Therefore, the tendency of carbamic acids to form adducts with, e.g., organic bases, would decrease as the number of sulphur atoms increases. This might well explain the higher biological reactivity of urethane as compared to its sulphur analogues.

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