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THE STABILITIES OF α-ISOCYANOCARBONIUM IONS

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Summary: Stabilization energies of three α-isocyanocarbonium ions relative to those of the parent carbonium ions have been found from fully geometry-optimized STO-3G total energies of all charged and neutral species and relevant isodesmic reactions. α-isocyanosubstitution, unlike α-cyanosubstitution, stabilizes all three carbonium ions considered here. The stabilization energy appears to depend upon a number of factors, electron delocalization, the inductive effect, and changes in steric repulsion, the latter of which arise from changes in bond angles in the formation of the carbonium ions from their neutral precursors.

Recent publications[1,2] have examined the effect of cyano substitution on the stabilities of carbonium ions. Experimental evidence[1] which suggested that cyano substitution in such cases may not have as large a destabilizing effect as had been anticipated was interpreted as demonstrating the ambivalence of the cyano group. An inductive destabilization and a stabilizing charge delocalization were both attributed to the cyano substituent. PRDDO and ab initio calculations have been employed[2] with geometry optimization of the CC and CN bond lengths to examine the effect of cyano substitution on these two bond distances in a number of different cyanocarbonium ions.

The present work considers three prototype carbonium ions CH_3^+, $C_2H_5^+$ (classical form), and $C_3H_7^+$ and the structures and the relative stabilities of these carbonium ions when α-substituted with another electron-withdrawing species, the isocyano group. Ab initio calculations[3] with an STO-3G basis were employed and complete optimization of all bond lengths and all bond angles was carried out to ±0.001 Å and ±0.1°, respectively, on the carbonium ions and their α-isocyano derivatives mentioned above as well as the neutral species obtained by addition of a hydride ion.

The energy required to form the α-isocyano substituted carbonium ion from its neutral parent can be compared with that needed where the isocyano group is replaced by hydrogen by employing the isodesmic reactions (1-3)

$$H_2CNC^+ + CH_4 \rightarrow H_3CNC + CH_3^+ \qquad (1)$$

$$H_3CCHNC^+ + C_2H_6 \rightarrow H_3CCH_2NC + C_2H_5^+ \qquad (2)$$

$$(H_3C)_2CNC^+ + C_3H_8 \rightarrow (H_3C)_2CHNC + C_3H_7^+ \qquad (3)$$

The changes in energy calculated for these reactions from the geometry-optimized energies of the individual molecules can be interpreted as stabilization energies of the particular α-isocyanocarbonium ion with respect to the corresponding carbonium ion where the isocyano group is replaced by hydrogen.

The three carbonium ions considered here are all positively stabilized by addition of the α-isocyano group (Table 1).

TABLE 1

Stabilization Energies[a] of α-isocyanocarbonium ions[b]

α-isocyanocarbonium ion	Stabilization Energy
H_2CNC^+	25.6
H_3CCHNC^+	15.9
$(H_3C)_2CNC^+$	10.6

a Relative to the parent carbonium ion (with H replacing NC) (Kcal/mole).

b STO-3G geometry-optimized energies were employed for both charged and neutral species.

However, the extent of the stabilization decreases with increasing size of the cation. It may be noted that the stabilization is largest for the primary carbonium ion and decreases as the degree of substitution increases. This trend is similar to that found with α-cyano substitution[4] where the stabilization energy is found to be slightly positive for the primary carbonium ion but negative for the secondary and tertiary species.

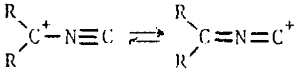
The atomic charges on the nitrogen and carbon atoms of the isocyano group as well as that on the carbon atom attached to the latter group are shown in Table 2 for the isocyanocarbonium ions and the corresponding neutral isocyanides.

TABLE 2

Atomic Charges on Isocyanocarbonium Ions and the Corresponding Neutral Isocyanides

	C	N	C
$(H_3C)_2HCNC$	+0.095	-0.341	+0.088
$[(H_3C)_2CNC]^+$	+0.405	-0.313	+0.408
$(H_3C)HHCNC$	+0.019	-0.338	+0.091
$[(H_3C)HCNC]^+$	+0.350	-0.296	+0.452
H_3CNC	-0.062	-0.332	+0.098
$[H_3CNC]^+$	+0.296	-0.273	+0.503

In all cases it can be seen that the positive charges are centered on the two carbon atoms and the negative charge remains on the nitrogen atom. It is interesting to note that the increases in positive charges on the two carbon atoms and the decrease in the magnitude of the negative charge on the nitrogen atom found in passing from the neutral isocyanide to the corresponding charged isocyanide are similar to those found with the corresponding cyanides. In the same way as with the cyanides, the stabilization found with the isocyanocarbonium ions can be represented as the result of resonance hybridization between two forms of these ions



Examination of the optimized nuclear configurations (Table 3) reveals that the NC and H-CNC bond lengths in the charged isocyano species are larger than those in the parent neutral isocyanide, while the C-NC distances are smaller in the former than in the latter. This observation provides evidence for an increased electron delocalization in the charged species which should presumably reduce the total energy. The C-NC bond length decreases in the isocyanocarbonium ions as the stabilization energy increases. Consequently it can be inferred that the stabilization energy increases as the extent ot the electron delocalization increases.

In the α-isocyanocarbonium ions the charge on the alkyl group increases as the size of that group increases. Thus the charges on CH_2, C_2H_4, and C_3H_6 are 0.770, 0.843, and 0.905, respectively, in the isocyanocarbonium ions, while in the unsubstituted carbonium ions, these charges are 0.741, 0.778, and 0.807, respectively. Thus the charges on the alkyl groups in the isocyanocarbonium ions become larger, compared to that in the unsubstituted cations, as the amount of substitution in the alkyl portion increases. This may be interpreted as resulting from a decrease in electron delocalization and an increase in the inductive effect.

Further information can be obtained by examination of the changes in the HCN(C) bond angles (Table 3).

TABLE 3

Bond Lengths[a] and Bond Angles[a] in α-isocyanocarbonium ions and parent neutral molecules

Molecule	H–CNC	C*–CNC	C–NC	N≡C	HCN(C)
CH_3NC	1.092	1.446	1.446	1.171	109.9
C_2H_5NC	1.094	1.544	1.454	1.171	108.2
C_3H_7NC	1.096	1.550	1.450	1.172	107.6
$(CH_2NC)^+$	1.117	-----	1.307	1.238	120.2
$(C_2H_4NC)^+$	1.117	1.516	1.322	1.226	116.8
$(C_3H_6NC)^+$	-----	1.525	1.340	1.217	-----

* C of CH_3

[a] Bond lengths (Å) and bond angles (°) optimized to ±0.001 Å and ±0.1°, respectively.

In the charged species this angle is considerably larger than that found in the neutral isocyanides so that, in the former case the separation of the substituent groups is significantly reduced. As a consequence the steric repulsion energy will increase proportionally to the size of the substituents involved. Of course, since the carbonium ions can be considered as formed from the neutral molecules by hydride extraction, the steric repulsion energy will be reduced.

There are apparently, then, at least three factors which must be considered in any rationalization of the size of the stabilization energy and the changes in this energy with substitution in the alkyl group of the isocyanocarbonium ion. The electron delocalization is largest for the smallest isocyanocarbonium ion and decreases as CH_3 groups are added, while the inductive effect correspondingly increases. The steric repulsion energy, which will be altered as a consequence of geometrical changes, will at least in part, counterbalance the energetic changes produced by shifts in the electronic densities.

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