

# THEORETICAL PREDICTION OF THE EXISTENCE OF STABLE DISTONIC RADICAL CATIONS

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## ABSTRACT

The preference of molecules of the form  $H_mX-YH_n$  to adopt hydrogen-shifted structures  $H_{m-1}X^{\cdot}-Y^+H_{n+1}$  on removal of an electron is theoretically examined. The latter structures are distonic radical cations with the formal charge and radical centres located on different atoms. The relative stabilities of distonic ions relative to classical isomeric forms have been modelled by means of idealized reactions involving small fragments. *Ab initio* energies for these model reactions indicate the existence of several distonic radical cations more stabilized than currently known systems. Distonic forms are particularly stabilized for the combinations:  $X = \text{Be, Si, P and S}$ ;  $Y = \text{N, O and F}$ .

## INTRODUCTION

CURRENTLY there is considerable interest in a novel class of radical cations whose formal charge and radical sites are centred on different atoms<sup>1-3</sup>. Such species have been termed as distonic radical cations<sup>1</sup>. The existence of several carbon containing distonic radical cations has been predicted by Radom and coworkers using *ab initio* molecular orbital theory<sup>1-4</sup>. In fact, distonic ions of the form  $\text{CH}_2(\text{CH}_2)_n \text{N}^+\text{H}_3$ ,  $\text{CH}_2(\text{CH}_2)_n \text{O}^+\text{H}_2$ , and  $\text{CH}_2(\text{CH}_2)_n \text{F}^+\text{H}$  ( $n = 0, 1$ ) are calculated to be more stable than the corresponding classical isomers  $\text{CH}_3(\text{CH}_2)_n \text{NH}_2^{+\cdot}$ ,  $\text{CH}_3(\text{CH}_2)_n \text{OH}^{+\cdot}$ , and  $\text{CH}_3(\text{CH}_2)_n \text{F}^{+\cdot}$ , respectively<sup>1,4</sup>. Many of these predictions have since been confirmed experimentally<sup>5-7</sup>.

Attempts to find more systems which prefer distonic structures have met with indifferent success. Radical ions of the form  $\text{CH}_3(\text{CH}_2)_n \text{XH}_m^{+\cdot}$  consistently adopt classical structures (i. e. structures of the parent neutral molecules) when  $X$  is not sufficiently electronegative<sup>3</sup>. Also, of the 29 other radical ions of the type  $X^{\cdot}\text{CH}_2\text{Y}^+\text{H}$  examined by Radom and coworkers, only five were calculated to prefer distonic structures<sup>2</sup>.

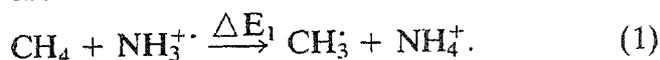
In this paper we employ a simple predictive scheme to look for potentially stable distonic radical cations in the series  $[\text{XH}_m\text{YH}_n]^{+\cdot}$ , in which  $X$  and  $Y$  have substantially different electronegativities. Based on earlier results, these ions seemed to be promising candidates to adopt distonic structures.

## THE COMPUTATIONAL MODEL

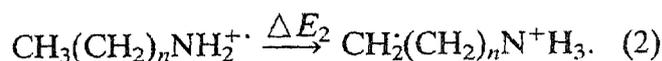
The theoretical procedure for quickly ascertaining the relative stability of a distonic radical cation is best described with a specific example. Consider the  $[\text{CNH}_5]^{+\cdot}$  system for which the preferred isomer is the ylid-ion  $\text{CH}_2\text{N}^+\text{H}_3$  rather than the radical cation of methyl amine,  $\text{CH}_3\text{NH}_2^{+\cdot}$  (contrast this structural preference with that for the neutral molecule: the ylide  $\text{CH}_2\text{NH}_3$  is probably not even a minimum on the potential energy surface and is at least 66 kcal/mol higher in energy than methyl amine<sup>8,9</sup>). The relative stability of the distonic radical cation can be traced to the differences in the electronic structures of the ylid-ion and its classical isomer. The classical isomer has a normal tetracoordinate carbon with an octet of electrons and a tricoordinate nitrogen with only an electronic septet. In the distonic form, the electron-deficient centre is the less electronegative carbon, while the hypercoordinate

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nitrogen has its full complement of eight electrons. These changes can be modelled by the following "reaction" involving simple fragments:

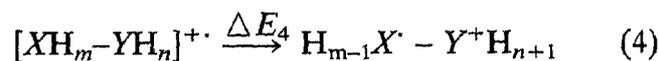
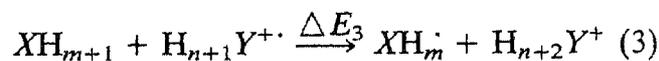


The energy changes associated with (1) may therefore be expected to parallel the relative energies of the distonic and classical isomers of  $[\text{CNH}_5]^+$  (and its homologues):



The energies  $\Delta E_1$  and  $\Delta E_2$  cannot, however, be expected to be identical<sup>2</sup>. In equation (1), the charge and radical centres are separated to infinity, which does not happen in (2). Short-range interactions in  $\text{CH}_2(\text{CH}_2)_n\text{N}^+\text{H}_3$  are expected to lead to differences in the two reaction energies. Also, the differential methyl substituent effects on  $\text{NH}_3^+$  and  $\text{NH}_4^+$  would lead to additional deviations<sup>2</sup>. However, if only general trends are sought equation (1) should prove an adequate model for rearrangement (2). The simple computational scheme is especially useful in screening a large number of systems which are likely to adopt distonic structures.

We have chosen to examine systems containing elements with very different electronegativities. Since the isomeric classical and distonic radical cations would then have electron-deficient centres localized on two widely disparate atoms, large energy differences may be expected. To confirm this hypothesis, a large number of such systems have been modelled using reactions of the type (3), which are generalized forms of (1). The energies of reaction (3) are taken to be representative of the true distonic-classical relative energies ( $\Delta E_4$ ).



[X = Be, B, C, Si, P, S; Y = N, O, F]

[m = 1, 2, 3, 3, 2, 1; n = 2, 1, 0; respectively].

The reaction energies  $\Delta E_3$  for the different systems have been obtained from *ab initio* total energies of the appropriate fragments. Data obtained with several different basis sets and including electron correlation to varying extents have been employed. Energies with a split-valence basis (3-21G), double zeta basis sets including *d* and *p* type polarization functions (6-31G\* and 6-31G\*\*, respectively), as well as with Moller-Plesset perturbation calculations to second, third and fourth orders to include electron correlation (MP2, MP3 and MP4)<sup>10</sup> have been used to test the method dependence of the theoretical predictions. Most of the reference energies have been taken from the literature<sup>11</sup>. When not available, we used the Gaussian 80 series of programs on a DEC-1090 computer to calculate the energies<sup>12</sup>.

## RESULTS AND DISCUSSION

The energies of reaction (3) calculated at various theoretical levels are presented in table 1. All the values are large and uniformly negative. The trends in the calculated energies at different computational levels are also rather similar. However, the results obtained at the highly correlated MP4/6-31G\*\* and MP3/6-31G\*\* levels represent the most reliable values.

The negative values for  $\Delta E_3$  in all the systems considered imply that distonic radical cations should be the preferred isomer in each case. To make a quantitative comparison, the data for X = C provide a convenient reference point. The  $\Delta E_3$  values at the MP4/6-31G\*\* level for X = C and Y = N, O and F are -19, -34 and -61 kcal/mol, respectively. The corresponding distonic radical cations  $\text{CH}_2(\text{CH}_2)_n\text{NH}_3^+$ ,  $\text{CH}_2(\text{CH}_2)_n\text{OH}_2^+$ , and  $\text{CH}_2(\text{CH}_2)_n\text{FH}^+$  are all calculated to be more stable than their classical counterparts<sup>3</sup>. However, the precise relative energies are smaller than  $\Delta E_3$  values for different *n*. This is because the model equation ignores short-range interactions and differential substituent effects, as mentioned earlier<sup>2</sup>.

The overestimation of the stability of distonic structures by the energies of the model

Table 1 Calculated reaction energies (kcal/mol) at different theoretical levels

Reaction	3-21G	6-31G*	6-31G**	MP2/ 6-31G**	MP3/ 6-31G**	MP4/ 6-31G**
BeH <sub>2</sub> + HF <sup>+</sup> → BeH <sup>·</sup> + H <sub>2</sub> F <sup>+</sup>	-55.6	-56.2	-61.8	-84.3	-77.3	-77.9
BeH <sub>2</sub> + H <sub>2</sub> O <sup>+</sup> → BeH <sup>·</sup> + H <sub>3</sub> O <sup>+</sup>	-43.2	-34.8	-39.3	-56.7	-50.8	-50.9
BeH <sub>2</sub> + H <sub>3</sub> N <sup>+</sup> → BeH <sup>·</sup> + H <sub>4</sub> N <sup>+</sup>	-27.0	-24.4	-26.0	-39.7	-35.7	-35.9
BH <sub>3</sub> + HF <sup>+</sup> → BH <sub>2</sub> <sup>·</sup> + H <sub>2</sub> F <sup>+</sup>	-42.7	-42.6	-48.1	-68.1	-61.5	-62.2
BH <sub>3</sub> + H <sub>2</sub> O <sup>+</sup> → BH <sub>2</sub> <sup>·</sup> + H <sub>3</sub> O <sup>+</sup>	-30.3	-21.1	-25.6	-40.5	-35.0	-35.1
BH <sub>3</sub> + H <sub>3</sub> N <sup>+</sup> → BH <sub>2</sub> <sup>·</sup> + H <sub>4</sub> N <sup>+</sup>	-14.2	-10.8	-12.2	-23.5	-19.9	-20.1
CH <sub>4</sub> + HF <sup>+</sup> → CH <sub>3</sub> <sup>·</sup> + H <sub>2</sub> F <sup>+</sup>	-43.2	-45.2	-50.5	-65.3	-60.4	-60.8
CH <sub>4</sub> + H <sub>2</sub> O <sup>+</sup> → CH <sub>3</sub> <sup>·</sup> + H <sub>3</sub> O <sup>+</sup>	-30.8	-23.7	-28.0	-37.6	-33.9	-33.8
CH <sub>4</sub> + H <sub>3</sub> N <sup>+</sup> → CH <sub>3</sub> <sup>·</sup> + H <sub>4</sub> N <sup>+</sup>	-14.6	-13.4	-14.7	-20.6	-18.8	-18.8
SiH <sub>4</sub> + HF <sup>+</sup> → SiH <sub>3</sub> <sup>·</sup> + H <sub>2</sub> F <sup>+</sup>	-60.7	-56.0	-61.1	-84.8	-78.5	-79.2
SiH <sub>4</sub> + H <sub>2</sub> O <sup>+</sup> → SiH <sub>3</sub> <sup>·</sup> + H <sub>3</sub> O <sup>+</sup>	-48.3	-34.5	-38.7	-57.2	-52.0	-52.1
SiH <sub>4</sub> + H <sub>3</sub> N <sup>+</sup> → SiH <sub>3</sub> <sup>·</sup> + H <sub>4</sub> N <sup>+</sup>	-32.1	-24.2	-25.3	-40.2	-36.9	-37.1
PH <sub>3</sub> + HF <sup>+</sup> → PH <sub>2</sub> <sup>·</sup> + H <sub>2</sub> F <sup>+</sup>	-74.2	-68.9	-73.8	-94.6	-88.8	-89.5
PH <sub>3</sub> + H <sub>2</sub> O <sup>+</sup> → PH <sub>2</sub> <sup>·</sup> + H <sub>3</sub> O <sup>+</sup>	-61.8	-47.4	-51.3	-67.0	-62.2	-62.4
PH <sub>3</sub> + H <sub>3</sub> N <sup>+</sup> → PH <sub>2</sub> <sup>·</sup> + H <sub>4</sub> N <sup>+</sup>	-45.6	-37.1	-38.0	-50.0	-47.2	-47.4
SH <sub>2</sub> + HF <sup>+</sup> → SH <sup>·</sup> + H <sub>2</sub> F <sup>+</sup>	-73.4	-66.1	-69.7	-87.0	-81.6	-82.3
SH <sub>2</sub> + H <sub>2</sub> O <sup>+</sup> → SH <sup>·</sup> + H <sub>3</sub> O <sup>+</sup>	-61.0	-44.6	-47.2	-59.4	-55.1	-55.3
SH <sub>2</sub> + H <sub>3</sub> N <sup>+</sup> → SH <sup>·</sup> + H <sub>4</sub> N <sup>+</sup>	-44.8	-34.3	-33.9	-42.4	-40.0	-40.3

equation does not lead to any ambiguity in the predictions involving the remaining systems because the  $\Delta E_3$  values for virtually all the systems considered are more negative than those calculated for  $X = C$ . Since the latter have been established to prefer distonic structures (for  $Y = N, O$  and  $F$ )<sup>1-6</sup>, the same must be true for the other systems. In fact, distonic isomers should prove to be stable to a greater extent in virtually all the radical ions considered, compared to the isomer energies of the carbon analogues. The only exception may be boron containing radical cations, since the  $\Delta E_3$  values for  $X = B, Y = N, O, F$  are almost identical to those calculated for  $X = C$  systems.

Two factors seem to be important in determining the magnitude of the calculated  $\Delta E_3$  values. For the series containing only second row elements,  $X = Be, B, C$  and  $Y = N, O, F$ , the large electronegativity difference between the heavy atoms principally determines the reaction energies. It is consistently preferable to have an electron-deficient centre at the electropositive  $X$  than at  $Y$ . Hence the  $\Delta E_3$  values are large negative quantities. While this factor is also present for  $X = Si, P$  and  $S$ , the  $\Delta E_3$  values are much too large to be attribut-

able solely to electronegativity differences. The ability of the third row elements to adopt subcoordinate and subvalent structures, increasing evidence for which is found in recent studies<sup>13,14</sup>, must be responsible for these anomalously high  $\Delta E_3$  values.

It is instructive to consider a few specific predictions resulting from table 1. Direct ionization of silanol leads to an isomer  $SiH_3OH^{+\cdot}$  which is less stable than the corresponding distonic form  $H_2Si^{\cdot}OH_2^+$ . The energy difference is predicted to be greater than that for the corresponding carbon analogues,  $CH_3OH^{+\cdot}$  and  $H_2C^{\cdot}OH_2^+$ . MNDO calculations on these isomers confirm these expectations. The ylid-ion  $H_2C^{\cdot}OH_2^+$  is calculated to be 21.6 kcal/mol more stable than the classical isomer. On the other hand,  $H_2Si^{\cdot}OH_2^+$  is as much as 67.4 kcal/mol lower in energy than  $SiH_3OH^{+\cdot}$  at the same theoretical level. While both these relative energies have probably been overestimated by the MNDO method, the trend is unambiguous. Silicon based distonic radical cations should be consistently more stable than their classical isomer. Interestingly, these are systems quite amenable to gas phase experimental examination.

The radical cations derived from molecules

with P-O bonds represent another interesting case. Among its neutral isomers,  $H_3P = O$  with a hypervalent phosphorus is clearly more stable than  $H_2P-OH$  or other alternatives<sup>15</sup>. Removal of an electron leads to a dramatic change in the preferred structure. In the gas phase<sup>16</sup>, it has been shown that  $H_2P-OH^{+\cdot}$  is more stable than  $[H_3P = O]^{+\cdot}$ . The present calculations suggest yet another intriguing alternative. The distonic isomer  $HP^{\cdot}-OH_2^+$  with a subvalent phosphorus may indeed be the most stable isomer. Generation and structural identification of such an isomer in the gas phase would be of considerable interest.

The method dependence of the calculated reaction energies in table 1 should prove useful in the selection of a suitable theoretical level for the direct evaluation of distonic-classical isomer energies in these systems. Inclusion of polarization functions leads to some changes in the calculated reaction energies, but the corrections are generally reversed when electron correlation is added (table 1). It may therefore be possible to obtain relative isomer energies correct to within about 10 kcal/mol even at the split-valence 3-21G level for a majority of the systems considered (with the exception of fluorine containing radical ions).

## CONCLUSION

Using a model equation, a number of radical cations containing electropositive and/or third row elements are predicted to adopt unusual distonic structures. The preference for distonic forms is much greater in these systems compared to all the currently known carbon containing distonic species. Silicon, phosphorus and sulphur-based systems should prove to be particularly amenable to gas phase experimental studies. Theoretical studies of the true relative isomer energies as well as barriers to rearrangement in these systems are currently under way.

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