Anions N[C(CN)_2]_3^- and P[C(CN)_2]_3^- and the superacidic properties of their conjugate acids

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Abstract

Computational (DFT B3LYP 6-311+G**) study of novel anions N[C(CN)_2]_3^- and P[C(CN)_2]_3^- – obtained by replacement of oxygen atoms –O– and –=O of nitrate and metaphosphate anions of by –C(CN)_2^- and –C(CN)_2 fragments, respectively – and the gas-phase acidity of their conjugate acids, reaching below 260 kcal mol^-1, is presented.

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1. Introduction

Superacids continue to attract attention from both practical and fundamental points of view. In an earlier report we suggested that when designing a superacid one should first of all design the anion [1]. According to the common knowledge the charge in the anion should be as delocalized as possible, using electron-accepting substituents with strong field-inductive and resonance-acceptor properties. It is the best if the anion does not have a well-defined protonation site and has instead a symmetric structure with many energetically equivalent protonation sites. In addition to these considerations one has to consider repulsion between closely situated electron-accepting substituents, possible steric hindrance to resonance and other effects. The complex interplay of effects complicates the search for superacidic structures and narrows the range of successful structures. During the recent years several advancements in design of superacidic systems have been reported: carborane acids [2,1], a generalized principle of substituent modification [3] (based on the earlier Yagupolskii’s principle [4]), different polycyanated hydrocarbons [5–7].

In this communication we report about computational design of two novel anions 1 and 2 and the superacidic properties of their conjugate acids (Fig. 1). To the best of our knowledge neither of the anions nor their conjugate acids have been described earlier.

Both 1 and 2 can be regarded as derivatives of anions of mineral acids (nitrate and metaphosphate, respectively) obtained by formal replacement of the oxygen atoms by dicyanomethylene fragments as follows:

\[ -\text{O}^- \quad \rightarrow \quad \text{CN} \quad \text{CN} \]

\[ =\text{O} \quad \rightarrow \quad =\text{CN} \quad =\text{CN} \]

(1)

2. Methods

The geometries and energies of the anions and their conjugate acids as well as the gas-phase acidities of the conjugate acids were calculated using the DFT B3LYP approach with the 6-311+G** basis set. The gas-phase acidity \( \Delta G_{\text{acid}} \) of an acid HA is the negative Gibbs’ free energy effect of
the reaction \( HA \rightarrow H^+ + A^- \). Full geometry optimizations and vibrational analyses were performed. All stationary points were found to be true minima (\( N_{\text{imag}} = 0 \)). Thermodynamic quantities \( \Delta G_{\text{acid}} \) and \( \Delta H_{\text{acid}} \) (at 298 K) were calculated using standard procedures taking into account zero-point energies, finite temperature (0–298 K) correction, and the pressure–volume work term.

### 3. Results and discussion

The results of acidity calculations are presented in Table 1.

The geometry of the anions is similar (Fig. 2). Images of \( 2a \) and \( 2b \) are presented, the respective forms of \( 1 \) are similar.

#### Table 1

<table>
<thead>
<tr>
<th>Species</th>
<th>( \Delta H_{\text{acid}} )</th>
<th>( \Delta G_{\text{acid}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{N(CN)}_2 \text{CH(CN)}_2^- )</td>
<td>266.5</td>
<td>259.4</td>
</tr>
<tr>
<td>( \text{N(CN)}_2 \text{CH(CN)}_2 \text{CNH}^- )</td>
<td>266.6</td>
<td>259.5</td>
</tr>
<tr>
<td>( \text{P(C(CN)}_2 \text{CH(CN)}_2^- )</td>
<td>258.1</td>
<td>252.1</td>
</tr>
<tr>
<td>( \text{P(C(CN)}_2 \text{CH(CN)}_2 \text{CNH}^- )</td>
<td>263.3</td>
<td>256.1</td>
</tr>
</tbody>
</table>

*All energies are given in kcal mol\(^{-1}\) and correspond to the most stable conformations of the species. The results for the most stable protonated species are given in bold.*

Both have \( D_3 \) symmetry. The most pronounced difference is the length of the bonds between the central atom and the C1 carbon (numbering in Fig. 1), which for \( 1 \) and \( 2 \) is 1.38 and 1.71 Å, respectively, and the value of the angles between the planes of the central NC3 or PC3 moiety and the C(CN)2 fragments: 34° and 30°, respectively. The shorter distance from C1 to the central atom might be the cause of the somewhat stronger distortion of the anion \( 1 \) and one of the factors responsible for somewhat higher acidity of protonated \( 2 \) compared to protonated \( 1 \).

In the C1 protonated species \( 1a \) and \( 2a \) the CN groups of the CH(CN)2 fragment are rotated out of the plane of the central moiety, which is still nearly planar in both cases (Fig. 2, \( 2a \)). The angles between the plane of the central moiety and the N–C–H and P–C–H planes are 12.5° and 5.9°, respectively. Distortion of this fragment out of the main plane enables the other two C(CN)2 fragments to decrease their angles with respect to the central plane to 21° and 11° for \( 1a \) and \( 2a \), respectively.

The geometry of the N3 protonated species \( 1b \) and \( 2b \) is rather similar to the anions (Fig. 2, \( 2b \)). The CNH angle is 124° and 127° in \( 1b \) and \( 2b \), respectively, and the proton is directed out of the plane of the C(CN)2 fragment to which it is attached towards the nearest CN group of the neighboring C(CN)2.

The protonated forms \( 1a \) and \( 1b \) have energies differing by only 0.1 kcal mol\(^{-1}\) (Table 1). Thus the anion \( 1 \) provides an example of an anion without a well-defined protonation site – although small it has nine protonation sites with virtually equal energies! The protonated form \( 2b \) is by 4.0 kcal mol\(^{-1}\) more stable than \( 2a \). The partial Mulliken atomic charge on the central nitrogen in \( 1 \) is +0.84, the partial charge on the central phosphorus atom in \( 2 \) is +0.08. As expected, the negative charge of the anions \( 1 \) and \( 2 \) mainly resides on the nitrogen atoms of the CN groups (partial charges −0.30 in both anions).

The acids \( 1b \) and \( 2b \) are predicted to be by 54.5 and 47.1 kcal mol\(^{-1}\) more acidic that their “parent” acids HNO3 and HPO3 [1], while \( 2b \) is by 3.4 kcal mol\(^{-1}\) more acidic than \( 1b \). These acids are among the strongest non-carborane superacids and confirm the superstrong acidifying effect of incorporation of multiple CN groups into an acidic molecule whose conjugate anion is able to form an extensive conjugated system with the anionic protonation.
The acid 2b is predicted to be in the gas phase stronger than any of the following acids: CF$_3$SO$_3$H, HAlCl$_4$, HPF$_6$ and the parent carborane acid CB$_{11}$H$_{12}$H [1]. Work is in progress to apply the principle given in (Eq. (1)) to other mineral acids.

Acknowledgements

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References


[7] Our calculations at DFT B3LYP 6-311+G** level show that introduction of eleven CN groups into the “curved” hydrocarbon fluoradene is expected to increase its gas-phase acidity by ca. 85 kcal mol$^{-1}$ (or ca. 63 power of ten) to 239.6 kcal mol$^{-1}$, even despite the not most favorable conditions for the resonance stabilization of the carbanion.