Structures and Stabilities of Gas-phase $C_6H_4X^-$ (X = F, Cl and Br) Anions: Benzyne–Halide Ion Complexes?

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High-level *ab initio* calculations predict that $C_6H_4X^-$ anions are stable donor–acceptor complexes with a dramatic decrease of binding energies on going from $C_6H_4F^-$ to $C_6H_4Cl^-$ and to $C_6H_4Br^-$ (226, 96 and 60 kJ mol^{-1}, respectively); the $C_6H_4Br^-$ ion is calculated to undergo a bromide ion transfer rather than hydrogen abstraction when reacting with methanol, in excellent agreement with experimental observation.

In a recent FT-ICR study, Linnert and Riveros have demonstrated that the gas-phase $C_6H_4Br^-$ and $C_6H_4I^-$ ions display the characteristics of halide–benzyne complexes.[1] $C_6H_4Br^-$ and $C_6H_4I^-$ were found to react with more acidic substrates (MeOH and halobenzene) by a halide ion transfer rather than proton abstraction. This is in marked contrast to similar anions containing a first or second row electron-bearing group, $C_6H_4X^-$ (X = F, Cl, CN and NO_2) anions, which were found to readily abstract a proton from the more acidic alcohol.

To shed light on the unusual reactivity and halide specificity for complex formation in the series of $C_6H_4X^-$ ions, we report here the first *ab initio*[2] investigation of the structures and stabilities of $C_6H_4F^-$, $C_6H_4Cl^-$ and $C_6H_4Br^-$ ions. Geometries were fully optimized at MP2/DZV+(d) levels. Improved relative energies were obtained at the QCISD(T)/TZV+(2df, 2p)//MP2/DZV+(d) level,[3] by using an additivity approximation [ΔE(QCISD(T)/TZV+(2df, 2p)] ≈ ΔE[QCISD(T)/DZV(d)] − ΔE[MP2/DZV(d)]+ΔE[MP2/TZV+(2df, 2p)]. Our best relative energies include zero-point vibrational correction, derived from HF/DZV+(d) scaled frequencies.[4] For the C, H, F and Cl atoms, the DZV(d), DZV+(d) and TVZ+(2df, 2p) basis sets refer to 6-31G*, 6-31+G* and 6-311+G(2df, 2p) basis sets, respectively, while for the Br atom, the SV4P and SV4+P basis sets of Andzelm *et al.*[5] and TZV basis set of McGrath and Radom[6] were used. All calculations were performed with the GAUSSIAN 92 system of programs.[7] The extent of charge transfer between X^- and benzyne were calculated by using the Bader approach[8] and the PROAIM program.[9] The optimized geometries of the $C_6H_4X^-$ ions and benzyne (C_6H_4) are shown in Fig. 1 and the calculated reaction energies are given in Table 1.

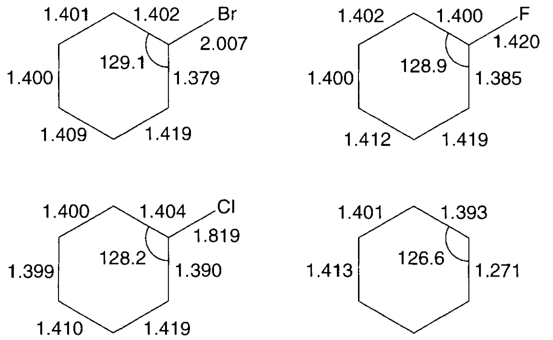

Fig. 1 Selected optimized geometries [MP2/DZV+(d)] of the $C_6H_4X^-$ ions and benzyne (bond lengths in Å and bond angles in degrees)

Table 1 Calculated energies[a] (kJ mol^{-1}) for $C_6H_4X^-$ reactions

Reaction	X = F	X = Cl	X = Br
$C_6H_4X^- \rightarrow C_6H_4 + X^-$	226.0	95.5	60.0
$C_6H_4X^- + MeOH \rightarrow C_6H_4 + MeOHX^-$	−18.8	−15.5	−8.8
$C_6H_4X^- + MeOH \rightarrow C_6H_5X + MeO^-$	104.6	28.4	−14.5

[a] QCISD(T)/TZV+(2df, 2p) + ZPVE values.

All $C_6H_4X^-$ ions are calculated to be stable equilibrium structures with C–X bond lengths (1.420, 1.819 and 2.007 Å for X = F, Cl and Br, respectively) close to those of typical C–X single bond lengths. For comparison, the C–X bond lengths in halobenzenes (C_6H_5F, C_6H_5Cl and C_6H_5Br) are 1.369, 1.742 and 1.901 Å, respectively [MP2/DZV+(d)]. These tightly bound complexes are in distinct contrast to the simple carbene–anion complexes which have very long C–X bond lengths (*ca.* 3 Å).[10] The short C–X bond lengths in the $C_6H_4X^-$ ions can be explained by the favourable orbital interaction between the unusually low-energy LUMO of benzyne[11,12] and the HOMO (*p* orbital) of the halide anion (Fig. 2). The strength of the donor–acceptor interaction is also reflected in the calculated charge transfer from X^- to benzyne, 0.33, 0.55 and 0.59 for X = F, Cl and Br, respectively. Note that in all cases there is a somewhat localized C=C double bond adjacent to the C–X bond (Fig. 1).

How stable are these $C_6H_4X^-$ ions? The $C_6H_4F^-$ ion is predicted to have a relatively large binding energy of 226 kJ mol^{-1}, significantly larger than that of aminoborane (129 kJ mol^{-1}).[13] In contrast, the stability of the $C_6H_4Br^-$ ion is just 60 kJ mol^{-1}, close to that of a weak molecular complex. The calculated binding energy of $C_6H_4Br^-$ is in excellent accord with the experimental estimate (50 kJ mol^{-1}).[1] The calculated trend of stabilities in the $C_6H_4X^-$ series is also consistent with the observed relative equilibrium constants for the dehalogenation reaction of $C_6H_4Cl^-$ and $C_6H_4Br^-$, eqn. (1).[14]

$$C_6H_4X^- = C_6H_4 + X^- \ (X = \text{Cl and Br}) \qquad (1)$$

The equilibrium favours benzyne more in the case of the bromide. Despite a similar energy difference between the benzyne LUMO and the halide ion HOMO, there is a large variation of the calculated binding energies of the $C_6H_4X^-$ ions (Table 1). What is the origin of the rapid decrease of binding energies on going from $C_6H_4F^-$ to $C_6H_4Cl^-$ to $C_6H_4Br^-$? The $C_6H_4X^-$ series involving bonding of benzyne to different halogens involves atoms which are very different in size. The halogen ends of the bonds are constructed from 2p, 3p and 4p orbitals, respectively. The orbital overlap, and therefore the resulting stabilization energy, will decrease rapidly across the series, X = F, Cl and Br. The importance of overlap dependence in determining the stabilization energies of donor–acceptor complexes is readily shown in the series of BH_3X^- ions; the calculated binding energies for X = F, Cl and Br are 275, 149

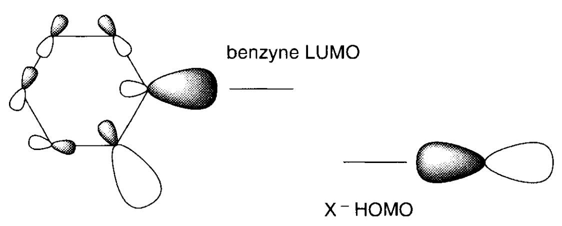

Fig. 2 The donor–acceptor interaction between the benzyne LUMO and the halide HOMO

and 117 kJ mol^{-1}, respectively.[15] The stabilities of the $C_6H_4X^-$ ions are important factors in understanding the benzyne mechanism[16] for nucleophilic aromatic substitution.[15]

Finally, we consider the energetics for the reactions of $C_6H_4X^-$ ions with methanol (Table 1). There are two possible channels for these reactions: a halide ion transfer [eqn. (2*a*)] and proton abstraction [eqn. (2*b*)]. For X = F and Cl, proton

$$C_6H_4X^- + MeOH \rightarrow C_6H_4 + MeOHX^- \quad (2a)$$

$$C_6H_4X^- + MeOH \rightarrow C_6H_5X + MeO^- \quad (2b)$$

abstraction is energetically more favourable than the corresponding halide ion transfer reaction. On the other hand, a bromide ion transfer is slightly favoured for the $C_6H_4Br^-$ ion. This result is in excellent accord with the experimental observations. Preliminary calculations also indicate that $C_6H_4I^-$ reacts with methanol by an iodide ion transfer.

In summary, $C_6H_4Br^-$ is predicted to have a small binding energy of 60 kJ mol^{-1}, in distinct contrast to the more stable $C_6H_4F^-$ and $C_6H_4Cl^-$ ions. The trend of calculated stabilities in the $C_6H_4X^-$ series can be rationalized in terms of the donor–acceptor interaction between the benzyne LUMO and the halide ion HOMO. Consistent with experimental observations, the $C_6H_4Br^-$ ion is predicted to undergo a bromide ion transfer rather hydrogen abstraction when reacted with methanol.

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