

A Self Consistent Reaction Field Calculation of the Fluorobenzonitrile Radical Ions

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A self consistent reaction field study has been carried out at the MINDO/3 level, in order to explain the decomposition of the species in solution.

In previous articles we have studied the cleavage reactions of aromatic radical anions [1–2]. We have shown the dependence of the decomposition rate on the position of an orbital crossing point [2]. If the singly occupied molecular orbital (SOMO) is σ^* the radical anion is unstable, while if it is π^* it is stable. Eventually, the crossing of these two orbitals allows for the decomposition of a stable radical anion, and the energy to reach this crossing point from the equilibrium governs the reaction rate. The antibonding character of the unpaired electron should be borne in mind. This means that the system is stable while the electron density excess due to the extra electron is spread over several centres (π character), so that the destabilization is distributed over the bonds associated to them. As soon as the electron density becomes localized to a certain extent (σ character), a larger destabilization is attached to the bond on which the electronic density is mainly localized [3]. The majority of these reactions is explained with such a simple scheme.

The isomers of fluorobenzonitrile radical, however, show a particular behaviour [4]. The *p*-fluorobenzonitrile radical yields fluoride and *p*-benzonitrile radical, while the metal derivative yields cyanide and *m*-fluorobenzene radical. This fact could not be explained in vacuum energetic terms (as usually used in standard molecular orbital calculations), since in both cases fluorine cleavage is favoured by 10 kcal/mol.

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The reaction field techniques provide a deeper insight in reactions which depend on the environment. A self consistent reaction field scheme proposed by Tapia and Constanciel [5] was applied on the MINDO/3 algorithm [6], so that we were able to carry out calculations for the systems under consideration, using the geometrical parameters optimized at the vacuum level. This method has widely been used in the literature in MINDO/3 [7] as well as CNDO/S-CI [8] calculations. We have used the charges obtained by this procedure to calculate electrostatic potential maps. Joining the positions of the minima of the electrostatic potential in several planes to the molecular one, we obtained the trajectory the cation would follow if its interaction with the radical anion were merely electrostatic, which is generally true in our case.

The results for the *para* derivative are shown in Figure 1. The full line indicates the vacuum level result, while the dotted one shows the path for an environment with a dielectric constant of 10. The trajectory lies in the molecular symmetry plane in both cases, showing that the interaction with the fluorine atom is dominant. The derivative shows a completely different behaviour (Figure 2). The vacuum level displays a similar behaviour to that observed for the *para* isomer. The environment, however, brings about an interaction with the nitrile group.

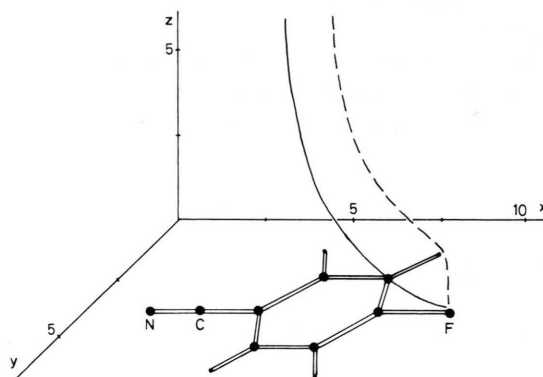


Fig. 1. Trajectories (axis units: Å) along the minimum of electrostatic potential generated by *p*-fluorobenzonitrile radical anion. Full line: vacuum level, dotted line: continuous dielectric with a dielectric constant of 10. The trajectories stay in the symmetry plane of the system.

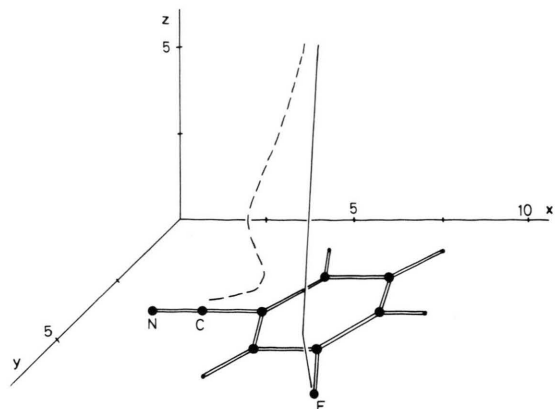


Fig. 2. As Fig. 1, but for *m*-fluorobenzonitrile radical anion. The trajectories do not stay in planes.

The presence of the cation favours the probability of localizing the antibonding electron on the same side of the molecule than the counter ion, weakening the bonding between the nearest prospective nucleofuge group and the aromatic moiety. A similar conclusion is reached as regard the products. The final state is certainly more stable when the cation is directly interacting with the anion formed as a consequence of the decomposition than the one reached if the counter ion were interacting with the radical formed. The experimental measurements

were carried out in solvents with moderate dielectric constants, as the one considered in this note. The values of the dielectric constant do not substantially affect the conclusions presented here, except for the para isomer in a medium with a large dielectric constant, where the ion remains in the neighbourhood of the nitrile group.

The meta derivative behaviour is explained taking into account that the charge defect on the carbon atom bonded to the fluorine is larger than that of the carbon atom attached to the cyanide. A similar behaviour was found for neutral molecules [9], where the positions the absolute minima depend on the dielectric constant of the media considered.

This note proves once more [10] the ability of the reaction field techniques, in particular that in reference [5], to deal with experimental situations where simple vacuum level calculations are not sufficient.

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- [1] H. O. Villar, E. A. Castro, and R. A. Rossi, *Can. J. Chem.* **60**, 2525 (1982).
- [2] H. O. Villar, E. A. Castro, and R. A. Rossi, *Z. Naturforsch.* **39a**, 49 (1984).
- [3] R. J. Houser, D. E. Bartak, and M. D. Hawley, *J. Amer. Chem. Soc.* **95**, 6033 (1973).
- [4] R. Constanciel and O. Tapia, *Theor. Chim. Acta* **48**, 75 (1978).
- [5] R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Amer. Chem. Soc.* **97**, 1285 (1975).
- [6] See for instance an interesting analysis in: G. Klopman and P. Andreozzi, *Theor. Chim. Acta* **55**, 77 (1980).
- [7] A. Botrel, A. le Beuze, P. Jacques, and H. Strub, *J. Chem. Soc. Faraday Trans. 2* **80**, 1235 (1984).
- [8] H. O. Villar and E. A. Castro, *Croat. Chim. Acta* **58**, 153 (1985).
- [9] See for instance: J. Angyán, M. Allavena, M. Picard, A. Potier, and O. Tapia, *J. Chem. Phys.* **77**, 4723 (1982).