The Radical Anion $[C_6F_5I]^-$

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Summary Electron attachment to iodobenzene gave the normal π^*-radical, but attachment to the pentafluoro-derivative gave a σ^*-radical, the excess electron being largely confined to the C–I σ^* orbital.

ELECTRON attachment processes, conveniently induced by exposure to ionizing radiation, often follow a variety of routes depending upon the nature of substituents and even upon solvent.[1] Accommodation of excess electrons in localised σ^* orbitals seems to be fairly common, even when relatively low-lying π^* orbitals are available, which might have been expected to act as acceptors. For example, Br–CN gave Br–CN$^-$, the unpaired electron being clearly confined to the Br–C σ^* orbital,[2] and various *N*-chloro, -bromo, and -iodo amides or imides gave similar anions with the electrons confined to the $\text{N}\dot{-}\text{hal}$ σ^* orbital.[3]

Hasegawa and Williams have now shown that F_3C–hal molecules (hal = Cl, Br, or I) give similar anions with the electron largely in the $\text{C}\dot{-}\text{hal}$ σ^* orbitals.[4] These results have led me to suppose that the tendency to form σ^* anions is related to the structure of the radical, R·, formed on loss of the hal$^-$ anions [equation (1)]. Thus, if R· radicals have

$$\text{R–hal} + e^- \rightarrow \text{R}\dot{-}\text{hal}^- \rightarrow \text{R}\cdot + \text{hal}^- \qquad (1)$$

a drastically different structure from that for the R-group in the parent molecule, dissociation is likely to be complete, but if there is little change, then, at least in the absence of a good anion solvating medium, dissociation may not be detected. The concomitant change in orbital hybridisation for the unpaired electron in R· is also likely to contribute. Thus, for alkyl halides, dissociation is virtually complete, although a weak residual interaction with the halide ions may be detected.[5] This follows, since alkyl radicals are almost certainly planar, and the unpaired electron is confined to a pure $2p$ orbital rather than to the *ca.* sp^3 hybridised orbital of the parent molecules. In contrast, $F_3C\cdot$ radicals are undoubtedly pyramidal, probably with bond angles close to those of the parent molecules,[6] and hence, at least in condensed phases, the tendency to complete separation is arrested. This also applies to the other radical anions mentioned above.

These considerations have led to the prediction that C_6H_5hal and C_6F_5hal molecules might also give $\text{C}\dot{-}\text{hal}^-$ σ^* adducts. Our e.s.r. results, for dilute solutions in methyltetrahydrofuran exposed to ^{60}Co γ-rays at 77 K show that, for C_6F_5I, this prediction is correct. The halogenobenzenes gave what appear to be π^*-radicals on electron capture, but C_6F_5I gave the spectrum shown in the Figure, from which we find $A_{\parallel}(^{127}I) = 550$ G† and $A_{\perp}(^{127}I) = 150$ G. The ^{19}F coupling on the parallel feature is either 28 G for four equivalent fluorine atoms, or 28 G for two and *ca.* 53 G for two more. (The latter, which I favour, requires that the outermost lines are extremely broad.) Coupling on the perpendicular features for one pair of fluorine atoms is *ca.* 18 G, and probably *ca.* 27 G for the other set. We stress that these are unlikely to be principle values.

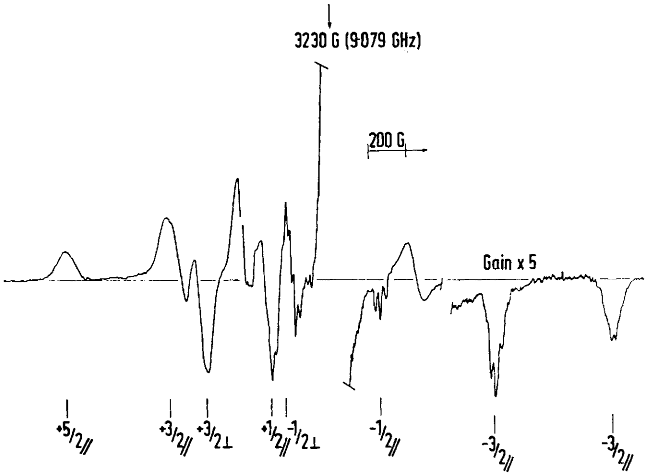

FIGURE. First derivative *X*-band e.s.r. spectrum for C_6F_5I in methyltetrahydrofuran after exposure to ^{60}Co γ-rays at 77 K, showing feature assigned to $[C_6F_5I]^-$ anions.

These results are similar to those of other σ^* iodides, especially the anion of *N*-iodosuccinimide.[3a] It is interesting to compare them with those for $C_6F_6^-$ anions, recently detected in an adamantane matrix by Yim and Wood.[7] The hyperfine coupling to 6 equivalent fluorine nuclei is extremely large (137 G) and led to the postulate that the anion has a planar σ^* structure rather than the expected π^* structure. On the basis of the changes that occur when the radical anions are rigidly held, we have postulated that the anions are buckled making each $C_2\dot{C}$–F unit pyramidal as in $\cdot CF_3$.[8] Clearly, the π^* orbital is less accessible than for benzene and its derivatives, which helps to explain the contrast between C_6H_5I and C_6F_5I.

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† G = 10^{-4} T.

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