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ANCHIMERIC STABILIZATION IN AN ANION RADICAL

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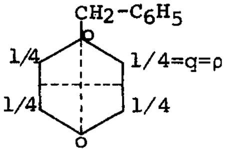
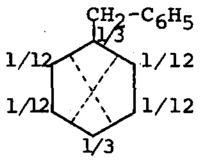
It has been established[1,2] that the odd electron in the diphenylmethane anion radical (DPM$^{\bar{\cdot}}$) occupies an antisymmetric (A) benzene-like MO (1) in preference to a symmetric (S) benzene-like MO (2) which, in the case of benzene itself, is degenerate with the A orbital. The question was of some interest since a 1,3 nonclassical covalent interaction (3) in DPM$^{\bar{\cdot}}$ should be maximized[3] in the S state and, to the first order,[4] vanish for the A state (*i.e.*, the state in which the A orbital is singly occupied). Since the A state is actually more stable it appears that any nonclassical interaction in the S state must be dominated by inductive destabilization of this state by the benzyl substituent. Actually, the ground state of DPM$^{\bar{\cdot}}$ has a small fraction of the S state vibronically mixed into it, so that C_1 is not truly nodal. However, the odd electron density is small (~0.07 electron), so that a substantial nonclassical interaction would not be expected. The close similarity of the hyperfine splittings of DPM$^{\bar{\cdot}}$ and *t*-butylbenzene anion radical supports this contention.[5]



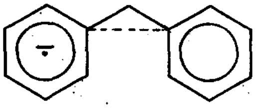
A

1



S

2



3

--- = nodal lines
q = charge density
ρ = odd electron density

It has now been found that, the above observations notwithstanding, *DPM$^{\overline{\cdot}}$ is thermodynamically more stable than the benzene anion radical (B$^{\overline{\cdot}}$)*, with reference to their respective neutral substrates. This is quite unexpected inasmuch as the benzyl group is electron donating[6] and should destabilize this anionic species. Reduction of a 2:1:1 mixture of B:DPM: dicyclohexyl-18-crown-6 ether[7] by NaK in 2-methyltetrahydrofuran (MTHF) yields only DPM$^{\overline{\cdot}}$, as shown by esr spectroscopy. In the absence of DPM, B$^{\overline{\cdot}}$ is generated quite routinely, and in the absence of B$^{\overline{\cdot}}$, DPM$^{\overline{\cdot}}$ is obtained as before. A 2:1 B:DPM ratio was used to compensate for the fact that one mole of DPM contains two moles of benzene rings. Radicals are not generated in high concentrations when the crown ether is omitted. Consequently, control of the crown ether concentration is essentially equivalent to, and more convenient than, limiting the supply of NaK. To further confirm these surprising results, a similar experiment was carried out in DME, omitting the crown ether. Again DPM$^{\overline{\cdot}}$ was obtained, and no vestige of B$^{\overline{\cdot}}$ was detectable. More predictably, both the toluene and *t*-butylbenzene anion radical proved less stable than B$^{\overline{\cdot}}$. Apparently DPM$^{\overline{\cdot}}$ is, after all, an unorthodox "alkyl" benzene radical, in terms of stability.

Moreover, *DPM$^{\overline{\cdot}}$ as formed in the MTHF-crown medium is localized*, *i.e.*, the odd electron is localized on a single benzene ring, in sharp contrast to previous observations in DME. The hfs (hyperfine splittings) are 4.50 (4H, *o* + *m*), 1.50 (1H, *p*) and 1.80 (2H, CH_2). These are almost exactly twice (except for the CH_2 splitting, which should remain the same) the hfs observed in DME, namely 2.23 (1H, *o* + *m*), 0.89 (2H, *p*), and 2.23 (2H, CH_2). In the latter case, the spin is equally distributed over both rings. Therefore the DME species is probably not fundamentally different from the MTHF one. The esr spectrum of the DME species probably represents a dynamic equilibrium between two equivalent localized species.

The MTHF species is impressively highly localized, as the hfs show. Delocalization, even to an unsymmetrical nonclassical ion, implies leakage of spin to the second ring. No such hfs are observed nor could as much as 2%, or 0.5 Gauss, of the total spin be lost to this ring. The ΔΔF for the formation of

$DPM^{\overline{\cdot}}$ compared to that of $B^{\overline{\cdot}}$ is established as about 500 cal by the competition experiments. Considering that the benzyl substituent of the former must engender an inductive destabilization, the anchimeric stabilization of $DPM^{\overline{\cdot}}$ is probably at least about 1 kcal.

The present data and conformational evidence to be presented discourage, but do not unequivocally rule out, an interpretation in terms of a nonclassical interaction of either the 1,3 or 1,5 type. However, an electrical polarization effect (attraction between a pole and its induced pi dipole) is plausible and compatible with the present results. Since the excess charge is heavily (-0.50) at the *o*-positions, it is reasonable to assume that *o*-*o* interactions (electrostatic) dominate the observed anchimeric effect. Condordant with this, 2,2-diphenylpropane (DPP) anion radical was found to cyclize to 9,9-dimethylflourene anion radical.[2] Note that the *o*-positions should be nearer in $DPP^{\overline{\cdot}}$ than in $DPM^{\overline{\cdot}}$ because of the diminished phenyl-c-phenyl angle in DPP.

The implication that other anchimeric effects, *e.g.*, in carbonium ions, may be engendered by electrical polarization rather than nonclassical covalent overlap should not be overlooked.

If, after all, a nonclassical interaction is involved, the conclusion is inevitable that small but significant energy effects can arise with but miniscule concomitants in molecular topography. In this case, even relatively sensitive probes may fail to diagnose nonclassicality.

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References

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4) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry"

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5) The hfs of *t*-butylbenzene anion radical are 4.66 (4H, *o* + *m*) and 1.74 (1H, *p*).

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