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ESR and Optical Spectra of Ion Radicals of Some Triptycene Derivatives

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It is important to study the delocalization interactions between the groups when a molecule contains two or more π-electronic groups separated by saturated chemical bonds. The mechanisms of CT (charge transfer) complex formation and of electron transfer reaction are cases closely connected with this problem. Hillier and Rice[1] studied theoretically the electronic state of *para*-cyclophane anion radicals and predicted appearance of a charge resonance band at 9000 cm^{-1} when the distance between the two molecular plane is *ca.* 3A. Ishitani and Nagakura[2] measured the optical and ESR spectra of 2,2′-*para*-cyclophane anion and showed that the absorption band at 760 nm could be interpreted as a charge resonance spectrum. If the two π-electronic systems are different, it might be possible, by means of ESR and optical measurements of the ion radicals, to examine directly the extent of the charge transfer in the ground state and the appearance of the CT band for a definite separation between the π-electronic groups. We have conducted such studies for 1,4-quinone triptycene anion (I) and dimethoxytriptycene cation (II).

Synthesized and purified samples of triptycene derivatives (supplied by Dr. F. Ogura of this University) were used without further purification. I was produced by reduction of corresponding molecule with metallic potassium in THF or DME solution. II was prepared by dissolving the molecule in concd sulfuric acid.

Optical absorption spectra were measured with Cary 14 and Cary 15 spectrophotometers. The ESR spectra were recorded with a JES-3BX spectrometer using X-band.

The absorption spectra of I in DME were almost the same as those of *p*-benzoquinone anion radical in the same solvent. No new absorption band which might be attributed to the interaction between the *p*-benzoquinone group and other parts of I was found in the spectra of I. We come across quite similar circumstances in the case of II, *viz.* absorption bands which correspond to the 437 nm and 282 nm bands of 1,4-dimethoxybenzene cation radical can be observed, but none due to the interaction between the dimethoxybenzene cation group and the other groups. Thus, the excess electron in I and the positive hole in II seem to be fairly well localized at quinone and dimethoxybenzene groups, respectively.

The same conclusion has been reached also from the ESR measurements. The ESR spectra of both I and II show no hfs due to the delocalization interaction between the component groups, *viz.*, the spectra of I shows the hfs due to the two protons in the quinone group, and the hfs constants of II are very close to the corresponding ones[3] of *cis*-form 1,4-dimethoxybenzene cation radical. In the case of free 1,4-dimethoxybenzene cation radical, both *cis*- and *trans*-isomers can exist in solution.[3] However, the 1,4-dimethoxybenzene group in II take only the *cis*-form owing to the barrier due to the bridge-head proton.

The fact that there are no significant intramolecular delocalization effects in the case of the above ion radicals may be of some interest from the viewpoint of the electronic structures of ions and molecular complexes in solution. According to recent experimental and theoretical studies,[4] it has become clear that the electronic structure of many TCNB (1,2,4,5-tetracyanobenzene) complexes with various aromatic hydrocarbons in the S_1 state can be considered to be a contact ion-pair with no significant delocalization interaction between the component TCNB anion and hydrocarbon cation. In the case of the TCNB complex in the S_1 state, quantum chemical calculations indicate clearly that it has a symmetrical overlapping structure where the intermolecular overlap integral is very small and the ion-pair structure may be stabilized strongly by solvation.[4] The intermolecular overlap integrals between the constituent groups of I and II may be rather small in view of their geometrical structure. On the other hand, the delocalization interaction between two identical aromatic groups is sufficiently strong for the "fast transfer" of the excess electron to occur when they are separated by one or two methylene groups.[5,6] In the case of I and II, we are concerned with the charge transfer between different groups, where the trapping of the excess electron or the positive hole at one group occurs very easily. The trapping may be facilitated by strong solvation of the ion radical groups.

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[4] H. Masuhara and N. Mataga, *Z. Phys. Chem.* N. F., **80**, 113 (1972); H. Masuhara, N. Tsujino and N. Mataga, This Bulletin, in press.

[5] H. M. McConnell, *J. Chem. Phys.*, **35**, 58 (1961); J. E. Harriman and A. H. Maki, *ibid.*, **39**, 778 (1963).

[6] In the case of dibenzotriptycene anion, the odd electron is delocalized completely over two naphthalene groups.