\(\pi\)-Conjugated Radical Cations Stabilized by Surrounding Bicyclic \(\sigma\)-Frameworks

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Benzene 1, naphthalene 2, biphenylene 3, and anthracene 4, fully annelated with bicyclo[2.2.2]octene were transformed into the corresponding radical cations, and their structures were clarified by X-ray crystallography. The remarkable stability of these salts are ascribed to the electronic and steric effects of the bicyclic frameworks. 1,4-Dithiin 5 annelated with the same bicyclic units was also oxidized into the stable salt of the radical cation, and the structure examined by X-ray crystallography. The ESR study indicated that the spin is effectively delocalized into the bicyclic frameworks. Dithiin 5 was further oxidized into the dication, which was shown to be 6\(\pi\) aromatic by the NMR and theoretical studies.

Keywords: cyclic voltammetry / X-ray crystallography / ESR / molecular orbital calculations

Organic radical cations have been of fundamental interest to organic as well as physical chemists in a variety of contexts. Their stabilization have in general been achieved by the extension of the \(\pi\)-conjugated system. In our group, however, it has been clarified that the remarkable stabilization of such a positively charged \(\pi\)-conjugated system can be attained by structural modification with \(\sigma\)-frameworks. Typical examples are demonstrated by the following studies.

1. Radical Cations of Benzenoid Aromatics.

A series of benzenoid aromatics, benzene 1 [1], naphthalene 2 [2], biphenylene 3 [3], and anthracene 4 [4], fully annelated with bicyclo[2.2.2]octene (abbreviated as BCO) exhibited reversible oxidation waves at remarkably low potentials (+1.08, +0.33, +0.25, and +0.17 V in tetrachloroethane vs Fc / Fc\(^+\), respectively). Accordingly these hydrocarbons were readily converted to the corresponding radical cation salts, Ar\(^+\)SbCl\(_6\)\(^-\), quantitatively by one-electron oxidation with 1.5 equivalents of SbCl\(_5\).

The salts were isolated as ruby red (1\(^+\)), dark green (2\(^+\)), blue violet (3\(^+\)), and dark green (4\(^+\)) crystals, which were stable in air at room temperature. This is the first examples of the isolation of the radical cation salts of alkyl-substituted benzene, naphthalene, and biphenylene as stable crystals. This stability is ascribed...
to both the electronic effects, such as inductive and σ-π conjugative effects, and the steric effects, such as steric and "Bredt’s rule" protection, of the rigid bicyclic σ-frameworks surrounding the π-system.

The X-ray crystallography was conducted for these radical cation salts to give the results shown in Figure. Here the change in bond lengths upon one-electron oxidation of $2^– 4^+$ is related to the coefficients of the relevant carbons’ HOMO of the neutral molecule: the bonds with the bonding nature in HOMO were elongated and those with antibonding in HOMO were shortened. The benzene radical cation appears to be subjected to the static Jahn-Tellar distortion, although the effect of crystal packing force can not be completely ruled out.

2. Radical Cation and Dication of 1,4-Dithiin [5, 6].

The 1,4-dithiin is a π-conjugated system isoelectronic to cyclooctatetraene, and its derivative annelated with BCO (5) is highly susceptible to the consecutive one-electron oxidation as shown by the oxidation potential in dichloromethane: $E_{1/2}$ (1) +0.0 V, $E_{1/2}$ (2) 0.82 V vs Fc / Fc$^+$. The oxidation with SbCl$_5$ afforded the radical cation salt $5^{+}$SbCl$_6^-$ as brown-colored crystals, which were characterized by X-ray crystallography.

The ESR spectrum of $5^{+}$ exhibited a 9-line signal due to the coupling with 8 anti-methylene protons ($\delta_{1H}$ 0.080 mT) and also a weak coupling with $^{33}$S (natural abundance 0.75%) ($\delta_{1S}$ 9.86 mT). The $\delta_{1H}$ value was even smaller than the value reported for the thianthrene radical cation (6). This is supported by the spin density calculated (B3LYP / 6-31+G* // B3LYP / 6-31G*) for these two sulfur atoms (spin density 0.2869 for $5^{+}$, 0.2874 for $6^{+}$), and indicates that the bicyclic σ-framework is even more effective for spin delocalization than the annelated benzene π-system [5].

The treatment of dithiin 5 with an excess amount of a stronger oxidant, SbF$_5$, in CD$_2$Cl$_2$ caused the formation of dication $5^{2+}$ as examined by $^1$H and $^{13}$C NMR spectroscopy. The downfield shift ($\Delta\delta$ 2.02 ppm) of the bridgehead proton of the BCO unit clearly demonstrates the presence of 6π-electron aromaticity in dication $5^{2+}$. This was further supported by the value of nucleus independent chemical shift (NICS) of -8.8 calculated for $5^{2+}$ (GIAO / HF / 6-31+G* // B3LYP / 6-31G*) [6].

References