The design of molecular devices critically depends on the preparation of molecules with predictable electrical, optical, and magnetic properties. An assembly of such devices within the framework of nanotechnology is a promising new field of research. Toward Molecular Charge-Transfer Relays. A Three-Dimensional Acceptor and Its Radical Anion

Przemyslaw Maslak,* Matthew P. Augustine, and Jeffrey D. Burkey

Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802
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Toward Molecular Charge-Transfer Relays. A Three-Dimensional Acceptor and Its Radical Anion

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tetraone I were susceptible to nucleophilic attack that resulted in a series of rearrangements, forcing us to carry out the radical anion experiments at low temperatures (see below).

The crucial information about the LUMO in I was provided by the measurement of reduction potentials of 1 (−0.90 V) and the appropriate model ketones, 4 (−1.51 V) and 5 (−1.36 V). The addition of a carbonyl group to 4 lowered its reduction potential by 0.15 V. Thus, if the effect were purely additive the estimated reduction potential of 1 should have been −1.21 V, instead of the observed −0.90 V. These results indicate a lowering of the LUMO in 1 by 0.31 eV in comparison to a hypothetical nonspiroconjugated model.

The radical anions of 1 and the half-molecule model, 2, were prepared at low temperature (195−173 K) in THF/HMPA (10% v/v) mixtures with radical anions of polycyclic aromatic compounds serving as electron donors. Figure 2 shows the UV/visible and ESR spectra of potassium salts of 1 and 2 recorded under identical conditions. The pale yellow solution of 2− exhibited the characteristic three-line spectrum resulting from the coupling to C-5 and C-6 protons. The ESR spectrum of the orange solution of 1− showed five lines, indicating coupling to four equivalent hydrogens. Both ESR spectra are in qualitative agreement with the relative sizes of the LUMO coefficients (Figure 1) and clearly indicate delocalization of the unpaired spin density over the entire molecule in 1−, at least on the ESR time scale. In THF/HMPA the ESR spectra were independent of the counterion (Li+, Na+, and K+), thus excluding any ion-pairing complications.

The distinction between simultaneous delocalization of the unpaired electron over the entire molecule of 1− and a rapid electron transfer (on the ESR time scale) between the halves can be obtained by UV/visible spectroscopy. In the latter case, the transitions between the highest doubly occupied MOs and the singly occupied MOs (intense π→π* bands in Figure 2) in 1− and 2− should be of identical energy and intensity. The spectra of these anions obtained in THF/HMPA (10% v/v) were, however, quite different (Figure 2). In agreement with a spiroconjugated SOMO, the π→σ* band in the spectrum of 1− is twice as intense as that in the spectrum of 2− and shifted significantly toward longer wavelengths.

The present results establish that the unpaired electron in 1− is simultaneously delocalized over two perpendicular π-planes. To our knowledge, this is the first example of an organic spiroconjugated radical anion. The “three-dimensional” character of the LUMO in this acceptor should lead to CT interactions of increased dimensionality. New materials based on such interactions are currently being prepared in our laboratory.

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Extremely High Rate Accelerations in Aldol Reactions of α-Alkoxy Ketones: Reactivity Governed by Substituent Field Effects

Goutam Das and Edward R. Thornton*

Department of Chemistry, University of Pennsylvania
Philadelphia, Pennsylvania 19104-6323

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Aldol reactions play a major role in modern synthesis, yet little is known about structural effects on reactivity. Consequently, we have targeted this area for study. We have discovered very large rate accelerations in aldol reactions of a-substituted ketones with the lithium enolate of pinacolone. Our results establish that (1) chelation is not responsible for these accelerations; (2) instead, a purely field/inductive (σ) effect is the major source of the high reactivities; and (3) the reactivity range is so large that it permits...