this case, the bell-shaped pH vs rate profile was determined to arise from a shift in the rate-determining step as the imidazole/imidazolium ratio was varied. On the basis of the results presented here, we propose that a bifunctional mechanism may be involved in the case of transition metal complex promoted RNA hydrolysis. In the case of $Cu(trpy)^{2+}$, a metal-bound hydroxide, or its equivalent, could function as the base while the metal center itself could act as a Lewis acid. That 2,3-cyclic AMP is detected as a product of the cleavage reactions argues against the direct attack of a metal-bound hydroxide on the phosphate center which has been proposed in the mechanism of Co(III)-promoted hydrolysis of AMP.[4] Further studies aimed at elucidating the mechanism of RNA hydrolysis by metal complexes are in progress.

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Toward Molecular Charge-Transfer Relays. A Three-Dimensional Acceptor and Its Radical Anion

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The design of molecular devices critically depends on the preparation of molecules with predictable electrical, optical, and magnetic properties.[1] An assembly of such devices within the framework of nanotechnology[1,2] is a promising new field of chemistry. Organic and organometallic materials based on charge-transfer (CT) interactions play an important role in this field.[3–5] The acceptor and donor molecules used to construct such devices (or materials) have been largely limited to flat conjugated π-systems.[3–6] As a consequence, the materials obtained are quasi one-dimensional. Here, we describe a "three-dimensional" acceptor that may serve as a relay of charge-transfer interactions between
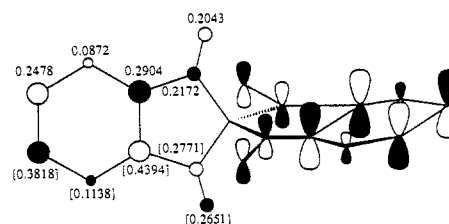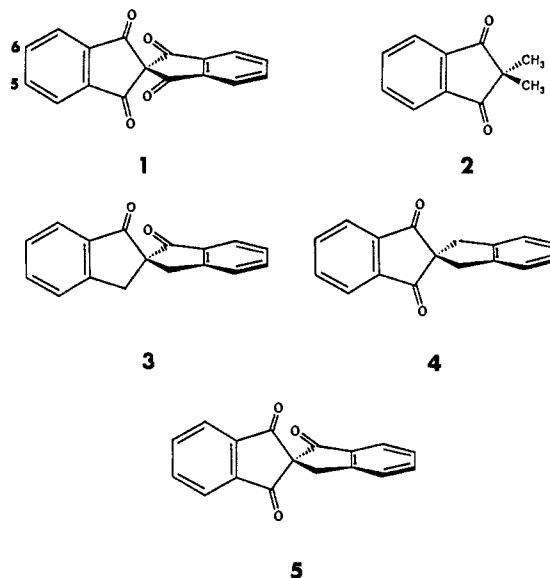

Figure 1. Coefficients (p_x or p_z) of the LUMO in 1 obtained by MNDO-PM3. The values in brackets are the corresponding LUMO coefficients for 2.

two perpendicular π-planes or two perpendicular stacks in a crystal. The radical anion of such an acceptor, $1^{\bullet-}$, is shown to simultaneously delocalize its unpaired electron in two perpendicular π-planes.

Our design of CT components with increased dimensionality is based on the phenomenon of spiroconjugation.[7,8] In the case of two identical perpendicular π–networks joined by a spiro atom (as in 1), the orbitals of the "halves" may interact only if they have the same symmetry. Such interactions lead to pairs of delocalized orbitals encompassing the entire molecule. From the point of view of CT interactions, it is essential that the frontier orbitals (LUMO for 1) satisfy this symmetry requirement. Figure 1 shows the p_x and p_z coefficients of the LUMO in 1 obtained by MNDO-PM3 calculations.[9] This molecular orbital may be formally considered as a bonding combination of the "half-molecule" orbitals.[10] Thus, the fully delocalized LUMO of 1 should allow for simultaneous CT interactions in two perpendicular planes.

To test this prediction, we have prepared tetraone 1 and probed its LUMO by an ultimate CT interaction, i.e., full electron transfer. The synthesis[11] of 1 involved oxidation of 3[12] with $CrO_3/AcOH$ to afford 5 (52% yield). The dibromination of the methylene group ($NBS/Br_2/h\nu$) followed by hydrolysis with silver acetate gave the tetraone (1) in 53% yield. Both trione 5 and

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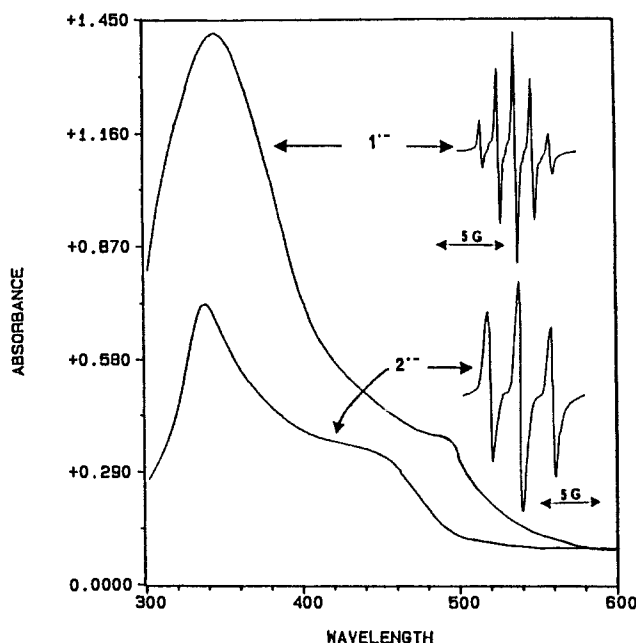*J. Am. Chem. Soc.* **1990,** *112,* 5360–5362

Figure 2. UV/vis and ESR spectra of 1·⁻ (a_H = 1.25 G) and 2·⁻ (a_H = 2.73 G) in THF/HMPA (10% v/v) at –90 °C (K⁺ as the counterion). The spectra presented were obtained under identical conditions[14] by reduction of 1 and 2 with identical amounts of the reducing agent (K⁺,biphenyl·⁻). The bands at 354 nm (1·⁻) and 338 nm (2·⁻) are assigned to the π → π* transitions.

tetraone 1 were susceptible to nucleophilic attack that resulted in a series of rearrangements,[11] forcing us to carry out the radical anion experiments at low temperatures (see below).

The crucial information about the LUMO in 1 was provided by the measurement of reduction potentials[13] 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 was 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.[10]

The radical anions of 1 and the half-molecule model, 2, were prepared[14] 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·⁻ showed the characteristic three-line spectrum[15] 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 → π* band in the spectrum of 1·⁻ is twice as intense as that in the spectrum of 2·⁻ and shifted significantly toward longer wavelengths.[16]

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.[8,17] 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.

(13) The reversible reduction potentials (vs SCE) were obtained by using cyclic voltammetry in 0.1 M solutions of tetraethylammonium perchlorate in acetonitrile at 25 °C.

(14) ESR and UV/visible spectra were independent of the reducing agent used. The relative intensities of the UV/visible spectra of 1·⁻ and 2·⁻ were also reproducible, but the absolute extinction coefficients have not been determined yet. The ketones were recovered unchanged in ca. 85–95% yield (GC vs internal standard) if the solutions of radical anions were treated with dioxygen.

(15) A similar coupling pattern ($a_{H5,H6}$ = 2.6 G) has been reported for 2·⁻ in DMSO. The coupling to ortho hydrogens ($a_{H4,H7}$ = 0.1 G) in this radical anion could be resolved only with difficulty: (a) Nelsen, S. F. *J. Org. Chem.* **1973,** *38,* 2693. (b) Russell, G. A.; Blankespoor, R. L.; Mattox, J.; Whittle, P. R.; Symalla, D.; Dodd, J. R. *J. Am. Chem. Soc.* **1974,** *96,* 7249.

(16) There are two degenerate (or near-degenerate) highest doubly occupied MOs in 1, but there is only one such orbital in 2. Both compounds should have similar transition dipoles since they have similar frontier orbitals (Figure 1). Therefore, the probability of the π → π* transition will double in 1·⁻ as compared to 2·⁻ (a model for a "localized" version of 1·⁻). The bathochromic shift is due to the lowering of the SOMO in 1·⁻ (ref 9). The weaker, longer wavelength bands correspond to n → π* transitions (Figure 2). They are also bathochromatically shifted. The neutral tetraone (1) also showed the effects of spiroconjugation in its UV/vis spectrum. In comparison to 2, both the π → π* and n → π* transitions in the spectrum of 1 were more intense and bathochromatically shifted. The extinction coefficients (in M⁻¹ cm⁻¹) in CH₃CN for 1 are as follows: π → π*, ϵ_{236} = 83 800; n → π*, ϵ_{305} = 2300; and ϵ_{344} = 900. Analogous data for 2 (in M⁻¹ cm⁻¹): π → π*, ϵ_{223} = 54 600; n → π*, ϵ_{300} = 700; and ϵ_{344} = 120.

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

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Aldol reactions play a major role in modern synthesis, yet little is known about structural effects on reactivity.[1-6] Consequently, we have targeted this area for study. We have discovered very large rate accelerations in aldol reactions of α-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_I) effect is the major source of the high reactivities; and (3) the reactivity range is so large that it permits

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