D_2SO_4 to make the solutions $0.08M$ (stoichiometric) in the acid. The diaminodurene (1,4-diamino-2,3,5,6-tetramethylbenzene) cation was generated by electrolytic oxidation of $0.002M$ solutions in 1,2-dimethoxyethane. The measurements were made with an X-band superheterodyne spectrometer.[1,2] Room-temperature data for the first three radicals have been reported previously.[3,4]

In the usual sigma–pi interaction theory,[5–7] the hyperfine splittings a_i are expressed as linear functions of the pi-electron spin densities ρ_k^π, $a_i = \Sigma_k Q_{ik}\rho_k^\pi$, where the Q_{ik} are the sigma–pi parameters. The temperature dependence of the a_i implies that either the Q_{ik}, the ρ_k^π, or both, are functions of temperature. The separation of the lines in a spectrum may not, however, give the true hyperfine splittings because of either electron[8] or Heisenberg[9] exchange, both of which would cause the lines to coalesce at high temperatures, i.e., cause an apparent negative temperature coefficient of the splittings. The positive temperature coefficient observed for the nitrogen splittings shows that some mechanism other than exchange effects plays a significant role.

The opposite signs of the temperature coefficients of the nitrogen and proton splittings can be used to demonstrate that the sigma–pi parameters are functions of temperature: The nitrogen hyperfine splitting in the pyrazine cation can be written[3] $a^N = Q_{N(C_2H)}{}^N\rho_N{}^\pi + 2Q_{CN}{}^N\rho_C{}^\pi$ where the first term is predominant[3] and is known to be positive.[10,11] The proton splittings are given by $a_{CH}{}^H = Q_{CH}{}^H\rho_C{}^\pi$ and $a_{NH}{}^H = Q_{NH}{}^H\rho_N{}^\pi$, and if all the Q's are assumed to be temperature-independent, it follows that the signs of the temperature coefficients of the nitrogen and proton splittings should be the same, in contradiction to experiment. Similar considerations apply to the other radicals in Table I, so that at least part of the observed temperature dependence arises because the Q's are functions of temperature.

Although there is a small but experimentally significant temperature coefficient for the CH-proton splittings in the dihydro- and dideuteropyrazine cations, the temperature coefficient for the methyl-proton splittings in the tetramethylpyrazine and diaminodurene cations is negligible. This result suggests that the methyl-proton Q parameter is independent of temperature and also perhaps that the spin densities do not change significantly with temperature.

Replacement of the N–H hydrogen atom by deuterium causes several effects: The ratio of the NH-proton splitting to the ND-deuteron splitting is about 6.33, a value 2.8% lower than the ratio of the magnetic moments, 6.514. A ratio of 6.3 was also found for this radical by Bolton *et al.*[4] Fessenden and Schuler[12] observed a -1.1% isotope effect for the a^H/a^D ratio in the methyl radical, and in the ethyl radical the methylene positions give -1.0% and the methyl-group positions $+1.1\%$. Deuterium substitution also causes a relatively large change in the nitrogen splittings and, in the pyrazine cation, a small but experimentally significant change in the CH-proton splitting. The change in the methyl-proton splitting in the tetramethylpyrazine cation on deuteration is considerably less, however, and is probably within the experimental errors. The fractional temperature coefficients of the splittings, $|a_i|^{-1}(d|a_i|/dT)$, in the deuterated radicals are not significantly different from those for the undeuterated species.

Preliminary calculations indicate that both the temperature dependence of the sigma–pi parameters and the effect of deuterium substitution may arise from a vibrational mechanism[13–15] although all the effects have not been adequately investigated.

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Heavy-Atom Effects on Radiative and Radiationless Processes in Charge-Transfer Complexes

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CHARGE-transfer complexes of acceptors containing heavy atoms (e.g., tetrachloro- or tetrabromophthalic anhydride) with aromatic hydrocarbons as donors show a drastic decrease in the *observed* (radiative and nonradiative) phosphorescence lifetime of the

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TABLE I. Change in lifetime[a] (seconds) due to charge-transfer complexing.

Donor	Naphthalene			Phenanthrene		
	Observed τ_{PD}	Observed τ_{PH}	Calculated[b] τ_{PH}	Observed τ_{PD}	Observed τ_{PH}	Calculated[b] τ_{PH}
Alone	21	2.4		15	3.7	
TCPA	4.2	1.5	1.6	2.6	1.6	1.7
TBPA	0.39	0.29	0.34	0.40	0.34	0.37

[a] τ_{PH} and τ_{PD} represent the phosphorescence life of the charge-transfer complex of protonated and deuterated donors, respectively.
[b] Calculated according to Eq. (1) (assuming that only the radiative lifetime changes).

donors.[1] The question immediately arises: how much of this observed change is due to an increase in the radiative transition probability, and how much of it is due to an increase in the radiationless transition probability? In previous work, an upper limit of the increase of the transition probabilities of these two processes is given.[2] In the present work, a new method is used to separate the heavy-atom effects on radiative and nonradiative processes of the donor. Protonated and deuterated aromatic hydrocarbons are used as donors. The radiationless transition probabilities of the latter compounds are negligible (it can be shown that the agreement obtained in Table I is not affected if this statement is not correct) because of the small vibration overlap factors.[3] In the present work one assumes that the heavy atom *affects only the radiative transition probability*. According to this assumption, the observed lifetime of the deuterated complexes is the actual radiative lifetime of the $T_1 \leftrightarrow S_0$ transition of the donor in the complex. These values are then to be used together with the radiationless lifetimes of the protonated hydrocarbons to predict the *observed lifetime* for four different complexed protonated donor hydrocarbons. The excellent agreement with the measured values supports the assumption that *the heavy-atom effect on the donor lifetime in a charge-transfer complex of this type is due mainly to an increase in the radiative transition probability.*

The acceptors used were TCPA (tetrachlorophthalic anhydride) and TBPA (tetrabromophthalic anhydride). $C_{10}H_8$, $C_{10}D_8$, $C_{14}H_{10}$, and $C_{14}D_{10}$ served as the donor components. The compounds were purified as follows: TCPA by zone melting; TBPA by recrystallization from ether solution; $C_{10}H_8$ and $C_{14}H_{10}$ by vacuum sublimation. Studies were carried out in hydrocarbon glasses at 77°K. The exciting radiation used was the 3660-Å mercury line. The recorded spectra corresponded to the donor phosphorescence. The decay was exponential for both TCPA complexes but not for the TBPA complexes. In the latter case the slight nonexponential behavior arose from the superimposed emission of the uncomplexed TBPA. Since the TBPA emission is short-lived, the lifetime of the donor was readily determined from the long-lived component of the decay.

The lifetimes given in Table I demonstrate the much greater sensitivity to charge-transfer complexing of the deuterated species relative to their protonated counterparts. These results suggest that the decrease in τ_P is due principally to the enhanced $T_1 \leftrightarrow S_0$ radiative transition. Thus if one assumes that the radiationless rate is unchanged by complexing, the observed phosphorescence lifetime τ_{PH} of the protonated donor in a charge-transfer complex can be predicted using the expression

$$1/\tau_{PH} = (1/\tau_{PD}) + (1/\tau_{NH}), \qquad (1)$$

where τ_{NH} is the nonradiative lifetime of the uncomplexed protonated hydrocarbon and τ_{PD} is the observed lifetime of the complex of the deuterated hydrocarbon with the same acceptor.

The comparison between the predicted and the observed values of τ_{PH} is given in Table I. If both the radiative and radiationless $T_1 \leftrightarrow S_0$ transitions were appreciably affected in forming a charge-transfer complex, it would be difficult to understand the excellent agreement shown in Table I. It would be specially surprising if there were significant changes in these two processes which compensate for each other, in four different cases, so as to produce the agreement found upon assuming that only the radiative corrections are important.

The results of Table I might then be taken to indicate that *the heavy atom in a charge-transfer complex of the type examined enhances the $T_1 \leftrightarrow S_0$ radiative transition probability and does not greatly affect the $T_1 \leftrightarrow S_0$ radiationless transition probability.*

The radiative $T_1 \leftrightarrow S_0$ transition of the donor in a complex can be enhanced by spin–orbit mixing with the S–S transitions of the donor,[4] of the acceptor[5] or with the charge-transfer[6] transition. The latter mechanism can be eliminated if the phosphorescence of the complex is found to be polarized perpendicular to the charge-transfer absorption. The degree of polarization of the donor phosphorescence emission of the compounds given in Table I is determined by the method of photoselection[7] using procedures similar to those described elsewhere.[8] In all the compounds examined the emission is found to be positively polarized[9] with respect to the charge-transfer excitation. This result eliminates neither the charge-transfer mechanism nor the other mechanisms unless the geometry of the charge-transfer complex is known. If one assumes a sandwich structure for the charge-transfer complex (which is more probable), one can safely eliminate the mechanisms involving the

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in-plane S–S transitions of the donor and of the acceptor. If the structure of head to tail is assumed, with molecular planes being parallel, the charge-transfer transition would be in-plane polarized, and the results obtained above eliminate the mechanisms involving *out-of-plane S–S* transitions of the complexing molecules.

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NMR Study of Paramagnetic Salts in Aqueous Mixtures of Tetrahydrofuran

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A PREVIOUS NMR study of electrolytes in dioxane–water mixtures[1] has indicated, contrary to interpretations of vapor pressure and some conductance data, that cations were solvated by only water, with negligible activity on the part of dioxane. This study was undertaken using tetrahydrofuran (THF), similar to dioxane, but polar, to discover if this molecule is more effective in competing for electrolytes.

The measurements were carried out on a Varian A60 spectrometer at 40°±1°C. Precision concentric sample tubes were used since aqueous solution studies necessitated an external reference, in this case, cyclohexane. Concentrations of salt were low enough, 0.05*M* or less, to prevent excessive broadening and to permit the measurement of volume magnetic susceptibilities by the NMR technique.[2] The salts were reagent grade and were dried under vacuum before weighing.

A summary of the chemical-shift data, corrected for susceptibility, is given in Table I, wherein a positive value of δ, defined as

$$\frac{H_{\text{solvent}}-H_{\text{solution}}}{H_0},$$

and expressed in parts per million, indicates a downfield displacement of a particular signal upon the addition of electrolyte to a solvent mixture. Water linewidths, in cycles per second, are listed in the column headed by $\Delta\nu$, and the subscripts α and β refer to the appropriate tetrahydrofuran protons.

In all solvent mixtures the water signal is the only one affected to any extent by the addition of salt. The water shift data may be treated semiquantitatively by use of Bloembergen's expression[3] for solvent shifts due to the presence of paramagnetic ions, that is, $\delta = c\,|\psi(0)|^2/n$, where $|\psi(0)|^2$ is the probability of the odd electrons of the paramagnetic ion being at the solvent proton, n is the concentration of solvent molecules, and the constant c includes the solution susceptibility, corrected for in this study, and the coordination number of the ion. In the three solvent systems, from 75% to 25% water, the molar ratios for water are about 3:2:1, respectively. Normalizing to equal salt concentration and assuming equal probability of interaction in all solvents, one would predict equal solvent shifts in the 25% and 50% water mixtures and shifts lower by about a third in the 75% water mixture. This is observed, to within 10%, in the $CoCl_2$ and $FeCl_2$ systems.

On the basis of measurements of spin–lattice relaxation times[4–9] in the presence of paramagnetic ions, the more extensive broadening of solvent linewidth should be produced by the addition of Mn^{++}, less by Fe^{++} and Ni^{++}, and least by Co^{++}. This is verified by the water linewidths in Table I, which can be compared to the normal water linewidth of 1.5 cps in these mixtures. No apparent shift displacements of the water line in the Mn^{++} solutions and in two of the Ni^{++} solutions were observed. In the former case, the water line was

Table I. Paramagnetic salts in aqueous mixtures of tetrahydrofuran (THF).

% THF	Salt (moles/liter)	H_2O δ	H_2O $\Delta\nu$	THF δ^α	THF δ^β
25	$CoCl_2$(0.05)	+0.39	4	−0.04	−0.03
	$FeCl_2$(0.05)	+0.88	12	0	0
	$MnCl_2$(0.001)	0	26	−0.06	−0.05
	$NiCl_2$(0.05)	0	13	0	0
50	$CoCl_2$(0.05)	+0.61	5	−0.02	0
	$FeCl_2$(0.05)	+1.31	18	+0.05	+0.07
	$MnCl_2$(0.001)	0	40	0	0
	$NiCl_2$(0.05)	0	17	−0.06	−0.03
75	$CoCl_2$(0.025)	+0.64	4	+0.02	+0.02
	$FeCl_2$(0.025)	+1.21	16	+0.03	+0.03
	$MnCl_2$(0.001)	0	90	0	0
	$NiCl_2$(0.025)	+0.10	19	+0.02	+0.02

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