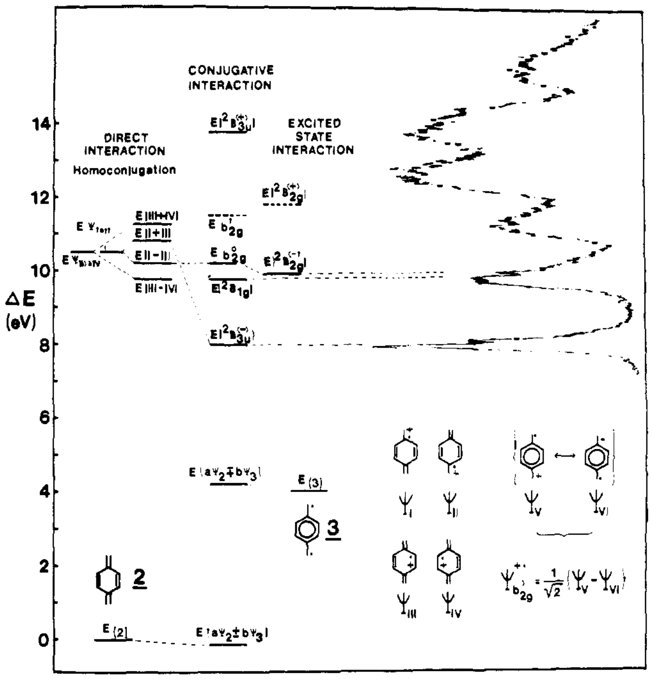

Figure 2.

tures of the conjugated diene units ($S_{1,3} \simeq 1.44$ eV). The observed positions of the first two bands in the spectrum of **2** are therefore in excellent agreement with the predictions of the simple SR method.

The zero-order SR method also predicts the position of the third Π band in the spectrum of **2** ($^2B_{2g}$, $1/\sqrt{2}(\Psi_{\mathrm{I}} - \Psi_{\mathrm{II}})$, Figure 2) at 10.2–10.5 eV. The value depends on the magnitude of the *direct* interaction between the ionic structures derived from the exocyclic ene units, which should be less than 0.3 eV. The observed spectrum shows no clear band maximum in this region although the measured total area under the second peak is greater (1.2:1) than that under the first. This observed second band could thus possibly arise from the unresolved superposition of the zero-order $^2B_{2g}$ and $^2B_{1g}$ stationary states.

We believe that a more likely explanation for both the low energetic position (band maximum less than 10.2 eV) and low apparent intensity of the third Π band is mixing of the zero-order b_{2g} structure ($b_{2g}{}^0$, $1/\sqrt{2}(\Psi_{\mathrm{I}} - \Psi_{\mathrm{II}})$) with the antisymmetric combination of the two *ionic* structures (Ψ_{V}, Ψ_{VI}, Figure 2) derived from the singlet diradical (**3**, Figure 2). The latter combination ($1/\sqrt{2}(\Psi_{\mathrm{V}} - \Psi_{\mathrm{VI}})$) corresponds to an optically excited (PES "forbidden")[8a] structure of the radical cation which is also of b_{2g} symmetry ($b_{2g}{}^1$).[8b] The stationary state giving rise to the lowest b_{2g} PES band must be a linear combination of the two b_{2g} ionic structures ($\Psi_{^2B_{2g}}{}^{\cdot+} = a^+\Psi_{b_{2g}{}^0}{}^{\cdot+} \pm b^+\Psi_{b_{2g}{}^1}{}^{\cdot+}$). The energy of the first $^2B_{2g}$ stationary state will be lowered by this "through structure interaction". The ratio of intensity of transition to the mixed $^2B_{2g}$ state over that to a relatively unmixed state ($^2B_{1g}$ say) can be approximated[9] as

$$\frac{I_{^1A_{1g}-{}^2B_{2g}}}{I_{^1A_{1g}-{}^2B_{1g}}} = \left[\frac{\langle\Psi_{^1A_{1g}}|\Psi_{^2B_{2g}}{}^{\cdot+}\rangle}{\langle\Psi_{^1A_{1g}}|\Psi_{^2B_{1g}}{}^{\cdot+}\rangle}\right]^2 \simeq [a^+]^2 \qquad (1)$$

The intensity contribution of the lowest $^2B_{2g}$ Π band should be somewhat low unless $[a^+]^2 \simeq 1$ (no mixing).

These qualitative considerations lead us to suggest that the lowest $^2B_{2g}$ band maximum is fortuitously near that for the $^2B_{1g}$ band (9.7 eV) and that the former contributes only a fractional intensity increment to the superposition. This assignment requires the $b_{2g}{}^1$ diradical ionic basis structure to be fairly close, in energy, to the $b_{2g}{}^0$ structure so that mixing is strong *in the ionic states.*[10] The assignments of the first two bands are more straightforward and indicate that the ground state structure of *p*-quinodimethane is that of a polyene as indicated by **2** though diradicals with lifetimes less than 10^{-5} sec (4,4′-dimethylylbibenzyl),[11] which intervene between **1** and **2**, would not be detected.

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(9) As shown in Figure 2, the ground state must also contain a component of the neutral diradical (**3**) ($\Psi_{^1A_{1g}} = a\Psi_2{}^0 \pm b\Psi_3{}^0$) and a less approximate expression for the intensity ratio is,

$$\frac{I_{^1A_{1g}-{}^2B_{2g}}}{I_{^1A_{1g}-{}^2B_{1g}}} \simeq \left[\frac{(a^{\bullet}a \pm b^{\bullet}b)}{a}\right]^2$$

The approximation in eq 1 neglects ground state mixing ($b \approx 0$). The mixing of excited structures in the $^2B_{3u}$ and $^2B_{1g}$ stationary states has also been neglected. These interactions as well as that for the ground state (**2** ↔ **3**) should be small because of the larger energy gap between zero- and first-order basis structures.
(10) This suggested assignment of the third Π band should be tested through the investigations of substituted analogs in which the accidental degeneracy would be lifted.
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Received November 16, 1974

Acidities of Carbon Acids. V. Correlation of Acidities in Dimethyl Sulfoxide with Gas-Phase Acidities

Sir:

The degree of dissociation of an acid in solution, relative to the gas phase, is enormous because solvation enthalpies of ions are exothermic to the extent of 50–90 kcal/mol. It is not surprising, then, to find that substituent effects on solution acidities are greatly attenuated compared to those observed in the gas phase. For example, the Hammett ρ for acidities of meta- and para-substituted benzoic acids is about 2.5 in dimethyl sulfoxide (DMSO)[1] as compared to about 10 in the gas phase.[2] In contrast to these results, we now report two examples where substituent effects on acidities in solution (DMSO) not only parallel those found in the gas phase,[3] but also approach them in magnitude (Table I, Figure 1).

These results suggest that the substituent effects on solution acidities in DMSO for these molecules correspond to a

Table I. Comparison of Intrinsic Gas-Phase Equilibrium Acidities and Solution Equilibrium Acidities

Acid	p*K* (DMSO)[a]	$\Delta G°$ (DMSO)[b]	$\Delta\Delta G°$ (DMSO)[c]	$\Delta G°$ (g)[d]	$\Delta\Delta G°$ (g)[c]
CH_3COCH_3	26.7	36.4	(0.0)	50.1	(0.0)
CH_3COPh	24.7	33.9	3.5	45.6	4.5
CH_3COCH_2Ph	19.4	26.6	9.8	36.2	13.9
$(CH_3CO)_2CH_2$	13.4[e]	18.3	18.1	28.0	22.1
CH_3COCH_2COPh	12.7[f]	17.4	19.0	24.2	25.9
CH_3CN	31.2	42.7	(0.0)	47.6	(0.0)
$PhCH_2CN$	21.9	30.0	12.7	35.0	12.6
$CH_2(CN)_2$	11.1[g]	15.1	27.6	17.2	30.4
	18.1	24.8		39.1	
$(Ph)_2CH_2$	32.3	43.2		47.0	

[a] Absolute acidities. As a result of anchoring our p*K* scale to absolute measurements in the 7–12 p*K* region the values reported earlier[4] have been adjusted upward by slightly more than 2 p*K* units; the p*K* of fluorene, which was previously used as a reference standard, is now 22.6. [b] At 25°. [c] Not statistically corrected. [d] Data of J. B. McMahon and P. Kebarle (ref 3) obtained at 327°. [e] Lit. p*K* 13.4.[5] [f] Lit. p*K* 12.1.[5] [g] Lit. p*K* 11.0.[5]

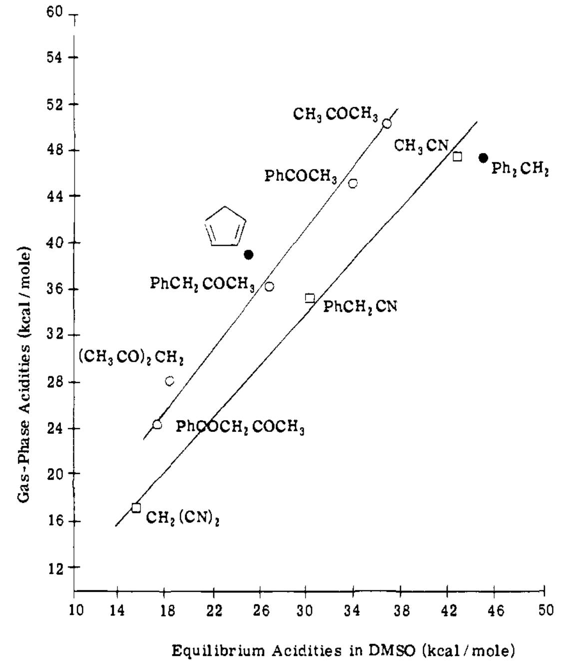

Figure 1. Equilibrium acidities of carbon acids in dimethyl sulfoxide (DMSO) solution plotted against intrinsic gas-phase acidities.

surprising degree to the intrinsic substituent effects revealed by gas-phase acidities. In other words, the solvent is exerting a relatively constant effect in both the nitrile series and the ketone series. The failure of substituent effects to be attenuated appreciably here is probably associated with the fact that the negative charge is delocalized in each instance essentially over the entire anion. This contrasts with the situation with meta- and para-substituted benzoic acids, where the charge is localized largely on the carboxylate ion. Solution substituent effects of a magnitude comparable to gas-phase substituent effects have also been observed for other highly delocalized ions, namely, aromatic radical anions,[6] and aryl carbocations.[7]

Although the substituent effects within the ketone and nitrile families are comparable in solution and in the gas phase (Figure 1), there is some indication of specific solvation effects. In the gas phase acetonitrile is a stronger acid than acetone by 2.5 kcal/mol,[8] whereas in DMSO solution acetonitrile is the weaker acid by 6.3 kcal/mol (Table I).

It may be significant that cyclopentadiene, which gives a symmetrically delocalized anion, is more acidic in DMSO, relative to the gas phase, than either the nitrile or ketone families (Figure 1). One might have expected on this basis that diphenylmethane would also be relatively more acidic in DMSO than in the gas phase, but it is not (Figure 1). This is consistent with other data, however, which indicate that twisting of the phenyl groups is required in $(Ph)_2CH^-$ anion.[9]

We anticipate that additional comparisons of gas phase and DMSO solution acidities will reveal further significant information concerning the nature of substituent effects and the nature of solvent effects.

Acknowledgment. We are grateful to the National Science Foundation (GP 42725X) for support of this research.

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Consecutive 3,5 Shifts in Pyridine 1-Oxide Rearrangements. One-Step Furopyridine Synthesis

Sir:

When the 3- and 5-positions are blocked in a pyridine 1-oxide, reaction with benzyne gives, under conditions of kinetic control, products resulting from 1,3- and/or 1,5-sigmatropic shifts in the original 1,2-dihydropyridine 1,3-cycloadduct.[1] With 3,5-dihalogenated pyridine 1-oxides (**1**) elimination of hydrogen halide from the 1,5-sigmatropic shift product leads to benzofuro[3,2-*b*]pyridines in good yield.[1] Furopyridines are of interest since perhydro derivatives occur in the alkaloids febrifugine and jervine[2] and furo[2,3-*b*]quinolines are present in dictamnine and related alkaloids.[3] Little work has been carried out on the synthesis