methyl sulfoxide solution [50% (v/v)] (Figure 1d), the presence of a significant amount of the conformer (**2B**) is clearly indicated. They also stated that methyl salicylate (**4**) did not form an intramolecular hydrogen bond to any significant degree. In contrast, the ^{13}C NMR spectra of methyl salicylate in the same "regular" deuteriodimethyl sulfoxide solution [50% (v/v)] clearly reveals the existence of the intramolecularly hydrogen-bonded conformer (**4A**) (Figure 1g and 1h), which is in accord with Curtin's and Byrn's infrared study.[14] The ratio of these two representative conformers (**4A/4B**) is 1.77.[15] Their equilibration rate is enhanced by acid and depends on temperature. At 118 °C the C_1 signals of **4A** (160.9 ppm at 25°C) and **4B** (160.7 ppm at 25 °C) coalesce, and the $^{13}C-^1H$ three-bond coupling vanishes. In view of these discrepancies, it must be cautioned against the use of the ortho-substituent constants derived from the earlier ^1H NMR studies.[12] Among the results of the complete analysis of the $^{13}C-^1H$ long-range coupling constant it is worth noting that the syn $^{13}C-^1H$ coupling constant ($^3J_{C_2-OH} = 4.4$ Hz) is considerably smaller than the anti coupling constant ($^3J_{C_6-OH}$ 8.3 Hz), analogous to the olefinic system.[5e] Therefore, $^{13}C-^1H$ long-range coupling constants can be useful in the conformational study of the hydroxy functional group.

The complete analysis of the ^{13}C spectrum of an isoflavone derivative (**5**) can further illustrate the potential usefullness
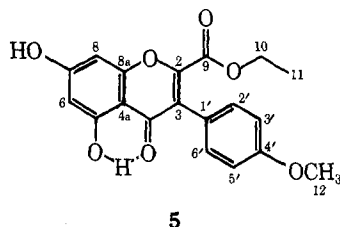
5

of $^{13}C-^1H$ long-range coupling constants (Figure 2).[16] Using the additivity principle of chemical shift theory, it is difficult to differentiate C_5, C_7, C_{8a}, and $C_{4'}$ and to distinguish the C_8 from C_6, and C_3 from $C_{1'}$ resonance signals. However, the detailed analysis of the long-range $^{13}C-^1H$ coupling constants allows one to completely resolve these ambiguities. In the proton-coupled spectrum in deuterioacetone solution, $C_{4'}$ shows as an unresolved multiplet at 160.2 ppm due to coupling with the methoxy protons, $H_{2'}$ and $H_{6'}$, and possibly with $H_{3'}$ and $H_{5'}$. C_{8a} has only one two-bond proton (H_8) and thus appears as a doublet at 157.5 ppm. A triplet at 161.1 ppm can be assigned to C_7, since only this carbon possesses two two-bond protons (H_6 and H_8). The C_5 signal is split into a double doublet owing to the coupling with H_6 and hydroxy proton which strongly indicates the intramolecular hydrogen bonding between this hydroxy group and the C_4 carbonyl group. This hydrogen bonding also results in the further splitting of C_6 signal ($^3J_{C_6-OH} = 7.0$ Hz), which is shown as double doublet of doublets at 99.6 ppm while the C_8 signal appears as double doublet at 94.0 ppm. C_{4a} is shown as a quartet due to the long-range coupling with H_6, H_8, and C_5-OH protons. Here, the stereospecificity of the three-bond $^{13}C-^1H$ coupling is disclosed again [$^3J_{C_{4a}-OH} = 4.3$ Hz (syn); $^3J_{C_6-OH} = 7.0$ Hz (anti)]. $C_{1'}$ can be easily distinguished from C_3 by its normal three-bond coupling constant ($^3J_{C_{1'}-H_{3'(5')}} = 8.0$ Hz), whereas the $^3J_{C_3-H_{2'(6')}}$ is reduced to 4.0 Hz. The carbons $C_{3'(5')}$ couples with $H_{5'(3')}$ through the oxygen-substituted carbon. The singlet at 151.2 ppm is assigned to C_2 simply because it is the only aromatic carbon without any two- or three-bond proton.

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(8) (a) From a large number of accumulation of high resolution spectra of aromatic compounds, this conclusion may be held for most electronegative substituents. Further results will be published soon. (b) First-order analysis was carried out. However the spectra of o-hydroxyacetophenone (**2**) appear non first order, and further detailed calculation will be necessary to unravel its precise long-range coupling constants.

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(10) In ether solution, this interconversion is considerably reduced; thus the intramolecular hydrogen bonding can be detected under this condition (Figure 1f), but the $^3J_{C-OH}$ (6.6 Hz) is smaller than the normal value (~7.4 Hz) suggestive of the moderate exchange rate between the two conformers.

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(15) The ratio seems to depend on the concentration. However, the critical factor is the water content in the laboratory deuteriodimethyl sulfoxide. The "regular" deuteriodimethyl sulfoxide used in the experiments contains 0.2–0.3% (w/w) water. Only intramolecular hydrogen-bonded conformer can be detected in "dry" deuteriodimethyl sulfoxide (distilled over calcium hydride twice just prior to use) solution. All ^{13}C NMR spectra were obtained in 10-mm spinning tube at ambient temperature (~25 °C). The ^{13}C resonances of deuteriodimethyl sulfoxide, deuterioacetone, and deuteriochloroform serve as internal references.

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Carbon Acids. 8. The Trimethylammonio Group as a Model for Assessing the Polar Effects of Electron-Withdrawing Groups

Summary: The relative size of polar and resonance contributions for CH_3CO, $PhCO$, $PhSO_2$, CN, and NO_2 groups in stabilizing a number of carbanions has been assessed from equilibrium acidity measurements by using the trimethylammonio group, Me_3N^+, as a model for the polar effect.

Sir: The trimethylammonio group, Me_3N^+, is unique in that it exerts a strong polar action and yet is incapable of acting as a π acceptor. As such, it has frequently been used as a model for judging the polar character of electron-withdrawing groups, G, and, from this, the extent to which G is capable of acting as a π acceptor when interacting with an acidic site across a benzene ring, as in p-$GC_6H_4NH_3^+$ or p-GC_6H_4OH.[1-3] We now wish to report results in which the effect of Me_3N^+ is used as a model to assess the resonance vs. polar character

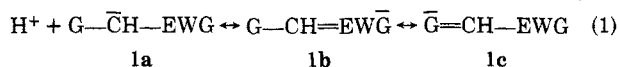**Table I. Equilibrium Acidities in Dimethyl Sulfoxide Solution for Carbon Acids, GCH_2EWG**[a]

G	pK (GCH_2CN)	pK (GCH_2SO_2Ph)	pK (GCH_2COPh)
H	31.3	29.0	24.6
Me	32.5[b]	31.0	24.4
Me_3C		31.2[c]	25.3[c]
Me_3N^+	20.6	19.4	14.6
CH_3CO		12.5	12.7
PhCO	10.2	11.4	13.1
$PhSO_2$	12.0	12.2	11.4
CN	11.1	12.0	10.2
NO_2		7.1	7.7

[a] The data for G = Me_3N^+ are from the present work; each acidity constant was determined from at least two three-point titrations with at least two indicators, and are reproducible to better than ± 0.1 pK unit. Other pK's are from ref 4 or 17, or from unpublished work from this laboratory. [b] Estimated assuming an average of ΔpK for $MeCH(CN)_2$ vs. $HCH(CN)_2$ and- $MeCH(Ph)CN$ vs. $HCH(Ph)CN$. [c] Determined with only one indicator.

of G when attached directly at the acidic site in a carbon acid, GCH_2EWG, where EWG is CN, $PhSO_2$, CH_3CO, PhCO, or NO_2.
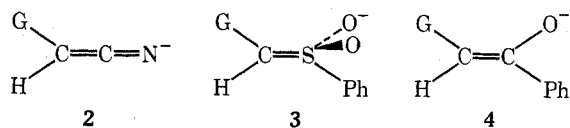
The positions of the equilibria described in eq 1, which can be determined indirectly by the competitive indicator method in dimethyl sulfoxide (Me_2SO) solution,[4] are governed for a given EWG, by the polar effect of G and by the ability of G to delocalize the charge in these highly basic anions.

$GCH_2EWG \rightleftharpoons$

$$H^+ + G\text{---}\bar{C}H\text{---}EWG \leftrightarrow G\text{---}CH\text{=}EW\bar{G} \leftrightarrow \bar{G}\text{=}CH\text{---}EWG \quad (1)$$

$$\text{1a} \qquad\qquad \text{1b} \qquad\qquad \text{1c}$$

When G is H, Me, *t*-Bu, or Me_3N^+ resonance contributor **1c** is of little or no importance. The increase in acidity when G is Me_3N^+, compared with when G is H, Me, or *t*-Bu, can then be taken as a measure of the polar effect of Me_3N^+, since the polar effects of H, Me, and *t*-Bu are close to zero. The data in Table I show that this increase is large, ranging from ~9 to 12 pK units (equivalent to 13 to 16.5 kcal/mol) depending on the carbon acid system and model chosen. Choosing ΔpK between $MeCH_2EWG$ vs. $Me_3N^+CH_2EWG$ as a reasonable model of the polar effect of Me_3N^+, we can use σ_I for Me_3N^+ (0.82[5]) to obtain ρ_I from the Taft equation, ΔpK $= \sigma_I\rho_I$. An estimate of the polar contribution for each group, G, can then be obtained from ρ_I and the σ_I constants for G (Table II).

We must emphasize at the outset that the results in Table II represent only a rough approximation of relative polar and resonance contributions of G. The Me group in $MeCH_2EWG$ is obviously a poor model, both sterically and electronically, for Me_3N^+.[11] Furthermore, the steric relationships of G to the negative charge center in the anions obviously change markedly in the three carbon acid systems (compare, e.g., **2**, **3**, and **4**). Nevertheless, despite the crudeness of the model, the dif-

ferences observed are so large and so consistent for the various carbon systems that we believe significant conclusions can be drawn from the data in Table II.

Note first that, although the ΔpK's for Me_3N^+ are large, the ΔpK's observed for the other groups are always larger. Since, by any account, the polar effect (σ_I) for Me_3N^+ is larger than

Table II. Estimate of Polar and Resonance Contributions to the Acidifying Effects of G in GCH_2CN, GCH_2SO_2Ph, and GCH_2COPh Carbon Acids

G	σ_I[a]	ΔpK$_{calcd}$[b]	ΔpK$_{obsd}$[c]	$\Delta\Delta$pK
GCH_2CN Carbon Acids; ρ_I = 14.5				
Me	-0.04[d]		(0.0)	
Me_3N^+	0.82[e]	(11.9)	11.9	
PhCO	0.30[f]	4.3	22.3	18.0
CN	0.56	8.1	21.4	13.3
$PhSO_2$	0.57[g]	8.3	20.5	12.2
GCH_2SO_2Ph Carbon Acids; ρ_I = 14.1				
Me	-0.04[d]		(0.0)	
Me_3N^+	0.82[e]	(11.6)	11.6	
CH_3CO	0.28	4.0	18.5	14.5
PhCO	0.30[f]	4.2	19.6	15.4
CN	0.56	7.9	19.0	11.1
$PhSO_2$	0.57[g]	8.1	18.8	10.7
NO_2	0.65	9.2	23.9	13.7
GCH_2COPh Carbon Acids; ρ_I = 11.9				
Me	-0.04[d]		(0.0)	
Me_3N^+	0.82[e]	(9.8)	9.8	
CH_3CO	0.28	3.3	11.7	8.4
PhCO	0.30[f]	3.6	11.3	7.7
CN	0.56	6.7	14.2	7.5
$PhSO_2$	0.57[g]	6.8	13.0	6.2
NO_2	0.65	7.8	16.7	8.9

[a] From ref 10 unless otherwise noted. [b] From ΔpK $= \sigma_I\rho_I$. [c] From the data in Table I relative to $MeCH_2EWG$.[11] [d] Taken as zero in the calculation of ρ_I. [e] See ref 5. [f] Estimate (assuming a slightly larger value than for CH_3CO). [g] See ref 8.

for any uncharged group, it follows that all of the other groups being considered (CH_3CO, PhCO, $PhSO_2$, CN, and NO_2) must be exerting stabilizing effects on the carbanions that are much larger than those expected from their polar contributions. The $\Delta\Delta$pK's in Table II provide a rough estimate of the sizes of these (resonance) effects. They range from 6.2 to 18.0 pK units, equivalent to 8.5 to 25 kcal/mol, depending on the group and the carbon acid system into which it is substituted. In the GCH_2CN and GCH_2SO_2Ph systems the resonance effects for all groups are much larger than their (calculated) polar effects. *This is contrary to the effect of p-G in benzene systems, where the polar contribution is usually dominant.*[3,10,12]

For a given group, G, $\Delta\Delta$pK always decreases as the acidity of the parent model acid, $MeCH_2EWG$, increases.[14] The size of $\Delta\Delta$pK is always larger for the carbonyl functions, CH_3CO and PhCO, than for the cyano or phenylsulfonyl functions, the latter two being nearly equal. (This is consistent with expectations from σ_R^- values.[10]) The large size of $\Delta\Delta$pK for $PhSO_2$ (7.0 to 13.2 pK units) supports the conclusion that this function is capable of a strong conjugative interaction with an α carbanion,[16] comparable in size with that of the cyano function, but somewhat smaller than that of carbonyl or nitro functions.

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(12) Polar contributions are clearly dominant according to the Swain–Lupton analysis.[3] Judging from the relative size of σ_I and σ_R^-, polar contributions are dominant according to the Ehrenson, Brownlee, and Taft dual parameter analysis.[13] These analyses are based on oxygen and nitrogen acid systems. For carbon acid systems, *p*-$G_6H_4CH_2EWG$ our results to date suggest that polar and resonance contributions are more nearly equal.
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Carbon Acids. 9. The Effects of Divalent Sulfur and Divalent Oxygen on Carbanion Stabilities

Summary: Using the trimethylammonio group, Me_3N^+, as a model to calculate the polar effect, the carbanion stabilizing effects of MeO and PhO groups have been found to be smaller than calculated, and the carbanion stabilizing effects of MeS and PhS groups have been found to be much larger than calculated.

Sir: There is long-standing and abundant evidence in the literature to indicate that divalent sulfur causes an adjacent C–H bond to be much more susceptible to cleavage by base than does divalent oxygen.[1] The greater kinetic acidity produced by α-RS (or α-PhS) than α-RO (or α-PhO) groups has been assumed by most experimentalists to be associated with a greater ability of divalent sulfur to stabilize an incipient carbanion in the transition state of the deprotonation reactions by a conjugative effect involving 3d orbitals.[1] On the other hand, theoreticians have generally been skeptical of the need to invoke such conjugative interactions.[2] For example, recent ab initio calculations have failed to reveal any role for 3d orbital conjugation in stabilizing the $HSCH_2^-$ anion, and the conclusion has been drawn that sulfur stabilizes carbanions by polarization, rather than by d-orbital conjugation.[3]

In the previous paper in this series[4] we used the difference in acidities (ΔpK) of $Me_3N^+CH_2EWG$ and $MeCH_2EWG$ (EWG = CN, $PhSO_2$, or PhCO) as a measure of the sensitivities of these carbon acids to polar effects, $\Delta pK = \sigma_I\rho_I$. The ρ_I values were then used in conjunction with σ_I to estimate the polar effect anticipated for a group, G, in the GCH_2CN, GCH_2SO_2Ph, and GCH_2COPh carbon acid systems. When G is a π acceptor it should stabilize the $GCHEWG^-$ anion by

Table I. Comparison of the Acidifying Effects of MeO, PhO, MeS, and PhO Groups with the ir Polar Acidifying Effects

G	$\sigma_I{}^a$	$\Delta pK_{calcd}{}^b$	$\Delta pK_{obsd}{}^c$	$\Delta\Delta pK{}^d$
A. GCH_2CN Carbon Acids; $\rho_I = 14.5$				
Me	-0.04^e	(0.0)	(0.0)	
Me_3N^+	0.82^f	(11.9)	11.9	
PhO	0.38	5.2	4.4	-0.8
PhS	0.30^g	4.4	11.7	7.3
B. GCH_2SO_2Ph Carbon Acids; $\rho_I = 14.1$				
Me	-0.04^e	(0.00)	(0.0)	
Me_3N^+	0.82^f	(11.6)	11.6	
MeO	0.27	3.8	0.3	-3.5
PhO	0.38	5.3	3.1	-2.2
MeS	0.23	3.2	7.6	4.4
PhS	0.30^g	4.2	10.5	6.3
C. GCH_2COPh Carbon Acids; $\rho_I = 11.9$				
Me	-0.04^e	(0.0)	(0.0)	
Me_3N^+	0.82^f	(9.8)	9.8	
MeO	0.27	3.2	1.5	-1.7
PhO	0.38	4.5	3.3	-1.2
PhS	0.30^g	3.6	7.3	3.7
PhSe	0.24^h	2.9	5.8	2.9
D. 9-G-Fluorene Carbon Acids; $\rho_I = 8.1$				
Me	-0.04^e		(0.0)	
Me_3C	-0.07^e	(0.0)		
Me_3N^+	0.82^f	(6.55)	6.55^i	
MeO	0.27	2.2	0.2	-2.0
PhO	0.38	3.1	2.4	-0.7
MeS	0.23	1.9	4.3	2.4
PhS	0.30^g	2.4	6.9	4.5

^{a} From ref 9 unless otherwise noted. ^{b} From $\Delta pK = \sigma_I\rho_I$. ^{c} Relative to the p$K$ of $MeCH_2CN$ (32.5, series A), or $MeCH_2SO_2Ph$ (31.0, series B), or $MeCH_2COPh$ (24.4, series C), or 9-methylfluorene (22.3, series D). ^{d} $\Delta\Delta pK = \Delta pK_{obsd} - \Delta pK_{calcd}$. ^{e} Taken as (0.0). ^{f} An average value; see footnote 5 of ref 4. ^{g} See ref 10. ^{h} Calculated from 0.45 $\sigma^*_{CH_2SePh}$ using the data of L. D. Pettit, A. Royston, C. Sherrington, and R. J. Whewell, *J. Chem. Soc. B*, 588 (1968). ^{i} Relative to 9-*tert*-butylfluorene (pK = 24.55).

conjugation, as well as by a polar effect, and the increase in acidity observed should be larger than that calculated from the $\sigma_I\rho_I$ relationship. This was found to be true when G is a strong π-acceptor group (CH_3CO, PhCO, NO_2, $PhSO_2$, CN), the $\Delta\Delta pK$'s ranging from 6.2 to 18.0 pK units.[4] If RS or PhS groups have π-acceptor capacity, we would then expect to find that the acidities are enhanced to an extent greater than expected on the basis of their polar effects; no enhancement is expected, of course, for RO and PhO groups. The results are summarized in Table I for four carbon acid systems.

For reasons given earlier,[4] we do not expect the Me group in $MeCH_2EWG$ to be a good model sterically or electronically for the Me_3N^+ group in $Me_3N^+CH_2EWG$. In addition, the steric relationships between G and the site of electron charge density changes for the various $GCHEWG^-$ anions.[4] Steric effects for 9-substituted fluorenes are more severe than in the GCH_2EWG carbon acids. In fluorene, substitution of Me_3C for H at the 9 position causes a 1.7 pK unit decrease in acidity, whereas substitution of Me for H causes a 0.5 pK unit *increase* in acidity. In the fluorene system 9-*tert*-butylfluorene has been used as a model for 9-trimethylammoniofluorene, but 9-methylfluorene has been used as a model to calculate ΔpK's for 9-MeO-, 9-PhO-, 9-MeS-, and 9-PhS-fluorenes. Although the difficulties in choosing proper models are such as to make the calculations of polar effects of an approximate nature, the