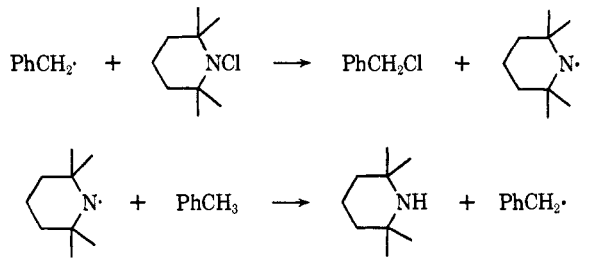
has often been rationalized on the basis of an unrealistically low value for $D[Me_2N\text{-}H]$. Tetramethylpiperidyl would, if anything, be expected to be less reactive in abstractions than dimethylamino. However, our results indicate that it is fairly active; in particular, it abstracts hydrogen from toluene at 24° (k^2_{abs} = 0.69 M^{-1} sec^{-1}) considerably more easily than *tert*-butylperoxy (k^2_{abs} = 0.05 M^{-1} sec^{-1}) or benzylperoxy (k^2_{abs} = 0.24 M^{-1} sec^{-1}) at 30°.[57] It should be possible, therefore, to set up a chain reaction at ambient temperatures in which one step in the propagation involves abstraction of a benzylic hydrogen by a dialkylamino radical. The chain length could be quite long if the second propagation step was rapid and if the amino radical were tetramethylpiperidyl. A reaction that might fulfill these conditions is the chlorination of toluene using the chloramine in nonacidic media.



The deuterium isotope effects observed in the reaction of tetramethylpiperidyl with toluene and with cyclohexane are remarkably large for hydrogen abstractions.[58] Thus, the isotope effect for abstraction from toluene *vs.* perdeuteriotoluene by dimethylamino at 136° yields k_H/k_D = 4.0.[7] Isotope effects are often enhanced in sterically hindered hydrogen transfers over the values found for their unhindered counterparts.[59,60] This is normally attributed to tunneling[59-61] and to a more extensive loss of zero-point energy as the barrier becomes more symmetric.[59-64] The rather low A factors found for hydrogen abstraction by tetramethylpiperidyl can also be ascribed to tunneling.[60-62] Low A factors are a common feature of hydrogen abstractions by sterically hindered radicals[57,65] and by unhindered radicals from sterically hindered positions.[57]

Tetramethylpiperidyl reacts rapidly and quantitatively with oxygen to yield the corresponding nitroxide. It must therefore be assumed that other dialkylamino radicals will react in a similar manner. Most workers[18,21] seem agreed that this is the case. The occasional reports[19,20] that dialkylamino radicals do not react with oxygen appear to be due to confusion of the amino radical with the nitroxide. The *N-tert*-butylanilino radical also reacts readily with oxygen[66] but product studies indicate that the *N*-phenyl-2-naphthylamino radical is relatively inert.[67]

(57) J. A. Howard, *Advan. Free-Radical Chem.*, 4, 49 (1971).
(58) There will, of course, be some contribution from secondary isotope effects.
(59) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, 40, 1851 (1962).
(60) E. S. Lewis and L. H. Funderburk, *J. Amer. Chem. Soc.*, **89**, 2322 (1967).
(61) See E. F. Caldin, *Chem. Rev.*, **69**, 135 (1969).
(62) F. H. Westheimer, *ibid.*, **61**, 265 (1961).
(63) C. A. Bunton and V. J. Shiner, Jr., *J. Amer. Chem. Soc.*, **83**, 3214 (1961).
(64) W. A. Pryor and K. G. Kneipp, *ibid.*, **93**, 5584 (1971).
(65) E. T. Denisov, "Konstanti Skorosti Homolyticheski Zhidkofaeni Reaktsii," Nauka, Moscow, 1971.
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(67) R. F. Bridger, *ibid.*, **94**, 3124 (1972).

Medium Effects on the Fluorine-19 Magnetic Resonance Spectra of Fluoropyridines

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Abstract: The effects of some 30 different solvents on the ^{19}F nmr shifts of 2-, 3-, and 4-fluoropyridine have been studied. These solvent-induced chemical shifts could not be correlated with the widely used solvent function which contained the dielectric constant. Instead good correlations were obtained using Dimroth's E_t or Kosower's Z values. Explanations for these observations are discussed.

In the course of our study of relationships of substituent parameters–chemical shifts of substituted fluoropyridines,[1] we observed some unusual medium effects on the chemical shifts. In particular, unsatisfactory results were obtained in our plots of the fluorine chemical shifts with the function $(\epsilon - 1)/(\epsilon + 1)$ or the function $(\epsilon - 1)/(\epsilon + 0.789)$ where ϵ is the dielectric constant of the solvent. This frequently used function was proposed by Emsley and Phillips[2] from the Onsager model to explain solvent effects on the fluorine chemical shifts in aromatic compounds. This led us to look for an alternate parameter which would better explain and predict the effects of solvents on the fluorine chemical shifts of these compounds.

One such solvent parameter which we considered was Kosower's Z which is defined[3] as the energy in kcal/mol of the first charge-transfer band of 1-ethyl-4-carboxymethylpyridinium iodide dissolved in the particular solvent. In general, proton chemical shifts have been found to give only *poor* correlations with Z values, pos-

(1) C. S. Giam and J. L. Lyle, *J. Chem. Soc. B*, 1516 (1970).
(2) (a) J. W. Emsley and L. Phillips, *Mol. Phys.*, **11**, 437 (1966); (b) J. W. Emsley and L. Phillips, *Progr. Nucl. Magn. Resonance Spectrosc.*, 7, 1 (1971); (c) W. T. Raynes and M. A. Raza, *Mol. Phys.*, 20, 555 (1971).
(3) E. M. Kosower, *J. Amer. Chem. Soc.*, **80**, 3253 (1958).

sibly due to important contributions from other effects.[4] However, Anderson and Symons[5] recently claimed that the 2,6-ring proton shifts of 1,4-diethylpyridinium cations correlate well with Z values. For other nuclei (*e.g.*, ^{13}C, ^{31}P), Z values–chemical shift correlations[6-10] have not been established.

We examined the medium effects on the chemical shifts of the fluorine nuclei in fluoropyridines and have found excellent linear relationships in our plots of the chemical shift *vs.* Z, and the related E_t values (see below for the definition of E_t).[11] 2- and 3-fluoropyridine were used as the fluorine probe at the 2 and 3 positions, respectively. 4-Fluoropyridine was too reactive and was not used to evaluate the solvent's influence at the 4 position; instead 4-fluoro-2-picoline was employed. The E_t rather than Z values were used in the plots presented here, because more E_t values are available for nonpolar solvents. E_t is linearly related to Z and is obtained in a manner similar to that used for Z. Our results and observations are reported below.

Experimental Section

Fluorobenzene. This compound was obtained from Aldrich Chemical Co. and was distilled before use, bp 84–85°, $n^{20}D$ 1.4659 (lit.[12] bp 84.5°, $n^{30}D$ 1.4610).

2-Fluoropyridine and 3-fluoropyridine were obtained as previously described; the former had bp 126–127° (lit.[13] 125°) and the latter bp 106–107° (lit.[13] bp 106–107°).

4-Fluoro-2-picoline was synthesized according to the procedure described, bp 128–129° (lit.[14] bp 128–130°).

All solvents were freshly distilled before use and only constant boiling middle fractions were employed.

The nmr spectra were obtained using a Varian Model HA-100 spectrometer equipped with a Hewlett-Packard Model 200 ABR auxilliary audio-oscillator. All measurements were made at 94.075 MHz with approximately 3% (v) solution of the fluoropyridines at ambient temperature. The chemical shifts are reported relative to fluorobenzene as an internal (1%) standard. Positive shifts designate upfield shifts. The fluoropyridines were carefully dried before use.

The spectra were obtained by locking onto an external sample of trifluoroacetic acid and off-setting with the external audio-oscillator.

Results and Discussion

In nmr spectroscopy, the applied magnetic field is related to the magnetic field at the nucleus ($H_{nucleus}$) by the equation

$$H_{nucleus} = (1 - S)H_{applied}$$

Table I. Solvent-Induced ^{19}F Chemical Shifts of 2-Fluoropyridine[a]

Solvent		Solvent	
Phenol	−42.84	2-Propanol	−45.17
Glacial acetic acid	−43.24	DMF	−45.25
Methanol–water (75:25)	−44.09	Benzonitrile	−45.30
Ethylene glycol	−44.34	*tert*-butyl alcohol	−45.31
Ethanol–water (80:20)	−44.54	Nitrobenzene	−45.41
Benzyl alcohol	−44.61	Acetone	−45.43
Methanol	−44.79	Pyridine	−45.45
DMSO	−44.81	Methylene chloride	−45.56
Ethanol	−45.02	2-Picoline	−45.60
Acetic anhydride	−45.04	1,4-Dioxane	−45.63
Nitromethane	−45.10	Methyl iodide	−45.64
1-Butanol	−45.11	Anisole	−45.69
1-Propanol	−45.12	2,6-Lutidine	−45.69
Carbon disulfide	−45.73	Chloroform	−45.90
Ethyl acetate	−45.74	Toluene	−46.06
Diphenyl ether	−45.76	Diethyl ether	−46.09
Chlorobenzene	−45.80	Benzene	−46.12
THF	−45.80	*n*-Hexane	−46.29
Ethyl bromide	−45.82	Carbon tetrachloride	−46.39
Ethyl iodide	−45.82	Cyclohexane	−46.59

[a] Ppm relative to internal fluorobenzene; 3% (v); exptl error = ±0.02 ppm.

where S is the screening constant. The screening constant can be subdivided into six contributions[10,15-17]

$$S = S_g + S_b + S_a + S_w + S_e + S_c$$

where S_g is the contribution to the total shielding of the isolated gaseous molecule, S_b is that due to the bulk magnetic susceptibility of the solvent, S_a the anisotropy of the susceptibility of the solvent molecules, S_w the van der Waals interactions, S_e the reaction field due to the medium, and S_c any complex or specific solvent–solute interaction.

By the use of the proper internal standard, the contribution to the total shielding by S_a, S_b, and S_w can be eliminated. In the cases where there is little or no hydrogen bonding or specific complex formation, the term S_c may be neglected and the only term left to determine the shielding in the isolated molecule is S_e.

For fluorine-19 nmr spectroscopy, the choice of the internal standard is very important. The most widely accepted internal standard has been Freon-11, but other standards have been commonly used and subsequently criticized.[18] Emsley and Phillips[2] suggested the use of hexafluorobenzene as the internal standard of choice for aromatic compounds and Freon-11 for aliphatic compounds. An internal standard with the size, shape, and character similar to those of the molecule under consideration minimizes all contributions to the total shieldings except for that arising from S_e, with a small amount of residual S_w. Taft and his coworkers[12] used fluorobenzene as an internal standard in the fluorine-19 nmr studies of substituted fluorobenzenes. For this study of the fluoropyridines, fluorobenzene was used as the internal standard because it is similar in size, shape, and character (aromatic) to the

(4) (a) A. D. Buckingham, T. Schaefer, and W. G. Schneider, *J. Chem. Phys.*, **32**, 1227 (1960); (b) F. W. Fowler, A. R. Katritzky, and R. J. D. Rutherford, *J. Chem. Soc. B*, 460 (1971).

(5) R. G. Anderson and M. C. R. Symons, *Trans. Faraday Soc.*, **65**, 2537 (1969).

(6) G. C. Maciel and R. V. James, *Inorg. Chem.*, **3**, 1650 (1964).

(7) G. C. Maciel and G. C. Ruben, *J. Amer. Chem. Soc.*, **85**, 3903 (1963).

(8) S. O. Grim, W. McFarlane, E. F. Davidhoff, and T. J. Marles, *J. Phys. Chem.*, **70**, 581 (1966).

(9) S. Brownstein, *Can. J. Chem.*, **38**, 1590 (1960); (b) G. Kotowycz, T. Schaefer, and E. Bock, *ibid.*, **42**, 2541 (1964).

(10) Some recent reviews on the subject of medium effects on nmr have appeared: (a) N. S. Bhacca and D. W. Williams, "Application of N.M.R. Spectroscopy in Organic Chemistry," Holden-Day, San Francisco, Calif., 1964; (b) P. Laszlo, *Progr. Nucl. Magn. Resonance Spectrosc.*, 3, 231 (1968); (c) J. Ronayne and D. H. Williams, *Annu. Rev. NMR (Nucl. Magn. Resonance) Spectrosc.*, 2, 83 (1969).

(11) (a) C. Reichardt and K. Dimroth, *Fortschr. Chem. Forsch.*, **11**, 1 (1968); (b) C. Reichardt, *Angew. Chem., Int. Ed. Engl.*, **4**, 29 (1965).

(12) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, *J. Amer. Chem. Soc.*, **85**, 709, 3146 (1963).

(13) A. Roe and G. F. Hawkins, *J. Amer. Chem. Soc.*, **69**, 2443 (1947).

(14) E. Profft and H. Richter, *J. Prakt. Chem.*, **9**, 164 (1959).

(15) A. D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960).

(16) W. G. Schneider, *J. Phys. Chem.*, **66**, 2653 (1962).

(17) A. D. Buckingham, T. Schaefer, and W. G. Schneider, *J. Chem. Phys.*, **32**, 1227 (1960).

(18) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, Oxford, 1968, p 871.

fluoropyridines except for the ring nitrogen. With this standard, the difference in the chemical shifts is a measure of the effect of the ring nitrogen in the fluoropyridines on the shielding due to the reaction field.

Tables I, II, and III list the chemical shifts of 2-fluoropyridine, 3-fluoropyridine, and 4-fluoro-2-picoline, respectively, in the solvents studied, relative to internal fluorobenzene. It can be seen that the solvent effects are quite large.

Figure 1 shows the plot of the chemical shifts of 3-fluoropyridine relative to the function $(\epsilon - 1)/(\epsilon + 1)$ which was proposed[2] to explain changes in the reaction field term (S_e). It is clear that no useful correlation can be obtained from this graph and this function fails to fit the data. Similar poor correlation plots were obtained for the other compounds.

On the other hand, Figures 2–4 show excellent linear plots of the fluorine chemical shifts with E_t (the values of E_t are summarized in Table IV). These correlations may in fact be used to estimate the solvent parameter, E_t, of solvents for which such values are not available.

It will be noted that increasing solvent polarity is accompanied by greater deshielding in 4-fluoro-2-picoline and 3-fluoropyridine, but by greater shielding in 2-fluoropyridine. These observations may be explained as follows. When a polar molecule, such as a fluoropyridine, is dissolved in a particular solvent, the dipole of the solute will either polarize the surrounding molecules as in the case of a nonpolar solvent, or orientate itself with the dipoles of the surrounding molecules as in the case of a polar solvent. The resulting field between the molecular dipole and that of the surrounding medium is the "reaction field" which gives rise to the S_e contribution to the total shielding (or deshielding). The only energetically favorable position for the polar or polarized solvent molecules will be opposite and parallel to the dipole of the solute. The reaction field is then parallel and in the same direction as the solute's

Table II. Solvent-Induced ^{19}F Chemical Shifts of 3-Fluoropyridine[a]

Solvent		Solvent	
Methanol–water (75:25)	9.52	Chloroform	12.81
Phenol	10.16	Acetic anhydride	12.88
Glacial acetic acid	10.72	Methylene chloride	13.28
Ethylene glycol	11.94	Benzonitrile	13.29
Benzyl alcohol	11.98	Nitrobenzene	13.34
Ethanol–water (80:20)	12.05	DMSO	13.40
Methanol	12.08	Pyridine	13.40
Nitromethane	12.34	Anisole	13.52
Ethanol	12.40	Diphenyl ether	13.53
1-Propanol	12.52	Chlorobenzene	13.53
1-Butanol	12.60	DMF	13.55
2-Propanol	12.61	Methyl iodide	13.55
tert-Butyl alcohol	12.77	Ethyl iodide	13.55
Ethyl bromide	13.56	Toluene	13.85
2-Picoline	13.57	THF	13.93
Acetone	13.65	Cyclohexane	13.93
1,4-Dioxane	13.69	Carbon disulfide	13.96
2,6-Lutidine	13.69	Carbon tetrachloride	13.96
Benzene	13.71	Diethyl ether	14.09
Ethyl acetate	13.79	*n*-Hexane	14.32

[a] Ppm relative to internal fluorobenzene; 3% (v); exptl error = ±0.02 ppm.

Table III. Solvent-Induced ^{19}F Chemical Shifts of 4-Fluoro-2-picoline[a]

Solvent		Solvent	
Ethylene glycol	−11.50	Pyridine	−8.11
Methanol	−11.46	Acetone	−8.08
Ethanol–water (80:20)	−11.32	Chlorobenzene	−8.05
Benzyl alcohol	−11.14	Ethyl acetate	−8.00
Ethanol	−10.93	2-Picoline	−7.99
1-Propanol	−10.84	Anisole	−7.98
1-Butanol	−10.73	2,6-Lutidine	−7.93
2-Propanol	−10.54	Diphenyl ether	−7.91
DMF	−10.12	THF	−7.69
Chloroform	−9.49	Benzene	−7.57
tert-Butyl alcohol	−9.15	Carbon tetrachloride	−7.57
Methylene chloride	−8.66	Diethyl ether	−7.52
Benzonitrile	−8.40	Toluene	−7.46
Nitrobenzene	−8.32	Carbon disulfide	−7.46
Nitromethane	−8.20	*n*-Hexane	−7.24
DMSO	−8.20	Cyclohexane	−7.10
1,4-Dioxane	−8.17		

[a] See footnote *a*, Table I.

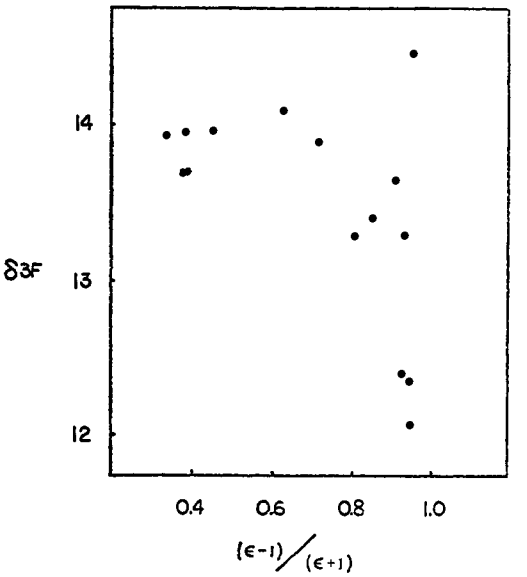


Figure 1. Plot of the solvent-induced ^{19}F shifts of 3-fluoropyridine (δ 3F) relative to fluorobenzene *vs.* the function $(\epsilon - 1)/(\epsilon + 1)$.

Table IV. E_T Values[a]

Solvent	E_T	Solvent	E_T
Ethylene glycol	56.3	Methylene chloride	41.1
Methanol	55.5	Pyridine	40.2
Ethanol–water (80:20)	53.6	2-Picoline	38.3
Ethanol	51.9	Ethyl acetate	38.1
Benzyl alcohol	50.8	Chlorobenzene	37.5
1-Propanol	50.7	THF	37.4
1-Butanol	50.2	Anisole	37.2
2-Propanol	48.6	2,6-Lutidine	36.7
Nitromethane	46.3	1,4-Dioxane	36.0
DMSO	45.0	Diphenyl ether	35.3
Aniline	44.3	Diethyl ether	34.6
tert-Butyl alcohol	43.9	Benzene	34.5
DMF	43.8	Toluene	33.9
Acetone	42.2	Carbon disulfide	32.6
Nitrobenzene	42.0	Carbon tetrachloride	32.5
Benzonitrile	42.0	*n*-Hexane	30.9

[a] Reference 11.

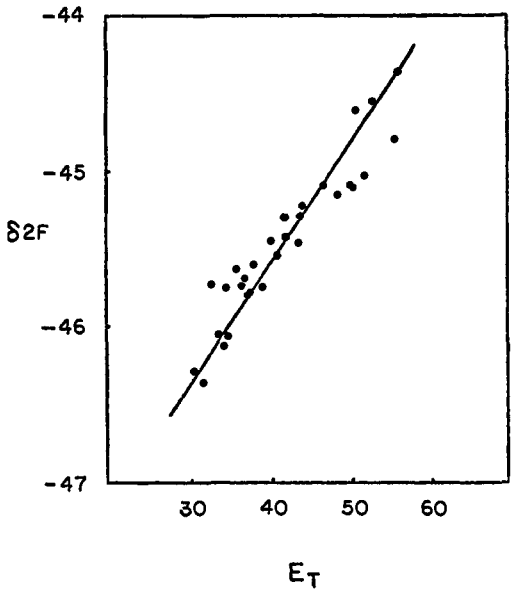


Figure 2. Plot of the solvent-induced ^{19}F shifts of 2-fluoropyridine (δ 2F) relative to fluorobenzene *vs.* E_t.

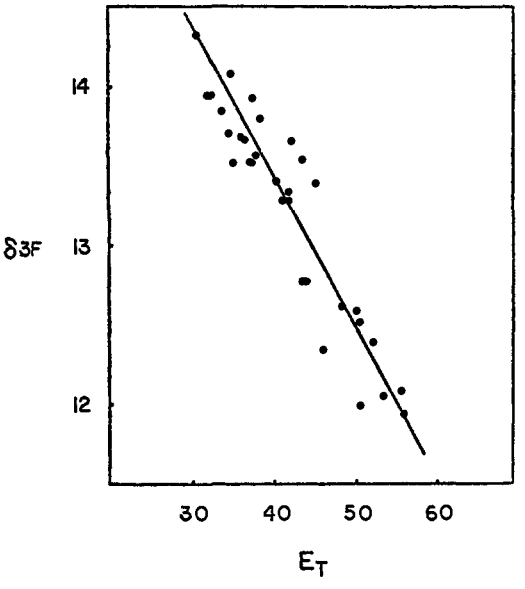


Figure 3. Plot of the solvent-induced ^{19}F shifts of 3-fluoropyridine (δ 3F) relative to fluorobenzene *vs.* E_t.

dipole. If a solvent of greater polarity is used, the reaction field (S_e) will be larger and the fluorine chemical shift will change accordingly. Thus, the deshielding by polar solvents on 4-fluoro-2-picoline (and 3-fluoropyridine) may be mainly influenced by the orientation of the positive end of the solvent dipoles toward the fluorine probe; in contrast, in 2-fluoropyridine, where the fluorine atom is situated adjacent to the lone pair of electrons on the ring nitrogen atom, the positive ends of the solvent dipoles are toward the nitrogen and the negative ends shield the fluorine probe giving the observed upfield shift. This model is consistent with the observation that the dielectric constant, ϵ, which is a "bulk" property, does not give good correlations. On the other hand, E_t is based on the transition energies of the intramolecular charge-transfer band of the pyridinium betaine (I, R = H or CH_3) in different solvents. It is

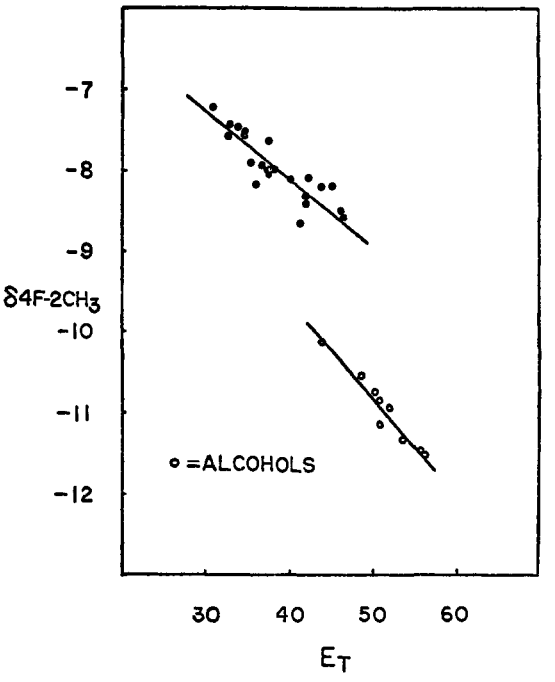
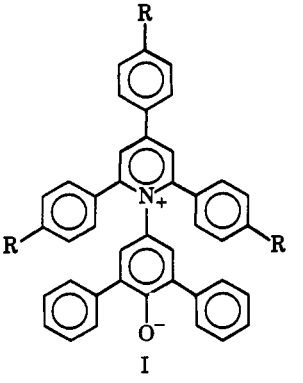


Figure 4. Plot of the solvent-induced ^{19}F shifts of 4-fluoro-2-picoline (δ 4F − 2CH_3) relative to fluorobenzene *vs.* E_t.



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thus a more sensitive measure of the dipolar interactions between the solute and the periphery solvent molecules, rather than solute–bulk-solvent properties. Chemical shifts in protic solvents also correlate well with E_t; hydrogen-bonding effects are probably the major factor responsible for the observed shifts in nmr as well as in uv spectroscopy.[3,19,20] In fact, Figure 4 shows the alcohols fall on a separate line because the fluorine probe, being para to the ring nitrogen, is extremely sensitive to hydrogen bonding by these solvents. The good linear correlations obviously suggest the changes in chemical shifts in different solvents, a ground-state phenomenon, roughly parallel the electronic transitions in these solvents; this type of correlation has been explained.[21]

Protonation

Table V lists the fluorine-19 chemical shifts of 2- and 3-fluoropyridine in several acids. It was expected that protonation of the ring nitrogen would cause a net drain of electrons from the ring and that this decrease

(19) S. Brownstein, *Can. J. Chem.*, **38**, 1590 (1960).
(20) C. Reichardt, *Angew. Chem., Int. Ed. Engl.*, 4, 29 (1965).
(21) E. M. Kosower, "Introduction to Physical Organic Chemistry," Wiley, New York, N. Y., 1968, p 184.

in electron density would cause the fluorine resonance to shift downfield. Thus, the shift for 3-fluoropyridine in 11.6 *N* hydrochloric acid is "normal," being shifted 11.8 ppm downfield from that in carbon tetrachloride.

However, 2-fluoropyridine in acids exhibits upfield rather than downfield shifts; this effect has also been observed by others[22] and may be attributed to magnetic anisotropic effects.

Table V. ^{19}F Chemical Shifts of 2- and 3-Fluoropyridine in Acid Solution[a]

Acid	2-Fluoropyridine	3-Fluoropyridine
HCl	1.52	35.50
HBr	1.67	35.61
HI	0.78	35.40
HNO_3	2.56	38.07
HOAc	−7.06	46.93
$HClO_4$	1.40	36.58
H_3PO_4	1.09	34.82

[a] Relative to external trifluoroacetic acid, ±0.1 ppm.

With electron-withdrawing groups in the 5 position, para to the 2-fluoro group, the effect of the 11.6 *N* hydrochloric acid on chemical shifts' difference is reduced.[1] As the electron-withdrawing ability of the substituent increases, the amount of upfield shift is reduced, because the dipole of the solute molecule is reduced, and as a result so is the reaction field shielding term, S_e. This is also in accord with the solvent model.

In conclusion, solvent-induced chemical shifts in fluoropyridines do not give good correlations with functions containing the dielectric constant. The solvent parameter, E_t, has been shown to correlate very well with the chemical shifts of these compounds. The use of E_t should also be extended to other systems.

Acknowledgment. We are grateful to the Robert A. Welch Foundation for the financial support of this project, and to Professor R. W. Taft for helpful discussions.

(22) Professor R. W. Taft, unpublished results.

Substituent Effects on Cyclopropenium Ions

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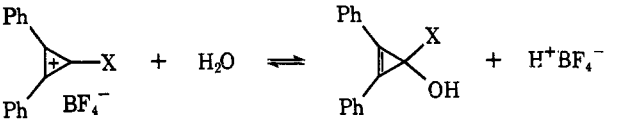
Contribution from the Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11790. *Received September 16, 1972*

Abstract: A series of substituted diphenylcyclopropenium tetrafluoroborates, $Ph_2C_3X^+BF_4^-$ (I), has been prepared, and their pK_{R^+} values have been measured by potentiometric titration. The trend observed, $R_2N \gg c\text{-}C_3H_5 > OEt > n\text{-}C_3H_7 \approx SMe > Ph > H$, indicates conjugative effects still to be predominant in stabilizing these cations, though less so than with most other cations. No evidence of abnormal phenyl effects is found. Dicyclopropylcyclopropenone (III) has been prepared from diallylcarbinol by Simmons–Smith cyclopropanation, chromic acid oxidation, dibromination, and hydrogen bromide elimination. III is more basic ($H_0 = -1.2$) than diphenylcyclopropenone (II) ($H_0 = -2.3$).

The early finding that alkyl groups stabilized cyclopropenium ions[1] (with respect to cyclopropenols) more effectively than phenyl groups did[2-4] raised the possibility that such ions, because of their closed 2π-electron shells, were less susceptible to stabilization by conjugative electron donation than traditional open-shell carbonium ions. More recently, Ciabattoni and Nathan[5,6] reported that alkyl groups stabilize cyclopropenium ions according to the Baker–Nathan order, though they were unable to ascribe the origin (*i.e.*, hyperconjugation or steric hindrance to solvation) of this ordering.

In order to further explore stabilization of cyclopropenium ions by substituents, in particular the importance of conjugative and hyperconjugative effects, we undertook to study a greater variety of substituted cyclopropenium ions. Since we proposed to measure their stability by the standard pK_{R^+} method,[4,6] we chose to study a series of substituted diphenylcyclopropenium ions, in which electronic stabilization of the covalent cyclopropenols is potentially the same (stilbene-like) regardless of the substituent X.



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These compounds also possess the merits that their expected pK_{R^+} values should be low enough to be significantly affected by X,[7] but yet high enough to be measured by potentiometric titration. They are also easily accessible.

Results

Substituted Diphenylcyclopropenium Ions. Reaction of appropriate Grignard reagents with diphenylcyclo-

(1) For reviews of early work on cyclopropenium ions, see (a) A. Krebs, *Angew. Chem., Int. Ed. Engl.*, **4**, 10 (1965); (b) G. L. Closs, *Advan. Alicyclic Chem.*, **1**, 53 (1966); (c) I. A. D'yakonov and R. R. Kostikov, *Russ. Chem. Rev.*, **36**, 557 (1967).

(2) R. Breslow and H. W. Chang, *J. Amer. Chem. Soc.*, **83**, 2367 (1961).

(3) R. Breslow, J. Lockhart, and H. W. Chang, *ibid.*, **83**, 2375 (1961).

(4) R. Breslow, H. Höver, and H. W. Chang, *ibid.*, **84**, 3168 (1962).

(5) J. Ciabattoni and E. C. Nathan, *Tetrahedron Lett.*, 4997 (1969).

(6) J. Ciabattoni and E. C. Nathan, *J. Amer. Chem. Soc.*, **91**, 4766 (1969).

(7) A series of alkyldi-*tert*-butylcyclopropenium ions, which are much more stable (pK_{R^+} = *ca.* 6.5) than alkyldiphenylcyclopropenium ions (pK_{R^+} = *ca.* 3.8), showed no differentiation among the various alkyl groups.[6]