Method II. Values of ΔH_f° determined through eq 2 depend strongly on the reliability of K_f. In view of the difficulty in obtaining K_f with high precision (and, more importantly, acceptable *accuracy*), a totally different approach was also used. Assume that at high dilution in pure aprotic B *as solvent*, each molecule of PFP is hydrogen bonded to one molecule of B. If we could correct for other interactions between PFP and the surrounding B molecules, the interaction energy due to hydrogen bonding alone could be isolated. To do this, anisole and *p*-fluoroanisole (PFA) are used as models. The measurement of heat of formation of C in pure B, which we shall call ΔH_f^B, is then simply a matter of measuring $\Delta \bar{H}_s$ for the phenol and its corresponding methyl ether, first in pure base and then in an inert solvent (carbon tetrachloride) to provide a suitable reference state. Then, for example

$$(\Delta H_f^B)_{\text{PFP}\cdots\text{B}} = (\Delta \bar{H}_s^{\text{PFP}} - \Delta \bar{H}_s^{\text{PFA}})_B -$$

$$(\Delta \bar{H}_s^{\text{PFP}} - \Delta \bar{H}_s^{\text{PFA}})_{\text{CCl}_4} \quad (3)$$

If all PFP molecules are converted to the 1:1 complex, no estimate of K_f is needed.

This approach assumes that there is not a large medium effect on the heat of hydrogen-bond formation (*i.e.*, $\Delta H_f^\circ \approx \Delta H_f^B$). Comparison of columns *c* and *d* in Table I provides striking evidence that this need not be a serious problem. For the three cases reported here, ΔH_f° values, at high dilution in CCl_4, and ΔH_f^B, in pure B, agree within experimental error. When allowance is made for uncertainties in K_f, the second method may actually be the more accurate and even be used to estimate K_f through eq 1 and 2. We find that agreement between the two methods is surprisingly general, but breaks down slightly for highly associated solvents such as dimethyl sulfoxide. The relative invariance of most hydrogen-bond strengths to environmental factors suggests that ΔH_f° for an A–H$\cdots$B bond determined at high dilution in CCl_4 might be used with little error as a model for a structurally similar situation under other conditions as, for example, within a protein helix.

Procedures for determining $\Delta \bar{H}_s$ and ΔH_{obsd} at 25° have been described previously.[6] The insensitivity of ΔH_f to temperature[7] was demonstrated (for the first time, to our knowledge) by a complete determination of ΔH_f° for the pyridine–PFP complex at high dilution in carbon tetrachloride at 12°. The value at this temperature to be compared with that in Table I is 7.2 ± 0.2 kcal/mole.[8]

(6) E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. McC. Duggleby, *J. Am. Chem. Soc.*, **87**, 1541 (1965).

(7) ΔH_{obsd} obtained by method I has a large temperature coefficient through K.

(8) K in this case was 130.6, calculated from the value at 25° by the van't Hoff equation.

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Regarding Proton Transfer in Hydrogen-Bonded Complexes as Measured by Fluorine Nuclear Magnetic Resonance[1]

Sir:

We wish to report the use of fluorine nuclear magnetic resonance (F nmr), with the *p*-fluorophenyl label, in the quantitative study of hydrogen bonding. The F nmr shielding of *p*-fluorophenyl derivatives provides a very sensitive probe of the interaction between the benzene ring and the functional substituent.[2] This probe has been used previously to investigate quantitatively Brønsted and Lewis acid–base equilibria,[3] as well as much weaker interactions of the dipole–dipole type.[4]

In the present study *p*-fluorophenol is used as the reference acid toward three typical bases. The work constitutes part of a collaborative investigation with Professor E. M. Arnett (*cf.* companion paper[5]), in which definitive hydrogen-bond parameters are being obtained through a combination of independent infrared, nmr, and calorimetric determinations.

The F nmr shielding results were obtained (D. G. and R. T.) with the use of a Varian HA-60 spectrometer equipped with a Varian 1024 computer of average transients and an NMR Specialties heteronuclear decoupler, Model SD60-B. The temperature-control probe was maintained at 25.0°. By decoupling the ring protons, F nmr shielding measurements at less than 0.01 M *p*-$\text{FC}_6\text{H}_4\text{OH}$ were obtained. Accordingly, all measurements were made under conditions for which infrared analysis indicates the existence of only the monomeric phenol. For base concentrations up to 0.02 M, the same F nmr shift (±0.02 ppm, the experimental error) of *p*-$\text{FC}_6\text{H}_4\text{OH}$ is obtained with the use of an external reference as with the internal reference, *p*-fluoroanisole (0.01 M). From 0.02 to 0.5 M base concentrations only the internal reference gives shifts which meet the analysis conditions discussed below. Since shielding effects of 2–4 ppm are measured to ±0.02 ppm, the F nmr method has sufficient sensitivity for a critical analysis.

The F nmr shifts, δ, for CCl_4 solutions with variable *p*-$\text{FC}_6\text{H}_4\text{OH}$ and base concentrations (covering a range of 30–80% complex formed) have been analyzed in terms of the assumed formation of a 1:1 complex to give values for the formation constant, K_f, and the corresponding change in shielding, Δ, between complexed and uncomplexed *p*-fluorophenol.[4] It is initially assumed that both Δ and K_f are independent of concentration effects. Our δ values upon such analysis yield fits to within the experimental error (condition 1). However, the precision of fit of the nmr shift alone is not a sufficient condition for accuracy of K_f and Δ values. Either experimental error or concentration effects could accumulate systematic errors in both parameters even though

(2) R. W. Taft, *et al.*, *J. Am. Chem. Soc.*, **85**, 3146 (1963).
(3) (a) R. W. Taft and P. L. Levins, *Anal. Chem.*, **34**, 436 (1962); (b) R. W. Taft and J. W. Carten, *J. Am. Chem. Soc.*, **86**, 4199 (1964); (c) R. G. Pews, Y. Tsuno, and R. W. Taft, *ibid.*, **89**, 2391 (1967).
(4) R. W. Taft, G. B. Klingensmith, and S. Ehrenson, *ibid.*, **87**, 3620 (1965).
(5) E. M. Arnett, T. S. S. R. Murty, P. von R. Schleyer, and L. Joris, *ibid.*, **89**, 5955 (1967).

Table I. Comparison of Formation Constants for p-FC$_6$H$_4$OH–Base Complexes Obtained by F Nmr, Infrared, and Calorimetric Methods in CCl$_4$ at 25.0°

	F nmr method[a]		Infrared method[b]		Calorimetric method[c]	
Base	Base range, M	K_f, M^{-1}	Base range, M	K_f, M^{-1}	Base range, M	K_f, M^{-1}
THF[d]	0.0241–0.201	19.1 ± 0.9	0.0221–0.0933	17.7 ± 0.5	0.00705–0.0211	19.4 ± 1.0
Pyridine	0.00690–0.0509	76.7 ± 2	0.00467–0.0240	76.2 ± 0.9	0.00344–0.0186	74.0 ± 5
DMF[e]	0.00665–0.0205	121 ± 2	0.00660–0.0427	116 ± 3	0.00361–0.0203	122 ± 9

[a] Obtained by best fit of δ_{obsd} values to fixed values of K_f and Δ (cf. footnote 4); p-FC$_6$H$_4$OH = 0.0093–0.013 M. [b] Obtained as indicated in text, with p-FC$_6$H$_4$OH $\leq$ 0.004 M. [c] Obtained as indicated in ref 5. [d] Tetrahydrofuran. [e] N,N-Dimethylformamide.

Table II. F Nmr Shifts of p-FC$_6$H$_4$OH–Base Complexes

	Δ values,[a,d] ppm		
Base	Titration curve (30–80% complexing)	Directly observed (97–99% complexing)	Apparent % proton transfer[a]
THF	2.03 ± 0.03[b]	...	14
Pyridine	2.48 ± 0.03[b]	2.53 ± 0.02 (0.698)[c]	18
DMF	2.71 ± 0.02[b]	2.73 ± 0.02 (0.457)[c]	20

[a] Cf. text. [b] Standard error of Δ from 6–12 points on "titration" curve calculated using K_f from the infrared method. [c] Base concentration employed. [d] Preliminary experiments[9b] carried out with 0.1 M p-FC$_6$H$_4$OH 'and relatively high base concentrations gave: Δ_{THF} = 2.10 ± 0.15, Δ_{pyr} = 2.55 ± 0.05, Δ_{DMF} = 2.75 ± 0.05.

condition 1 is met. However, the analysis and assumptions are confirmed by the further conditions: (2) agreement of the value of K_f obtained by the F nmr method with those obtained by two reliable independent methods (cf. Table I), and (3) agreement of the value of Δ obtained in the analysis with a directly measured value (for 97–99% complex formation which is corrected to 100%).

Tables I and II summarize the confirmatory results obtained for the three typical bases.[6] In Table I the values of K_f obtained by the three independent methods are given together with the conditions of the measurements. In Table II are given the directly observed values of Δ and those calculated from the observed shifts, δ, for solutions in which 30–80% complex formation occurs (Δ = (δ/[complex])[acid]$_s$, where [complex] = equilibrium concentration of complex and [acid]$_s$ = stoichiometric concentration of p-FC$_6$H$_4$OH). The third confirmatory condition (above) is limited to bases for which K_f > ca. 50 because of medium effects in the F nmr method (i.e., at base concentrations > ca. 0.5 M). For bases with K_f < ca. 50, only condition 2 may be applied as illustrated by the results for THF.

The infrared formation constants given in Table I have been obtained (L. J. and P. von R. S.) using a Perkin-Elmer 421 double-beam grating spectrophotometer to measure the transmittance of the fundamental OH stretching vibration (3610 cm^{-1}) of the uncomplexed p-fluorophenol in equilibrium with the complex. No reproducible systematic variation of K_f with base concentration beyond the precision measure was found.

Values of Δ are directly proportional to (at least approximately) the change in π-electron charge density at the p-carbon atom,[7] and, probably, of the

(6) Immediately before use, reagent-grade CCl$_4$, DMF, and pyridine were distilled from CaH$_2$, p-FC$_6$H$_4$OH was sublimed, and THF was distilled from Na–benzophenone.
(7) R. W. Taft, F. Prosser, L. Goodman, and G. T. Davis, J. Chem. Phys., 38, 380 (1963).

oxygen atom,[8] of p-fluorophenol which occurs on complex formation. The Δ value for complete proton transfer as obtained from the shielding effects of p-FC$_6$H$_4$OH in CCl$_4$ and p-fluorophenoxide ion in dimethyl sulfoxide solution is approximately 14 ppm.[9,10] Consequently, the F nmr of the p-fluorophenyl label provides a *novel measure of the extent of proton transfer in the H-bonded complex*, i.e., the apparent % proton transfer = 100Δ/14 (cf. results listed in Table II). The apparent per cent proton transfer is of particular concern in linear free-energy relationships between log K_f and pK_A of the base. The order of both Δ and log K_f values is THF < pyridine < DMF, whereas $-\Delta H_f$ values[5] give THF < DMF < pyridine. These matters will be examined in detail for wide structural variation in the base in a subsequent publication.

(8) F. Prosser, Ph.D. Thesis, The Pennsylvania State University, Aug 1961.
(9) (a) Unpublished results of Dr. George Allen; (b) Ph.D. Thesis of M. G. Schwartz, The Pennsylvania State University, Dec 1965.
(10) The complementary shift for complete protonation of p-FC$_6$H$_1$-OH is not available. However, the coordination of oxygen with BCl$_3$ is expected to give rise to a similar value.[3c] The Δ value for complexation of p-fluoroanisole with BCl$_3$ in CH$_2$Cl$_2$ solutions is −12.6 ppm (unpublished results of Mr. J. W. Carten). This figure may be taken as support for the direct relationship assumed between shift and extent of protonation.
(11) National Institutes of Health Predoctoral Fellow, Princeton University, 1967; Ph.D. Thesis, Princeton University, 1967.

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The Photochemical Decomposition of Geminal Diazides.
I. Dimethyl Diazidomalonate

Sir:

Photolysis of alkyl azides proceeds with loss of molecular nitrogen to yield products which may derive from a nitrene intermediate.[1] Photochemical decomposition of a geminal diazide could proceed analogously with loss of one, two, or three molecules of nitrogen.[2] The respective intermediates would be

(1) R. M. Moriarty and M. Rahman, Tetrahedron, 21, 2877 (1965); D. H. R. Barton and A. N. Starratt, J. Chem. Soc., 2444 (1965). For reviews, see L. Horner and A. Christmann, Angew. Chem. Intern. Ed. Engl., 2, 599 (1963); R. A. Abramovitch and B. A. Davis, Chem. Rev., 64, 149 (1964).
(2) L. Barash, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, reported that irradiation of benzophenone diazide in several matrices at 77°K yielded an epr spectrum identical with that of diphenylmethylene obtained by photolysis of diphenyldiazomethane. In the accompanying communication, we report on the photolysis of benzophenone diazide. See also L. Barash, E. Wasserman, and W. A. Yager, J. Am. Chem. Soc, 89, 3931 (1967).