

For **3**, the aromatic carbons of **3** were assigned in a manner identical with that for **2**. Thus assigned, it was observed that the same relative order of coupling constants occurred, viz., $J_{C-C_8} < J_{C-C_6} < J_{C-C_7} \sim J_{C-C_5}$ in both **2** and **3**. To verify that the α carbons in **3** (C-8 and C-5) were downfield from the β carbons (C-6 and C-7), a proton-coupled pattern²⁴ carbon NMR spectrum of **3** was recorded.

The analysis of **4** has been previously described.²⁵

For **5**, a proton-coupled pattern²⁴ spectrum differentiated the α and β carbons; furthermore, C-3, with no three-bonded carbon-proton coupling, appeared merely as a doublet. The three α carbons C-4, C-5, and C-8 were differentiated by: (1) the expectation that C-4 should be the furthest downfield;^{23,26} (2) steric perturbation of the carboxyl group on C-8 rendering its signal the furthest upfield.^{3a,26} The β carbons C-2, C-3, C-6, and C-7 were differentiated by: (1) the proton-coupled pattern of C-3 (vide supra); (2) the expectation that C-2 should be the furthest downfield;^{23,26} (3) the expectation that C-7 should be downfield from C-6.²³ The two γ carbons C-9 and C-10 were assigned by the expectation that $^3J_{CC} > ^2J_{CC}$. Thus assigned, the C-9 signal was upfield to the C-10 signal, consistent with previous reports of this "steric perturbation effect" on C-9 of 1-substituted naphthalenes.²³ These chemical shift assignments for **5** are consistent with the published chemical shifts of the structurally related 1-acetylnaphthalene.²⁷

For **6**, chemical shift assignments were done as previously reported for 9-anthracene derivatives.²² Chemical shifts for **6** thus parallel those for other 9-anthracene derivatives: (1) C-1 (C-8) and C-12 (C-13) are shielded relative to anthracene.²⁸ This imitates the "steric perturbation effect" observed in **5**. (2) The chemical shift of C-11 (C-14) is about the same as in anthracene²⁸ (compare 132.0 and 132.4 ppm).

Acknowledgment. The authors are indebted to the Robert A. Welch Foundation (Grant B-325), to North Texas State University Faculty Research, and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this work. The services of the University of Arizona Computer Center are also gratefully acknowledged. The authors further express their gratitude to Dr. P. G. Gassman of the University of Minnesota for providing the services of a Varian CFT-20 NMR spectrometer for verifying some of the data in Table I.

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An Experimental Determination of the Free Energy of Hydrogen Bonding to an Anion Radical

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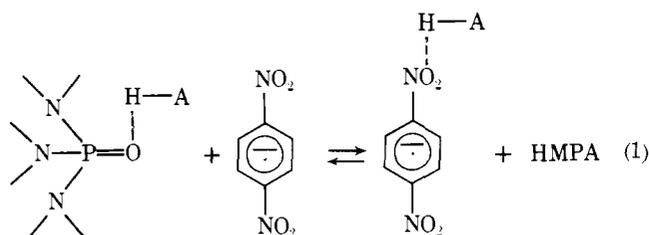
Abstract: The free energies for the hydrogen bond exchange reaction between the proton acceptors hexamethylphosphoramide (HMPA) and *p*-dinitrobenzene (PDNB) anion radical ($X\text{-PhC}\equiv\text{CH}\cdots\text{HMPA} + \text{PDNB}\cdot^- \rightleftharpoons X\text{-PhC}\equiv\text{CH}\cdots\text{PDNB}\cdot^- + \text{HMPA}$) were determined by the use of ESR. The free energies of hydrogen bond formation between the substituted phenylacetylenes and HMPA were determined separately from the NMR chemical shifts. These two free energies were then added in a thermochemical cycle to yield the free energies of hydrogen bonding to the anion radical, ΔG_a° . ΔG_a° was found to vary linearly with the σ^+ value for the para substituent on the donor. When this σ^+ value is zero or greater, ΔG_a° is negative, indicating that the *p*-dinitrobenzene anion radical is a strong proton acceptor, whereas the neutral molecule is a very poor proton acceptor. This represents the first report of free energies of hydrogen bonding to an anion radical.

A wealth of information has been compiled on the thermodynamic parameters controlling the formation of hydrogen bonds between proton donors and neutral proton acceptors.¹ However, the literature is essentially devoid of reports of thermodynamic parameters for systems where anion radicals

serve as the hydrogen bond acceptor. This is true despite the fact that the extra negative charge should make these acceptors particularly viable proton acceptors and the fact that a number of reports dealing with equilibrium constants for systems with anion radicals as proton acceptors have appeared.²

In most solvent systems the hydrogen bonding to anions is very complex due to the existence of many different types of complexes, including ion pairs and hydrogen bonded ion pairs.^{3,4} These complexes and several others were observed by Kuntz and Cheng⁵ in a recent report. Their elegant use of NMR and ir spectroscopy even allowed the estimation of several association constants between cations and HDO or methanol. However, the association constant for a pure hydrogen bond to an anion radical in solution still remains unmeasured.

It has been recently shown that the addition of small amounts of proton donor to the anion radical of *p*-dinitrobenzene (PDNB^{•-}) in hexamethylphosphoramide (where this anion exists free of ion pairing) affords an increase in the difference between the nitrogen hyperfine coupling constant (A_N) and the proton hyperfine coupling constant (A_H) upon ESR analysis.⁶ This difference (δ) is due to the formation of hydrogen bonds between the proton donor and the nitro groups of the anion radical.⁶ The two nitrogens remain magnetically equivalent even in the presence of proton donor due to the rapid intermolecular exchange of proton donor. Further, the concentrations of hydrogen-bonded anion and hydrogen-bonded hexamethylphosphoramide (HMPA) was shown to be controlled by the hydrogen bond exchange reaction (eq 1).



Since the equilibrium is fast on the ESR time scale, the equilibrium constant for reaction 1 can be obtained by the use of time-averaged equations.⁶ For the rapid formation of any weak molecular complex (X'), a most useful expression has been developed for the case where only the spectroscopic parameter (Γ) for the time-averaged species can be observed. The equilibrium constant for reaction 2 can be determined by the use of eq 3 without direct measurement of the spectroscopic parameter for the complex (Γ').⁷ However, the use of this expression does require the concentration of Y to be known.



$$1/(\Gamma - \Gamma^0) = 1/\{K_{eq}(\Gamma' - \Gamma^0)[Y]\} + 1/(\Gamma' - \Gamma^0) \quad (3)$$

The spectroscopic parameter (Γ^0) for X can be measured before the addition of Y to the solution.

In a previous report we described the estimation of the enthalpy of hydrogen bonding of methylacetylene (acting as the proton donor) to PDNB^{•-}.⁸ This was done by the use of a thermochemical cycle, where the enthalpy of the hydrogen bond exchange reaction (eq 1) was added to the enthalpy of hydrogen bonding between the methylacetylene and the HMPA. This latter enthalpy was taken from an NMR measurement.⁸ The free energies could not be obtained due to a series of experimental difficulties, including the fact that it was impossible to obtain the NMR chemical shift for hydrogen-bonded HMPA. The difference in A_N and A_H (δ) for the hydrogen-bonded anion radical could not be accurately obtained from the ESR experiment, and a noninert solvent (CCl_4) had to be used to avoid solubility problems and interference with the NMR resonance of methylacetylene.

In order to gain some understanding of hydrogen bonding to anion radicals and some insight as to the proton accepting abilities of anion radicals, we wish to report the first experimental free energies of hydrogen bonding to an anion radical

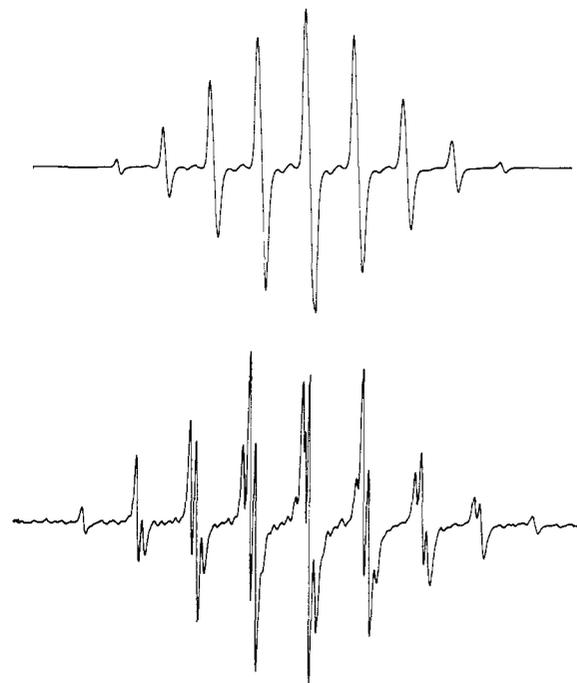


Figure 1. ESR spectra of the system PDNB-HMPA-Na at 25°: (upper) without added proton donor; (lower) containing 2.01 M phenylacetylene.

along with a positive correlation of these free energies with the σ values of the substituents on the proton donor. Phenylacetylenes were chosen as the proton donors, since it is well known that the acidities of the acetylenic proton can be varied with the para substituent.

Results and Discussion

ESR. Reduction of PDNB in HMPA results in a solution of the free anion radical, which upon ESR analysis yields a pattern due to two equivalent nitrogens ($A_N^0 = 1.155$ G) and four equivalent protons ($A_H^0 = 1.099$ G). The difference in A_N^0 and A_H^0 is (δ^0), which is 0.056 G. Addition of substituted phenylacetylenes to this HMPA solution affords an increase in this difference (Figure 1) due to the formation of hydrogen-bonded anion radical (eq 1).

Taking the value of δ as a weighted average between the hydrogen-bonded anion radical and the free ion, eq 3 can be used in terms of δ . Equation 3 predicts that a plot of $1/(\delta - \delta^0)$ vs. the reciprocal of the concentration of added proton donor is linear with an intercept of $1/(\delta' - \delta^0)$ and a slope of $[HMPA]/K_{eq}(\delta' - \delta^0)$. This is true for the following reasons: (1) the HMPA is the solvent, and $[HMPA]$ is large and constant; (2) the concentration of the added proton donor is much larger than that for PDNB^{•-}, and (3) all of the proton donor can be considered to be hydrogen bonded to the solvent, since $[X-PhC\equiv CH\cdots HMPA] \gg [X-PhC\equiv CH\cdots PDNB^{\bullet-}]$. For all of the proton donors studied, such a plot is linear (Figures 2 and 3). The equilibrium constants and δ' values obtained from least-squares analysis of these plots are given in Table I. Subjecting the equilibrium constants in Table I to a Hammett-type correlation yields a linear correlation between $\log K_{eq}$ and σ^+ for the para substituent on phenylacetylene (Figure 4). ρ taken from the slope of the line is 0.48 ± 0.06 . The positive value for ρ indicates that the anion radical is more sensitive to changes in the acidity of the donor than is the HMPA.

A similar set of experiments was carried out with para-substituted phenols used as the proton donor instead of the phenylacetylenes (Table II). The phenols are much more acidic than the phenylacetylenes. In fact, *p*-nitrophenol killed (protonated) the anion radical and consequently was not studied.

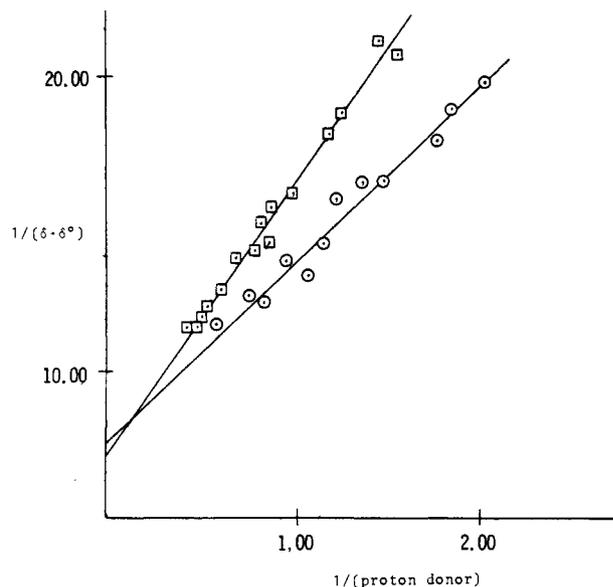


Figure 2. Plots of $1/(\delta - \delta^0)$ vs. the reciprocal of the proton donor concentration (O, *p*-chlorophenylacetylene; □, phenylacetylene).

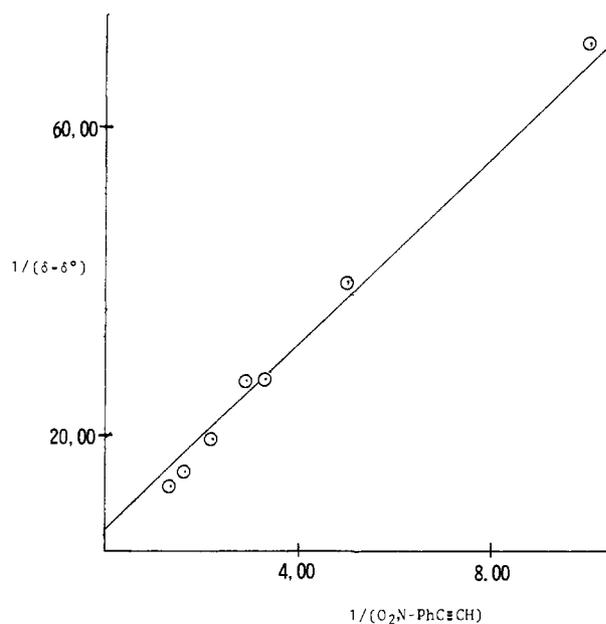


Figure 3. Plot of $1/(\delta - \delta^0)$ vs. the reciprocal of the concentration of added *p*-nitrophenylacetylene.

Table I. Equilibrium Constants for Reaction 1, δ' Values, and σ^+ Values for the Para-Substituted Phenylacetylenes Used as Proton Donors at 35°

Substituent	δ', G	K_{eq}	σ^+	$\Delta G^\circ, kcal/mol$
H	0.28	1.44 ± 0.17	0.00	-0.21 ± 0.07
CH ₃	0.30	1.21 ± 0.12	-0.31	-0.11 ± 0.06
C(CH ₃) ₃	0.29	1.18 ± 0.12	-0.26	-0.10 ± 0.06
OCH ₃	0.52	0.92 ± 0.17	-0.76	-0.05 ± 0.11
Cl	0.26	2.35 ± 0.40	0.11	-0.51 ± 0.10
NO ₂	0.24	4.60 ± 0.86	0.79	-0.91 ± 0.11

However, it is clear that no semblance of a straight line can be obtained from the data in Table II. The lack of a linear free energy relationship for the systems where para-substituted phenols were used as proton donors may be due to other competing interactions such as charge transfer effects that could

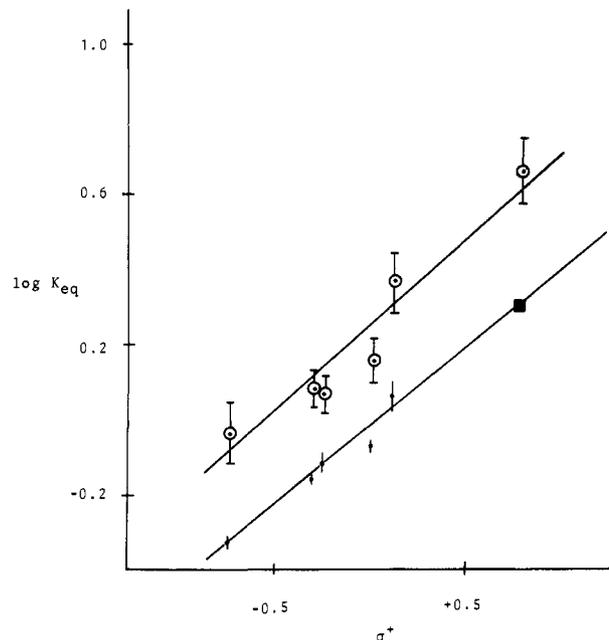


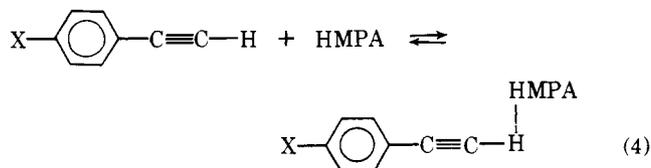
Figure 4. Hammett plots for both the hydrogen bond exchange reaction (O) and for the hydrogen bond formation to HMPA (●). The point indicated by ■ was not determined experimentally.

Table II. Free Energies for Reaction 1, δ' Values, and σ^+ Values for the Para-Substituted Phenols Used as Proton Donors at 35°

Substituent	δ', G	$\Delta G^\circ, kcal/mol$	σ^+
H	0.180	-1.12 ± 0.08	0.0
NHCOCH ₃	0.117	-1.94 ± 0.04	0.0
OCH ₃	0.117	-1.97 ± 0.04	-0.76
NH ₂	0.106	-2.40 ± 0.03	-1.3
CH ₃	0.100	-2.71 ± 0.09	-0.31
C ₂ H ₅	0.101	-2.72 ± 0.05	-0.30
I	0.107	-2.96 ± 0.02	0.13

alter the expected linear function, but the explanation is not obvious.

NMR. Upon NMR analysis, phenylacetylene and all of the para-substituted phenylacetylenes studied yield a multiplet for the phenyl protons and a sharp singlet for the acetylenic proton in both HMPA and cyclohexane. The chemical shift of the acetylenic proton is dependent upon the concentration of HMPA in the cyclohexane-phenylacetylene HMPA mixture. The sharp peak of cyclohexane was used as an internal standard, and all of the chemical shifts for the acetylenic protons were measured relative to this standard. The chemical shift of the monomeric-substituted phenylacetylene (ν^0) was obtained by extrapolating a plot of this shift vs. the concentration of the substituted phenylacetylene to infinite dilution in pure cyclohexane. The strong dependence of the chemical shift for the acetylenic proton upon the HMPA concentration is due to the formation of a hydrogen-bonded complex between the substituted phenylacetylene and the HMPA as shown below.



Since the formation and dissociation of the hydrogen bond complex is fast on the NMR time scale, the observed chemical

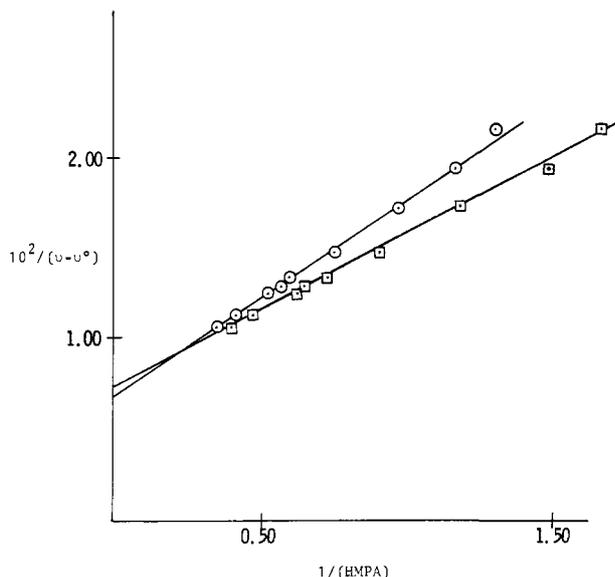


Figure 5. Plots of $10^2/(\nu - \nu^0)$ vs. $1/(\text{HMPA})$. The plot denoted by \circ was obtained by assuming that the HMPA concentration is equal to the added HMPA concentration. The plot denoted by \square was used to obtain K_{eq} , and the HMPA concentrations were taken from the last iteration. The proton donor is phenylacetylene.

Table III. Equilibrium Constants for Reaction 4, ν^0 Values, ν' Values, and σ Values for the Para-Substituted Phenylacetylenes Used

Substituent ^a	ν' , cps	ν^0 , cps	K_{eq}	σ^+
H	220.63	81.9	0.86 ± 0.02	0.00
CH ₃	231.48	79.0	0.69 ± 0.01	-0.31
C(CH ₃) ₃	214.91	78.3	0.75 ± 0.06	-0.26
OCH ₃	222.85	79.5	0.47 ± 0.02	-0.76
Cl	231.48	84.4	1.15 ± 0.08	0.11

^a *p*-Nitrophenylacetylene could not be studied because it is not sufficiently soluble in the solvent medium.

shift of the acetylenic proton is a weighted average between that of the monomeric and hydrogen-bonded species. This allows the use of eq 3, where Γ is replaced by ν and K_{eq} is given by

$$K_{\text{eq}} = [\text{X-PhC}\equiv\text{CH}\cdots\text{HMPA}] / [\text{X-PhC}\equiv\text{CH}][\text{HMPA}] \quad (5)$$

Replacing $[\text{Y}]$ in eq 3 with the concentration of monomeric HMPA, we obtain

$$1/(\nu - \nu^0) = 1/\{K_{\text{eq}}(\nu' - \nu^0)[\text{HMPA}]\} + 1/(\nu' - \nu^0) \quad (6)$$

where ν and ν' represent the observed chemical shift and the chemical shift for the hydrogen-bonded complex, respectively. The problem of not knowing the concentration of the monomeric HMPA was overcome by the use of an iterative process.⁹ Using the total HMPA concentration as a first approximation of $[\text{HMPA}]$, K_{eq} was calculated from a plot of $1/(\nu - \nu^0)$ vs. $1/[\text{HMPA}]$. This first estimate of K_{eq} was put into eq 7, which was solved for $[\text{X-PhC}\equiv\text{CH}\cdots\text{HMPA}]$. Equation 7 is true

$$[\text{X-PhC}\equiv\text{CH}\cdots\text{HMPA}]^2 + [\text{X-PhC}\equiv\text{CH}\cdots\text{HMPA}] \times ([\text{HMPA}]_{\text{initial}} + [\text{X-PhC}\equiv\text{CH}]_{\text{initial}} + K_{\text{eq}}^{-1}) + [\text{HMPA}]_{\text{initial}}[\text{X-PhC}\equiv\text{CH}]_{\text{initial}} = 0 \quad (7)$$

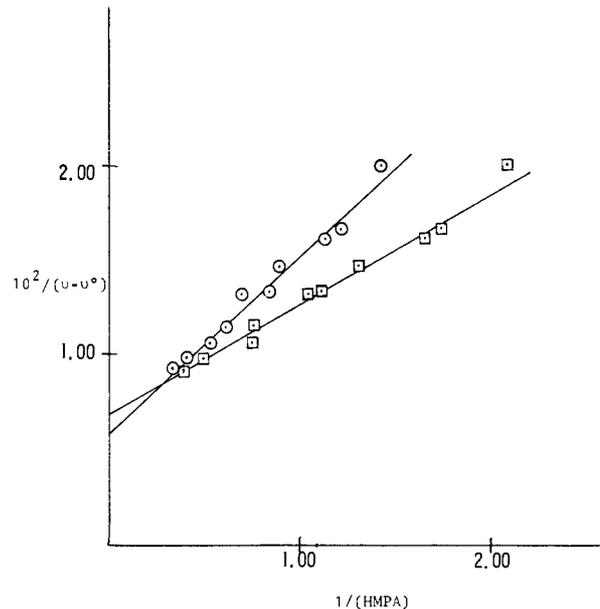


Figure 6. Plots of $10^2/(\nu - \nu^0)$ vs. $1/(\text{HMPA})$. The plot denoted by \circ was obtained by assuming that the HMPA concentration is equal to the added HMPA concentration. The plot denoted by \square was used to obtain K_{eq} , and the HMPA concentrations were taken from the last iteration. The proton donor is *p*-chlorophenylacetylene.

Table IV. Free Energies^b and ρ Values Obtained for the Reactions Used in the Thermochemical Cycle (Eq 8)

Substituent	ΔG_t°	ΔG_s°	ΔG_a°	
H	-0.21	0.09	-0.12 ± 0.04	
CH ₃	-0.11	0.22	0.11 ± 0.01	$\rho_t = 0.48 \pm 0.06$
C(CH ₃) ₃	-0.10	0.17	0.07 ± 0.03	$\rho_s = 0.45 \pm 0.03$
OCH ₃	-0.05	0.45	0.40 ± 0.03	$\rho_a = 0.93 \pm 0.09$
Cl	-0.51	-0.08	-0.59 ± 0.03	
NO ₂	-0.91	-0.4 ^a	-1.3 ^a	

^a These values were not determined experimentally. ^b All free energies are in kcal/mol.

since $[\text{HMPA}] = [\text{HMPA}]_{\text{initial}} - [\text{X-PhC}\equiv\text{CH}\cdots\text{HMPA}]$ and $[\text{X-PhC}\equiv\text{CH}] = [\text{X-PhC}\equiv\text{CH}]_{\text{initial}} - [\text{X-PhC}\equiv\text{CH}\cdots\text{HMPA}]$. The new value for $[\text{HMPA}]$ was submitted back into eq 6 to obtain a new value for K_{eq} . This iterative process was continued until the value for K_{eq} and $[\text{HMPA}]$ remained constant (Figures 5 and 6). The equilibrium constants and ν' values are given in Table III.

Conclusions

From the ESR and NMR experiments described above, a simple thermochemical cycle can now be constructed from which the actual free energy (ΔG_a°) and ρ value for hydrogen bonding to the anion radical can be calculated (eq 8). The results obtained from the use of this thermochemical cycle are given in Table IV.

The linear free energy relationship obtained for the substituted phenylacetylene systems could not be obtained when para-substituted phenols were used as proton donors. However, by comparing the free energies listed in Tables I and II, it is clear that the more acidic phenols have a greater affinity for the anion radical than do the phenylacetylenes. Consistent with

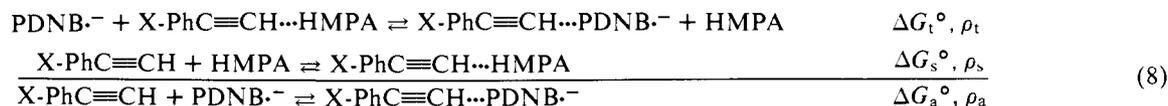


Table V. Range of s Values Calculated for the NMR and ESR Experiments Where Para-Substituted Phenylacetylenes Act as the Proton Donor

Substituent	s value range (NMR)	s value range (ESR)
H	0.34–0.68	0.14–0.36
CH ₃	0.30–0.62	0.12–0.30
C(CH ₃) ₃	0.40–0.73	0.09–0.27
OCH ₃	0.46–0.69	0.10–0.31
Cl	0.34–0.74	0.17–0.38
NO ₂		0.07–0.41

this is the fact that the more acidic the phenylacetylene, the more negative is ΔG_t° ($\rho_t > 0$). From comparison of the para-substituted phenol and phenylacetylene systems and ρ_a with ρ_s , it is evident that the formation of hydrogen bonds to the anion radical is more sensitive to changes in the acidity of the proton donor than is hydrogen bond formation to HMPA.

Despite the fact that nitro compounds are known to be relatively weak hydrogen bond acceptors,¹⁰ the anion radicals of nitro compounds are good proton acceptors as evidenced by the fact that ΔG_a° is negative when σ for the para substituent on phenylacetylene is greater than zero.

Since this report represents the first determinations of free energies of hydrogen bonding to anion radicals, it is important that a discussion of the possible sources of error¹¹ in this type of analysis be included. First, the solvation of phenylacetylene by HMPA must include more than the hydrogen bonding interaction. That is, there is an arrangement of solvent (HMPA) molecules around the phenyl moiety. In order to utilize the thermochemical cycle (eq 8), it is necessary to assume that this bulk solvation of the phenyl moiety is not significantly different whether the phenylacetylene is hydrogen bonded to HMPA or the anion radical. Second, large errors in K_{eq} are obtained when the plots of $1/(\Gamma - \Gamma^0)$ vs. $1/[Y]$ have small intercepts, that is, when K_{eq} is very small.¹² For the experiments described here, the intercepts are relatively large, and this error is not important. Third, the concentration ranges of the variables for the ESR and NMR experiments were sufficiently different that the direct comparison of ESR and NMR results may lead to errors originating from the fact that the solutions are not ideal, and activity terms may be important. Finally, Deranleau¹³ has recently pointed out that equilibrium constants for weak molecular complexes are most reliable when they are based upon spectral data that extend as much as possible into the region where the saturation factor (s) is between 0.2 and 0.8. The saturation is defined as

$$s = [X'] / ([X'] + [X]) = (\Gamma - \Gamma^0) / (\Gamma' - \Gamma^0) \quad (9)$$

By replacing Γ with ν for the NMR experiments and Γ with δ for the ESR experiments, the s values for the systems studied here were calculated and are given in Table V.

Experimental Section

All ESR spectra were recorded on a Varian E-9 ESR spectrometer, and the NMR spectra were recorded on a Varian T-60 NMR spectrometer. The purification of the HMPA and the method used to prepare the ESR samples have been previously described.¹⁴

The phenols were purified and dried as described in the literature.¹⁵ All of the para-substituted phenylacetylenes were prepared by the methods described in the literature: *p*-chlorophenylacetylene,¹⁶ *p*-methylphenylacetylene and *p*-*tert*-butylphenylacetylene,¹⁷ *p*-methoxyphenylacetylene,¹⁸ *p*-nitrophenylacetylene.¹⁹ Phenylacetylene was purchased from Columbia Chemical Co. and distilled under reduced pressure before use. All of the proton donors gave melting points and spectral data consistent with the literature values.

The cyclohexane was purchased from Aldrich Chemical Co. and purified as previously described.²⁰

Acknowledgment. We wish to thank the National Institute of Health for partial support of this work.

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