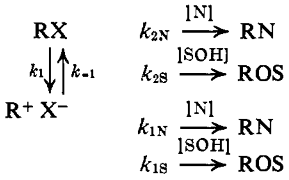
The experimental infinity titer is V_∞, the initial titer ($t = 0$) is V_0, and V_t is the titer at any time, t.

Appendix

Demonstration that $k_{1N}/k_{1S} = k_{2N}/k_{2S}$ for Simultaneous SN1 and SN2 Reactions. It can be shown that $k_{1N}/k_{1S} = k_{2N}/k_{2S}$ if a plot of [RN]/[ROS] *vs.* [N] is linear and if simultaneous SN1 and SN2 mechanisms are operative. The reaction scheme for simultaneous SN1 and SN2 reactions is shown in Scheme IA.

Scheme IA



The ratio [ROS]/[RN] is shown in eq A.

$$\frac{[\mathrm{ROS}]}{[\mathrm{RN}]} = \frac{k_{2S} + \dfrac{k_1k_{1S}}{k_{1S} + k_{1N}[\mathrm{N}] + k_{-1}}}{k_{2N}[\mathrm{N}] + \dfrac{k_1k_{1N}[\mathrm{N}]}{k_{1S} + k_{1N}[\mathrm{N}] + k_{-1}}} \qquad (\mathrm{A})$$

$$\frac{[\mathrm{ROS}]}{[\mathrm{RN}]} = \frac{k_{1S}k_{2S} + k_{2S}k_{1N}[\mathrm{N}] + k_{2S}k_{-1} + k_1k_{1S}}{k_{2N}[\mathrm{N}]k_{1S} + k_{2N}k_{1N}[\mathrm{N}]^2 + k_{2N}k_{-1}[\mathrm{N}] + k_1k_{1N}[\mathrm{N}]} \qquad (\mathrm{B})$$

Experimentally, a plot of [RN]/[ROS] vs. N is a straight line. Therefore

$$C_1 = \frac{k_{1S}k_{2S} + k_{2S}k_{1N}[\mathrm{N}] + k_{2S}k_{-1} + k_1k_{1S}}{k_{2N}k_{1S} + k_{2N}k_{1N}[\mathrm{N}] + k_{2N}k_{-1} + k_1k_{1N}} \qquad (\mathrm{C})$$

where C_1 is a constant.

$$k_{1S}k_{2S} + k_{2S}k_{1N}[\mathrm{N}] + k_{2S}k_{-1} + k_1k_{1S} = C_1(k_{2N}k_{1S} + k_{2N}k_{1N}[\mathrm{N}] + k_{2N}k_{-1} + k_1k_{1N}) \qquad (\mathrm{D})$$

$$[\mathrm{N}](k_{2S}k_{1N} - C_1k_{2N}k_{1N}) = C_1k_{2N}k_{1S} + C_1k_{2N}k_{-1} + C_1k_1k_{1N} - k_{1S}k_{2S} - k_{2S}k_{-1} - k_1k_{1S} \qquad (\mathrm{E})$$

The right side of eq E is a constant.

$$[\mathrm{N}](k_{2S}k_{1N} - C_1k_{2N}k_{1N}) = C_2 \qquad (\mathrm{F})$$

Since [N] is a variable and C_2 is a constant

$$k_{2S}k_{1N} - C_1k_{2N}k_{1N} = 0 \qquad (\mathrm{G})$$

Solving eq 6 for C_1 and substituting this value into eq D gives

$$k_{1S}k_{2S}k_{2N} + k_{2S}k_{1N}k_{2N}[\mathrm{N}] + k_{2S}k_{-1}k_{2N} + k_1k_{1S}k_{2N} = k_{2N}k_{1S}k_{2S} + k_{2N}k_{1N}k_{2S}[\mathrm{N}] + k_{2N}k_{-1}k_{2S} + k_1k_{1N}k_{2S} \qquad (\mathrm{H})$$

Rearranging and simplifying this equation gives

$$k_{1S}/k_{1N} = k_{2S}k_{2N} \qquad (\mathrm{I})$$

Thus if simultaneous SN1 and SN2 reactions are operating, a linear plot of [RN]/[ROS] *vs.* [N] leads directly to the condition

$$k_{1N}/k_{1S} = k_{2N}/k_{2S}$$

The Effect of Solvents on Anion Structure[1]

Robert C. Kerber and Albert Porter

Contribution from the Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11790. Received August 1, 1968

Abstract: The nmr and electronic spectra of salts of 1-nitroindene and 9-nitrofluorene show significant changes between hydroxylic and nonhydroxylic solvents. These changes demonstrate that hydrogen bonding to the oxygens of the anions tends to localize the charge on the oxygens, and thereby causes alterations in the structure of the anions. Cation coordination to the oxygens in nonpolar aprotic solvents produces similar effects, but of smaller magnitude. Analogous effects are observed for some phenoxide salts.

Our interest in the equilibria between 9-*aci*-nitrofluorene and 1-*aci*-nitroindene and their tautomers[2] led us to prepare the potassium salts of these compounds.[3] In the process of confirming the identity of these salts, we observed that their spectra showed substantial differences when measured in different solvents. Since a search of the literature failed to reveal any unequivocal examples of the effect of solvents on anion *structure* as revealed by spectra or other means, we undertook an investigation of this phenomenon, for the cases of these nitro salts and a pair of substituted phenoxide salts.

Nitro Salts. The potassium salts of 1-nitroindene (**1**) and 9-nitrofluorene (**2**) are high-melting, relatively stable solids, soluble in hydroxylic and in polar aprotic solvents but not very soluble in nonpolar solvents. Aqueous solutions are essentially neutral to pH paper, indicating the high acidity of the conjugate nitro compounds.

The infrared spectra of salts **1** and **2** in Nujol or hexachlorobutadiene mulls show lower C=N stretching frequencies (1527 and 1504 cm^{-1}, respectively) than typical secondary nitroalkane salts (1579-1603 cm^{-1}).[4]

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[1] Presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 3, 1968, Abstract P-130.

[2] R. C. Kerber and M. Hodos, *J. Org. Chem.*, **33**, 1169 (1968).

[3] (a) W. Wislicenus and K. Pfeilsticker, *Ann.*, **436**, 36 (1924); (b) W. Wislicenus and M. Waldmüller, *Ber.*, **41**, 3334 (1908).

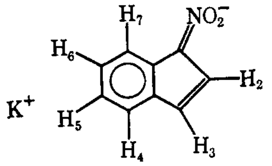
[4] H. Feuer, C. Savides, and C. N. R. Rao, *Spectrochim. Acta*, **19**, 431 (1962).

This apparently reflects greater delocalization of negative charge into the five-membered rings, and consequent lowering of the C=N bond order in the nitrocyclopentadiene derivatives.[5]

The salt **1** in particular provides a sensitive probe for solvent effects, because it contains a strongly polar functional group bearing the greater part of the charge density, and a hydrocarbon portion in conjugation with the polar functional group. Hydrogen-bonding or counterion association should occur almost entirely at the electron-rich oxygen atoms. The 2- and 3-protons provide a convenient probe of solvent effects on anion structure, since both their chemical shifts and coupling constant may be readily measured from the proton magnetic resonance spectrum.

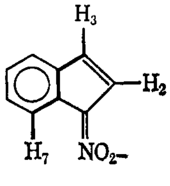
The nmr spectra of **1** in all solvents (Table I) show some common features: a one-proton resonance at *ca.* τ 2.0, which is due to the 7-proton, deshielded by the anisotropic effect of the *peri*-nitro group;[7] a complex multiplet in the range τ 2.6–3.4 due to the remaining three aromatic protons; and a pair of doublets in the range τ 3.0–4.0 due to the 2- and 3-protons on the five-membered ring. Of the latter two doublets, the lower field one is assigned to the 2-proton because that proton, like the 7-proton, should be subject to anisotropic deshielding by the proximate nitro group. Moreover, the high-field doublet usually shows broadening or splitting (0.7 Hz) due to a five-bond coupling to the 7-proton, such as is found in other indene derivatives.[8]

Table I. Effect of Solvent on the Nmr Spectra of

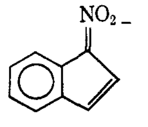


Solvent[a]	τ_2	τ_3	τ_{4-6}	τ_7	J_{23}[b]	J_{37}[b]
H⁺, $CDCl_3$[c]	3.3	3.3	2.5–2.8	2.0	...	...
D_2O	3.22	3.40	2.65–3.00	2.05	5.7	0.6
CF_3CH_2OH	3.18	3.39	2.70–3.00	1.96	5.6	...
Methanol	3.06	3.55	2.75–3.10	1.88	5.5	...
Acetone	3.05?	3.75	2.70–3.15	1.85	5.1	0.7
PC[d]	?	3.78	2.65–3.30	1.96	5.0	0.7
DMSO[e]	3.07?	3.87	2.70–3.25	1.98	5.1	...
HMP[f]	3.00?	4.04	2.80–3.40	1.92	5.0	...

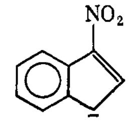
[a] All solutions *ca.* 5%. [b] ±0.1 Hz. [c] Spectrum of O-protonated form in $CDCl_3$ solution. *Cf.* ref 2. [d] Propylene carbonate. [e] Dimethyl sulfoxide. [f] Hexamethylphosphoramide.



The data of Table I show that in the strong hydrogen-bonding solvents, water and trifluoroethanol, the coupling constant of the protons in the five-membered ring, J_{23}, is 5.6–5.7 Hz, the same as in indene itself.[8,9] Since *cis*-geminal coupling constants in five-membered rings are related to the C=C bond order,[10] one can conclude that *in these hydroxylic solvents* the C_2–C_3 bond of **1** is essentially a pure double bond, and that therefore structures such as **1b** do not contribute significantly to the ground state. This is consistent with the chemical shift of the 3-proton (τ 3.4), which is not significantly shielded with respect to that of indene itself (τ 3.34).[9]



1a



1b

In contrast to these results in the strong hydrogen-bonding solvents, the spectra of **1** in aprotic solvents are substantially changed. Some of the aromatic ring protons are shifted upfield; more noticeably, the resonance of the 3-proton shifts upfield by as much as 0.6 ppm[11] (in HMP). At the same time, the coupling constant J_{23} decreases to 5.0 Hz.[12] We interpret these changes in the nmr spectra as reflecting increased electron density at C-3 and a lower π-bond order between C-2 and C-3[13] in aprotic solvents. This strongly suggests that the contribution of structures such as **1b** to the ground state of **1** is greater in aprotic solvents, where charge dispersion is favored by the nature of the available solvation,[14] than in hydroxylic solvents, where the primary solvation of anions is through hydrogen bonding.

It may be noted that even among the hydrogen-bonding solvents small differences in spectra can be seen; in particular, methanol seems to be less effective than water or trifluoroethanol as a hydrogen-bond donor.[15]

The nmr spectra of **2** in a number of solvents indicate the same trends as those of **1** in that the aromatic multiplet falls at higher field in the aprotic solvents than in the hydroxylic solvents. However, **2** lacks the sensitive probe afforded by the 2- and 3-protons of **1**.

The suggestion that the ground-state structure of the diamagnetic anions **1** and **2** is affected by the solvent is strongly supported by work on the electron spin

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[5] Protonation on oxygen reduces such charge delocalization and raises the C=N stretching frequencies to 1654 and 1652 cm^{-1} for **1** and **2**.[2,6]

[6] J. P. Freeman and K. S. McCallum, *J. Org. Chem.*, **21**, 472 (1956).

[7] Similar *peri* deshieldings are observed in 1-nitronaphthalene and 1-nitroazulene: P. R. Wells and P. G. E. Alcorn, *Australian J. Chem.*, **16**, 1108 (1963); D. Meuche and E. Heilbronner, *Helv. Chim. Acta*, **45**, 1965 (1962).

[8] J. A. Elvidge and R. G. Foster, *J. Chem. Soc.*, 590 (1963).

[9] D. D. Elleman and S. L. Manatt, *J. Chem. Phys.*, **36**, 2346 (1962).

[10] W. B. Smith, W. H. Watson, and S. Chiranjeevi, *J. Am. Chem. Soc.*, **89**, 1438 (1967).

[11] This shift, if due only to changes in electron density at C-3, would correspond to an increase of 0.06 electron charge at that position.

[12] Using Smith's correlation,[10] the 0.7-Hz decrease in coupling constant found here corresponds to a 10% reduction in π-bond order.

[13] The changes in J_{23} could also be explained by changes in hybridization at C-2 and/or C-3, with consequent changes in the HCCH dihedral angle. However, no reason for such deviations as a function of solvent is evident, nor would such deviations explain the changes in chemical shifts. Vicinal coupling constants are not normally sensitive to solvent effects: P. Laszlo, *Progr. Nmr Spectry.*, **3**, 348 (1967). However, see S. Castellano and R. Kostelnik, *J. Am. Chem. Soc.*, **90**, 141 (1968); S. Castellano and C. Sun, *ibid.*, **88**, 4741 (1966), for results concerning the effect of electronegativity of substituents on aromatic rings on the *ortho-meta* coupling constants, which parallel those reported here.

[14] See, for example, R. Alexander, E. C. F. Ko, Y. C. Mac, and A. J. Parker, *ibid.*, **89**, 3703 (1967), and references therein.

[15] Similar conclusions have been drawn from phenoxide and naphthoxide alkylation studies: N. Kornblum, P. J. Berrigan, and W. J. le Noble, *ibid.*, **85**, 1141 (1963); W. J. le Noble, *ibid.*, **85**, 1470 (1963).

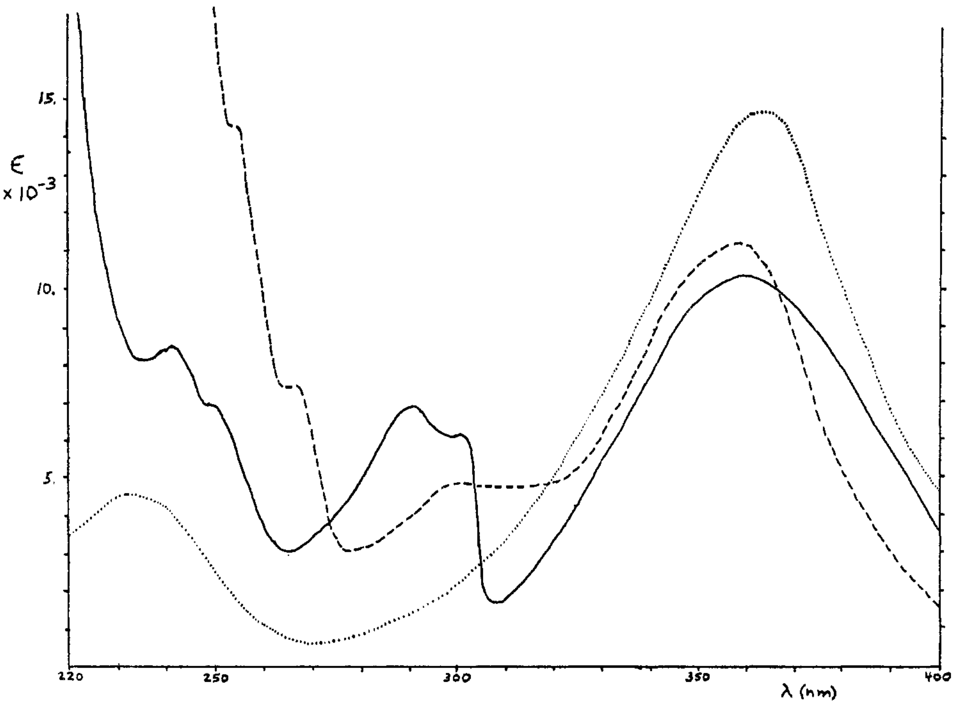

Figure 1. Ultraviolet spectra of **1** (——), **2** (----), and **4** (····) in water.

resonance spectra of nitroaromatic radical anions and other radical anions bearing good hydrogen-bond acceptor groups.[16] In such anions, the esr spectra in hydrogen-bonding solvents provide direct evidence of polarization of electron density toward the site(s) of hydrogen-bond acceptance.

Analogous, but smaller, effects have even been observed in neutral dipolar molecules. Thus, the sum of the coupling constants $|J_o + J_p|$ for *p*-nitroanisole (**3**) increases slightly with increasing solvent polarity, due to increased contribution of structure **3b** to the ground state in the more polar solvents.[17] Moreover, the ^{19}F nmr spectrum of *p*-fluoronitrobenzene shows the

3a **3b**

fluorine to be more deshielded (relative to fluorobenzene) in polar solvents, particularly hydrogen-bond-donating solvents, due to the greater electron-withdrawing ability of the hydrogen-bonded nitro group.[18]

If the effect of solvents on the nmr spectra of anions **1** and **2** is due to alterations in ground-state structure of the anions, then analogous effects of solvents on other spectra of these ions should be observable. The electronic spectra of these salts in water solution are relatively complex (Figure 1). Both salts (as well as the sodium salt of nitrocyclopentadiene (**4**)[19]) show intense, broad absorptions at *ca.* 360 nm, as well as other absorptions at lower wavelength. The longest wavelength absorption maximum in simple nitro salts, which appears at 226–239 nm, is thought to be due to a $\pi \rightarrow \pi^*$ transition having the character of an intramolecular charge transfer from the oxygens of the anion to the carbon.[20] This transition shifts appreciably to longer wavelength on conjugation (*e.g.*, salts of phenylnitromethane absorb at 293 nm[21]) and is probably also responsible for the 360-nm absorption of salts **1**, **2**, and **4**. The transfer of charge from the oxygens to the hydrocarbon portion of these salts in the excited state should result in lesser stabilization of the excited state by hydrogen bonding, and accordingly the transition should occur at higher energy (shorter wavelength) in hydrogen-bonding solvents than in aprotic solvents.

Indeed, a marked effect of solvent on the long-wavelength bands is observed (Table II). The transition energies do not correlate with spectrochemical indices of solvent polarity such as Z[22] (Figure 2); rather, they divide into two sets, one for hydroxylic solvents and one for nonhydroxylic solvents. As expected, the absorption is strongly blue shifted in the hydrogen-bonding solvents; water and trifluoroethanol are noticeably more effective at stabilizing the ground state by hydrogen bonding than the other alcohols, as judged by both the electronic and nmr spectra.

The difference in the transition energies of the anions in HMP and in water is more than 12 kcal. If this corresponds to the energy of the hydrogen bonds in the ground state,[23] then it is clear that both oxygen atoms in the nitro salts must be tightly hydrogen bonded within a sheath of solvent molecules.[24]

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(16) (a) L. H. Piette, P. Ludwig, and R. N. Adams, *ibid.*, **84**, 4212 (1962); (b) J. Gendell, J. H. Freed, and G. K. Fraenkel, *J. Chem. Phys.*, 37, 2832 (1962); (c) J. Q. Chambers, T. Layloff, and R. N. Adams, *ibid.*, **68**, 661 (1964); (d) P. B. Ayscough, F. P. Sargent, and R. Wilson, *J. Chem. Soc.*, 5418 (1963); (e) P. L. Kolker and W. A. Waters, *ibid.*, 1336 (1964).

(17) H. M. Hutton and T. Schaeffer, *Can. J. Chem.*, **43**, 3116 (1965).

(18) R. W. Taft, *et al.*, *J. Am. Chem. Soc.*, **85**, 3146 (1963).

(19) R. C. Kerber and M. J. Chick, *J. Org. Chem.*, 32, 1329 (1967).

(20) F. T. Williams, Jr., P. W. K. Flanagan, W. J. Taylor, and H. Shechter, *ibid.*, 30, 2674 (1965).

(21) W. Kemula and W. Turnowska-Rubaszewska, *Roczniki Chem.*, 37, 1597 (1963).

(22) E. M. Kosower, *J. Am. Chem. Soc.*, 80, 3253 (1958).

(23) G. J. Brealey and M. Kasha, *ibid.*, 77, 4462 (1955).

(24) This hypothesis provides a ready explanation of the blue shift produced in nitroalkane anion spectra in water by bulky alkyl groups.[20] We would interpret this as due to steric hindrance to solvation by the

Table II. Effect of Solvent on Long-Wavelength Electronic Absorptions of Nitro Salts

Solvent	Absorption max, nm 1	 2
H^+, ether or ethanol[a]	338	338
Trifluoroethanol	352	...
Water	359	357
Ethanol	378	373
t-Butyl alcohol	376	371
Ether	393	381,[b] 396
Dioxane	395	385, 400[c]
Tetrahydrofuran (THF)	406	387,[b] 406
Acetone	414	395,[b] 419
PC	414	394,[b] 414
DMSO	417	396,[b] 419
HMP	418	401,[b] 424

[a] Spectrum of O-protonated form in ether or ethanol. Not solvent sensitive. *Cf.* ref 2. [b] Shoulder on larger peak. [c] Both peaks of equal intensity.

In addition to the large differences in the spectra between hydroxylic and aprotic solvents, there is also a consistent trend within the group of aprotic solvents: the wavelength shows a red shift with increasing solvent polarity. The values in DMSO or HMP probably approach that of the free ion, but as the solvent becomes less polar and less able to solvate the potassium ion, the ions associate more tightly, and the spectrum becomes shifted to shorter wavelength.[25] That these shifts are due to cation association in the less polar solvents is shown by the effect of changing the K^+ ion in **1** for Na^+, and by the effect of adding the potassium chelatent, 2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene (**5**)[26] to solutions of the potassium salt (Table III). In the hydroxylic solvents these changes produce essentially no effect, because the anions are tightly hydrogen bonded to solvent molecules and do not form sufficiently tight ion aggregates.[27a] Similarly, in the polar aprotic solvents, the metal ions are strongly coordinated to solvent molecules and do not affect the spectra of the anions. However, in the nonpolar solvents the normal state of the salts is presumably as relatively tight ion aggregates, with sodium forming tighter ion aggregates (which absorb at shorter wavelength) than potassium, which in turn is able to form tighter ion aggregates than potassium complexed with **5**.[27b]

Table III. Ion Association Effects on Electronic Transitions of Salts of 1-Nitroindene

Solvent	Absorption max, nm Na^+ salt	 K^+ salt	 K^+ salt + **5**
Trifluoroethanol	350	352	352
Water	359	359	359
t-Butyl alcohol	374	378	379
Ether	383	393	403
Dioxane	~390	395	407
THF	398	406	410
Acetone	416	414	413
HMP	418	418	417

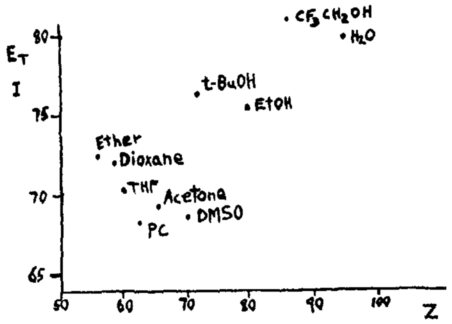

Figure 2. Lack of correlation between transition energy of **1** (kilocalories/mole) with *Z* in indicated solvents.

It is notable that either protonation, hydrogen bonding, or cation coordination to the oxygens of **1** or **2** produces qualitatively the same blue shift in the spectra of the anions, as expected if all three occur at the same site (oxygen). The effect of hydrogen bonding is considerably greater than that of cation coordination. This is analogous to the chemical results of Kornblum[15,28] who found that either hydrogen bonding or cation coordination to the oxygen of phenoxide anions favors carbon alkylation, with hydrogen bonding having the larger effect. This analogy suggested that spectra of some phenoxide salts should show similar effects.[29]

Phenoxide Salts. The phenoxides chosen for study were the sodium salts of 2,3-dimethyl-4-chlorophenol (**6**) and 2,3,6-trimethylphenol (**7**). These highly substituted phenols were chosen because each has only one pair of *ortho* aromatic protons, which should give a nearly first-order pattern in the nmr spectrum, and because the added hydrocarbon substituents should raise the solubility of the phenoxide salts in nonpolar media.

A summary of the spectral data for the sodium salts of these phenols is given in Tables IV and V.

In **6**, the higher field ring proton is assigned as the 6-proton, since protons *ortho* to the hydroxyl group in phenol[30] and in methylated phenols[31] invariably resonate at higher fields than those *meta* to the hydroxyl group. Similarly, in **7**, the higher field ring proton is taken to be the 4-proton because of the normal higher field resonances of *para* protons relative to *meta*.[30,31a,32] No unequivocal assignment of the methyl resonances in **6** is possible; we have, however, assigned the higher field resonance as the 2-methyl group by analogy with

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bulky alkyl groups, rather than to loss of coplanarity, as previously hypothesized.[22] One would predict from our hypothesis that the effect should be much smaller in aprotic solvents.

(25) (a) J. F. Garst, *et al.*, *J. Am. Chem. Soc.*, **87**, 4080, 4084 (1965); (b) H. E. Zaugg and A. D. Schaefer, *ibid.*, **87**, 1857 (1965).

(26) C. J. Pedersen, *ibid.*, **89**, 7034 (1967). This polyether also increases the solubility of **1** and **2** in nonpolar solvents by large factors.

(27) (a) Our experiments provide no distinction between ion pairs and higher ion aggregates. Consequently the latter, more general, term is used, even though one might not expect higher aggregates at the low concentrations used for the ultraviolet spectra. (b) In no case have we been able to observe separate absorptions for different types of ion pairs, as has been done for some alkali carbanion salts: L. L. Chan and J. Smid, *ibid.*, **89**, 4547 (1967); T. E. Hogen-Esch and J. Smid, *ibid.*, **88**, 307 (1966).

(28) N. Kornblum, R. Seltzer, and P. Haberfield, *J. Am. Chem. Soc.*, **85**, 1148 (1963).

(29) The effects of cation coordination and hydrogen bonding on the electronic spectra of a number of phenoxide and enolate salts have been reported. See ref 25 and also A. J. Parker and D. Brody, *J. Chem. Soc.*, 4061 (1963). No studies of these effects by nmr are known to us.

(30) J. C. Schug and J. C. Deck, *J. Chem. Phys.*, **37**, 2618 (1962).

(31) (a) I. Yamaguchi, *Bull. Chem. Soc. Japan*, **34**, 744 (1961); (b) Sadtler Standard NMR Spectra No. 82, 193, Sadtler Research Laboratories, Philadelphia, Pa., 1967.

(32) (a) R. R. Fraser, *Can. J. Chem.*, **38**, 2226 (1960); (b) Sadtler Standard NMR Spectra No. 36, 82 Sadtler Research Laboratories, Philadelphia, Pa.

Table IV. Spectral Data for Sodium 2,3-Dimethyl-4-chlorophenoxide (6)

Solvent	Nmr data					Uv[a]
	τ_2 or τ_3		τ_5	τ_6	J_{56}	
H^+, chloroform-*d*[b]	7.85	7.73	3.01	3.45	8.6	
H^+, *t*-butyl alcohol[b]	*c*	*c*	*c*	*c*	*c*	283
H^+, methanol[b]	7.84	7.73	3.06	3.38	8.6	284
H^+, water[b]	*c*	*c*	*c*	*c*	*c*	281
D_2O	7.91	7.76	3.08	3.50	8.6	298[d]
Methanol	7.82	7.78	3.22	3.51	8.6	299
t-Butyl alcohol	7.87	7.79	3.27	3.61	8.6	305
THF	7.88	7.78	3.24	3.71	8.6	307
Acetonitrile	*c*	*c*	*c*	*c*	*c*	308
Diglyme	7.93	7.85	3.37	3.81	8.6	312
DMSO-d_6	8.02	7.89	3.41	3.90	8.6	324[d]
HMP	7.96	7.91	3.56	3.80	8.7	328

[a] Position of longest wavelength maximum, in nm. [b] Spectra of the phenol. [c] Not sufficiently soluble for nmr. [d] Solvent for uv not deuterated.

Table V. Spectral Data for Sodium 2,3,6-Trimethylphenoxide (7)

Solvent	Nmr data					Uv[a]
	$\tau_{2,6}$	τ_3	τ_4	τ_5	J_{45}	
H^+, $CDCl_3$[b]	7.85, 7.90	7.82	3.36	3.24	7.8	
H^+, methanol[b]	7.83, 7.86	7.83	3.40	3.28	7.8	273
H^+, water[b]	*c*	*c*	*c*	*c*	*c*	272
D_2O	7.88	7.76	3.59	3.15	7.4	288[d]
Methanol	7.85	7.74	3.81	3.39	7.5	290
t-Butyl alcohol	7.89	7.75	3.82	3.37	7.5	294
THF	7.93	7.93	4.07	3.43	7.4	
Diglyme	7.96	7.94	4.16	3.48	7.4	
DMSO	8.08	8.03	4.30	3.57	7.4	311
HMP	8.01	8.01	4.39	3.60	7.2	

[a] Position of longest wavelength maximum, in nm. [b] Phenol spectrum. [c] Not sufficiently soluble for nmr. [d] Not deuterated for uv.

the ring proton resonances, and by analogy with **7**. In the spectra of the salt, **7**, one finds two methyl groups of identical chemical shift at high field, and the other at lower field. Since the 2- and 6-methyl groups are both *ortho* to the oxygen, these are most likely to show the same chemical shifts; they are therefore assigned the high-field resonance. The 3-methyl is thus assumed to fall at the lower field.

The nmr and ultraviolet spectra of the phenols do not exhibit marked solvent sensitivity. Conversion to the phenoxide salts, however, causes the ultraviolet absorption to move to longer wavelength, and the resonances of the ring protons to be shifted to higher field. The spectra of the phenoxides are noticeably solvent dependent: the ultraviolet absorption is at longer wavelength, and the ring proton chemical shifts are at higher field in aprotic solvents. These effects closely duplicate those of the nitro salts **1** and **2**, and presumably also reflect polarization of the anion structure by hydrogen bonding to the oxygen. No effect on the *ortho–meta* proton coupling constant of **6** can be discerned; however, the *meta–para* proton coupling constant of **7** clearly decreases on converting the phenol to the salt, and possibly also on transferring the phenoxide from protic to aprotic media.[33] Again analogously to the nitro salts, the salts **6** and **7** show slightly different spectra even in the different aprotic media, presumably due to the effects of cation association.

Conclusions

The electronic and nmr spectra of some phenoxide and nitronate salts indicate that hydrogen bonding (and to a lesser extent, cation association) causes polarization of the structure of the anions. The charge density tends to shift toward the acceptor site(s), causing detectable changes in bond orders and charge densities elsewhere in the molecules.

It has become evident in recent years that weak acids such as nitro compounds and phenols, with whose conjugate bases we deal here, show great variations in pK_a between protic and aprotic solvents.[34] This effect, in which oxy acids such as these are much weaker acids in aprotic solvents than in protic, has been explained as due to hydrogen bonding of hydroxylic solvents to the conjugate bases.[34] This results in stabilization of the conjugate bases through extramolecular charge dispersion into the solvent *via* the hydrogen bonds. In the absence of this stabilization, these materials become much weaker acids, since charge dispersion can occur only within the anion and to a small extent through dispersion interactions with the aprotic solvent. Hydrocarbon acids, whose conjugate bases do not enjoy extensive stabilization by hydrogen bonding, show about the same or slightly stronger acidity in aprotic solvents as in hydroxylic solvents.

These ideas find strong support in the results of this paper, which show that the extramolecular charge dispersion *via* hydrogen bonding occurs to some extent at the expense of intramolecular delocalization. Consequently, one is dealing with equilibria between a common acid and conjugate bases of somewhat different structure in the different types of solvents. It is therefore not surprising that acidities change so much with different solvents, and that a uniform H_- acidity scale cannot be set up.[34a,b]

These results also suggest a simple criterion for choosing indicators of widest utility in constructing basic acidity scales: those acids whose conjugate bases are least sensitive to solvent effects in their spectroscopic behavior should show the least change in absolute acidity between different solvents. This simple rule may be violated for a variety of reasons, such as chelation effects of the anions,[25b] conformational effects, and steric effects, but may nonetheless prove useful as a "rule of thumb."

Experimental Section

Materials. The potassium salts **1** and **2** were prepared as described elsewhere.[2,3] The infrared spectrum of **1** (Nujol or hexachlorobutadiene mulls, Perkin-Elmer 137-B Infracord, polystyrene film calibration) showed major bands at 6.45 (s), 7.24 (m), 7.54 and 7.63 (m) doublet, 8.13 (s), 8.81 (s), 10.04 (s), and 13.26 (s) μ; **2**

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[33] Hückel molecular orbital calculations and consideration of valence bond structures both predict an increase in the 2–3 bond order and decrease in the 3–4 bond order in converting phenol to phenoxide ion. W. B. Smith and T. J. Kmet [*J. Phys. Chem.*, 70, 4084 (1966)] have previously reported a 0.5-Hz increase in J_{23} on converting 4-nitrophenol to its conjugate base, due to an increased contribution of the quinonoid resonance structure in the phenoxide. Comparable increases were not observed in 4-bromo- and 4-cyanophenols on conversion to the phenoxides.

[34] (a) C. D. Ritchie and R. E. Uschold, *J. Am. Chem. Soc.*, **89**, 1721, 2752 (1967); **90**, 2821 (1968); (b) E. C. Steiner and J. D. Starkey, *ibid.*, **89**, 2751 (1967); (c) I. M. Kolthoff, M. K. Chantooni, and S. Bhowmik, *ibid.*, **90**, 23 (1968); (d) B. W. Clare, D. Cook, E. C. F. Ko, Y. C. Mac, and A. J. Parker, *ibid.*, **88**, 1911 (1966).

at 6.55 (m), 8.17 (s), 9.10 (m), 9.95 (s), 10.60 (m), 13.03 (s), and 13.60 (m) μ. 4-Chloro-2,3-dimethylphenol (Aldrich) was recrystallized from hexane to mp 83–84° (lit.[35] 84.5°). 2,3,6-Trimethylphenol (Aldrich) was recrystallized from hexane to mp 60–62° (lit.[36] 62°). Solvents used for spectra were dried and purified by standard methods: distillation from lithium aluminum hydride or sodium for the ethers; from calcium hydride for the polar aprotic solvents. **5** was prepared according to Pedersen's Method X,[26] in 15% yield, mp 161.5–163.5° (lit.[26] 164°).

Sodium Salt of 1-Nitroindene. A solution of 0.1 g of **1** in 5 ml of water was passed through a column (10 cm high × 1 cm diameter) of Dowex 50W-X1 resin which had been first washed with 30 ml of 1 *N* NaOH solution then 60 ml of water. Washing with 70 ml of water sufficed to remove the sodium salt from the column as judged by the color of the effluent. The water was stripped off at room temperature under vacuum, and the resulting dark yellow solid was dried at 0.2 mm pressure and room temperature. The infrared spectrum was essentially the same as that of **1**. On heating, the material darkened at *ca.* 200°, but did not melt even at 250°. A flame test showed a brilliant sodium coloration, but no potassium color through cobalt glass.

Sodium 4-Chloro-2,3-dimethylphenoxide (6). Sodium hydroxide (1.095 g, 27.4 mmol) was partially dissolved in 50 ml of methanol, then 4.184 g (26.7 mmol) of 4-chloro-2,3-dimethylphenol was added. The mixture was stirred at room temperature under a nitrogen atmosphere until homogeneous, then stripped on a rotatory evaporator. The residue was dried at 0.1 mm and room temperature for 24 hr. The material did not melt below 200°. The neutralization equivalent was 177 (calcd for C_8H_8ClNaO, 178.6).

Comparable attempts to prepare **7** gave only material of very high neutralization equivalent. Consequently, the spectra of **7** were obtained by dissolving the phenol in a solution containing excess sodium methoxide, and, if necessary, filtering quickly under nitrogen pressure.

Spectra. The electronic spectra were obtained using a Perkin-Elmer Model 202 or Beckman DK-2A spectrophotometer. All solutions were deoxygenated by passing dry nitrogen through them for several minutes before running the spectra. Concentrations of **1** and **2** were typically 1-5 × 10^{-5} *M*; those of **6** and **7**, 1-5 × 10^{-4} *M*. Nuclear magnetic resonance spectra were obtained using a Varian A-60, with tetramethylsilane as internal standard (τ 10.00). The spectral data are given in the text. Excess sodium alkoxide was used in obtaining the phenoxide spectra in protic solvents. None of the salts was sufficiently soluble in the ethers (5%) to give usable nmr spectra.

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(35) L. E. Hinkel, W. T. Collins, and E. E. Ayling, *J. Chem. Soc.*, **123**, 2968 (1923).

(36) G. T. Morgan and A. E. J. Pettet, *ibid.*, 418 (1934).

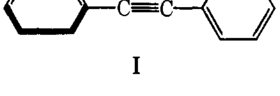
The Interactions and Chemistry of 1,8-Bis(phenylethynyl)-naphthalene and 1,8-Bis(1-alkynyl)naphthalenes

B. Bossenbroek, D. C. Sanders, H. M. Curry, and H. Shechter

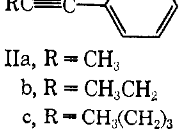
Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received August 28, 1968*

Abstract: The *peri*-diacetylenes, 1,8-bis(phenylethynyl)naphthalene (I) and 1,8-bis(1-alkynyl)naphthalenes (IIa–c), have been prepared from 1,8-diiodonaphthalene (III) and appropriate cuprous acetylides in pyridine. The ultraviolet absorption maxima of I are at slightly longer wavelengths than those of 1,5-bis(phenylethynyl)naphthalene (IV). The moderate nmr shielding and the absorption in I indicate that its phenyl groups may be moved apart and there may be some transannular acetylenic interaction upon its electronic excitation. Thermolysis or photolysis of I yields 7-phenylbenzo[*k*]fluoranthene (VI); reaction of I with iron pentacarbonyl gives acecycloneiron tricarbonyl (XIV). Bromination of I occurs by transannular 1,4 addition yielding 1,2-bis(α-bromobenzylidene)acenaphthene (XVI). XVI reacts with magnesium or *n*-butyllithium to give I, VI, and 7-bromo-12-phenylbenzo[*k*]fluoranthene (XXIII). Photolysis or thermolysis of XVI results in XXIII. Absorption in IIa occurs at slightly longer wavelengths than in 1,5-bis(1-propynyl)naphthalene (XXVII); transannular electronic interaction of the acetylene groups in IIa upon excitation is not large. Addition of 2 equiv each of bromine, hydrogen bromide, and hydrogen iodide to IIa occurs without net transannular structural change to yield 1,8-bis(1,2-dibromo-1-propenyl)naphthalene (XXVIII), 1,8-bis(1-bromo-1-propenyl)naphthalene (XXIXa), and 1,8-bis(1-iodo-1-propenyl)naphthalene (XXIXb), respectively. *peri*-Diacetylene I adds 2 equiv of hydrogen bromide to give the adduct $C_{26}H_{18}Br_2$.

The present research involves synthesis and study of 1,8-bis(phenylethynyl)naphthalene (I)[1] and 1,8-bis(1-alkynyl)naphthalenes (IIa–c). These *peri*-naphthalene derivatives contain near-rigid acetylene groups



I



IIa, R = CH_3
b, R = CH_3CH_2
c, R = $CH_3(CH_2)_3$

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[1] (a) In the present publication the synthesis and chemistry of I reported is a summary of the Ph.D. dissertation of B. Bossenbroek, The Ohio State University, 1967. (b) Synthesis and chemistry of 1,8-bis-(phenylethynyl)naphthalene (I) have been described preliminarily as a communication by B. Bossenbroek and H. Shechter, *J. Am. Chem. Soc.*, **89**, 7111 (1967). (c) Essentially simultaneously J. Ipaktschi and H. A. Staab, *Tetrahedron Letters*, 4403 (1967), submitted a communication in which syntheses, properties, and conversions of I to 7-phenylbenzo[*k*]-fluoranthene (VI), 12-phenylindeno[1,2-*a*]phenylene (XI), and acecycloneiron tricarbonyl (XIV) are reported. (d) Subsequently E. Müller, J. Heiss, M. Sauerbrier, D. Streichfuss, and R. Thomas, *ibid.*, 1195 (1968), described conversion of I by platinum tetrachloride to XI, its photolysis to VI, 7-phenylazuleno[1,2-*a*]acenaphthylene (XII, tentative) and an unassigned red product, and its thermolysis to VI. (e) For further communications and publications of the rapidly expanding field of parallel acetylenes see H. A. Staab, H. Mack, and E. Wehinger, *ibid.*, 1465 (1968); H. A. Staab, A. Nissen, and J. Ipaktschi, *Angew. Chem.*, 80, 241 (1968); and R. H. Mitchell and F. Sondheimer, *Tetrahedron*, **24**, 1397 (1968).