clearly preferentially incorporated into the solid phase as the temperature is lowered below 32 °C. Perhaps the most interesting feature of the present results is the quantitative discrepancy between the observed and calculated temperature dependence of the ^{13}C line broadening. In essence, the observed DPPC* resonance senses the onset of the lateral phase separation more strongly than expected on the basis of the theoretical calculations. The calculation assumes that ^{13}C nuclei in fluid domains are only broadened by lateral diffusion to solid domains. The calculated line broadening at the onset of the phase separation is small since the typical distance a molecule must diffuse ($\sim 1\ \mu$) is too far for this motion to be an efficient broadening mechanism for all ^{13}C nuclei in fluid domains.

A possible source of this "early" line broadening is nucleation throughout the fluid phase. If this process is sufficiently rapid, and extensive, then a large proportion of ^{13}C nuclei in the fluid phase may sense a relatively rigid environment, for a short period of time, without the need for long-range lateral diffusion. Unfortunately, it is difficult to give any theoretical estimate of the nucleation rate, since it depends critically on the number of molecules required for a nucleation center. Random composition fluctuations of the magnitude of those related by tie lines connecting the fluidus and solidus curves are very probable for groups of molecules of the order of ten, and become rapidly less probable for larger groups of molecules. Freeze-fracture electron microphotographic studies of lipid mixtures such as DEPC and DPPC as yet show no evidence of such nucleation centers; however, when membrane proteins are included in these mixtures one often observes patterns of solid phase crystallinity that indicate that such proteins can serve as nucleation centers for the growth of large solid phase domains (W. Kleemann and H. M. McConnell, unpublished).

In previous work, studies have been made of the temperature dependence of the active uptake of β-galactosides and β-glucosides into $E.\ coli$ cells having simple fatty acid compositions.[1] In one case ($E.\ coli$ 30Eβox$^-$ grown on elaidic acid) there is a virtually discontinuous marked $increase$ in the transport rate with $decreasing$ temperature, at the same temperature shown by the spin-label TEMPO method to

mark the onset of a lateral phase separation.[1] It has been suggested that density fluctuations (nucleation) in the immediate vicinity of the transport proteins may be responsible for this enhancement of transport.[1] The possible density fluctuations reported in the present work fall in a frequency domain that is consistent with this earlier proposal, and the present study provides the only physical evidence yet available for such fluctuations.

References and Notes

(1) C. Linden, K. Wright, H. M. McConnell, and C. F. Fox, *Proc. Natl. Acad. Sci. U.S.A.*, **70**, 2271 (1973).
(2) B. J. Wisnieski, Y. O. Huang, and C. F. Fox, *J. Supra. Struct.*, **2**, 593 (1974).
(3) N. Tsukagoshi and C. F. Fox, *Biochemistry*, **12**, 2822 (1973).
(4) G. K. Humphries and H. M. McConnell, *Proc. Natl. Acad. Sci. U.S.A.*, in press.
(5) For other views concerning lateral phase separations in membranes, and for references to additional literature relating the physical properties of membrane lipids and function, see A. G. Lee, N. J. M. Birdsall, J. C. Metcalfe, P. A. Toon, and G. B. Warren, *Biochemistry*, **13**, 3699 (1974).
(6) C. W. F. McClare, *Anal. Biochem.*, **39**, 527 (1971).
(7) E. Cubero Robles and D. Van den Berg, *Biochim. Biophys. Acta*, **187**, 520 (1969).
(8) F. M. Davidson and C. Long, *Biochem. J.*, **69**, 458 (1958).
(9) R. D. Kornberg and H. M. McConnell, *Biochemistry*, **10**, 1111 (1971).
(10) R. Lohrmann and H. G. Khorana, *J. Am. Chem. Soc.*, **88**, 829 (1966).
(11) E. J. Shimshick and H. M. McConnell, *Biochemistry*, **12**, 2351 (1973).
(12) S. H. Wu and H. M. McConnell, *Biochemistry*, **14**, 847 (1975).
(13) C. W. M. Grant, S. H. Wu, and H. M. McConnell, *Biochim. Biophys. Acta*, **363**, 151–158 (1974).
(14) C. W. M. Grant and H. M. McConnell, *Proc. Natl. Acad. Sci. U.S.A.*, **71**, 4653 (1974).
(15) W. Kleemann, C. W. M. Grant, and H. M. McConnell, *J. Supra. Struct.*, **2**, 609 (1974).
(16) J. Zernike, "Chemical Phase Theory", Antwerp, N.V. Uitgevers-Maatschappij AE. E. Kluwer, 1955, p. 220.
(17) P. Devaux and H. M. McConnell, *J. Am. Chem. Soc.*, **94**, 4475 (1972).
(18) H. Träuble and E. Sackmann, *J. Am. Chem. Soc.*, **94**, 4499 (1972).
(19) C. J. Scandella, P. Devaux, and H. M. McConnell, *Proc. Natl. Acad. Sci. U.S.A*, **69**, 2056 (1972).
(20) P. Brûlet and H. M. McConnell, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 1451 (1975).

π-Spin Distribution in the Radical Anions of [2.2]Paracyclophane and Some of Its Symmetric Benzo Derivatives

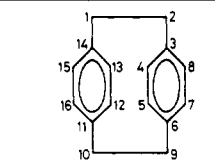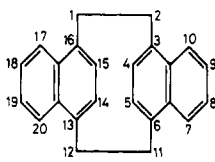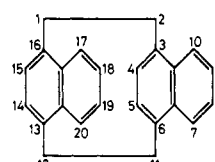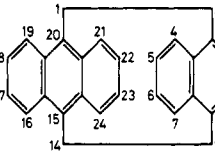**F. Gerson,* W. B. Martin, Jr., and Ch. Wydler**

Contribution from the Physikalisch-Chemisches Institut der Universität, 4056 Basel, Switzerland. Received July 1, 1975

Abstract: The radical anions of [2.2]paracyclophane (**1**), *syn-* and *anti-*[2.2](1,4)naphthalenophanes (**2** and **3**, respectively), and [2.2](9,10)anthracenophane (**4**) have been studied by ESR and ENDOR spectroscopy. The results confirm the expectation that the spin distribution between the two equivalent π systems is governed by the association of the radical anion with its positively charged counterion. Thus, a non-uniform spin distribution is favored by decreasing solvation of the cation and by an increasing π-charge localization in the sequence $\mathbf{4}\cdot^- < \mathbf{2}\cdot^- \approx \mathbf{3}\cdot^- < \mathbf{1}\cdot^-$.

We would like to report on ESR and ENDOR studies of the radical anions of [2.2]paracyclophane (**1**), *anti-* and *syn-*[2.2](1,4)naphthalenophanes (**2** and **3**, respectively), and [2.2](9,10)anthracenophane (**4**). Table I lists the perti-

nent coupling constants observed with three different solvents: 1,2-dimethoxyethane (DME), tetrahydrofuran (THF), and 2-methyltetrahydrofuran (MTHF); the counterion, K$^+$, and the temperature, -90 °C, are the same

Table I. Coupling Constants (G) for 1·⁻ to 4·⁻ᵃ

Radical anion of	DME	THF	MTHF	Assignment
1	2.97 (8)ᵇ	{3.79 (4)ᵇ {1.93 (4)ᵇ	3.84 (4) 1.71 (4)	4, 5, 7, 8 12, 13, 15, 16
	1.03 (8)ᵇ	{1.25 (4)ᵇ {0.70 (4)ᵇ	1.28 (4) 0.65 (4)	2, 9 1, 10
		0.12 (³⁹K)	0.13 (³⁹K)	Counterion
2 (anti)	3.00 (4)	3.02 (4)	{4.48 (2) {1.09 (2)	7, 10 17, 20
	2.13 (4)	2.11 (4)	{3.80 (2)} {0.42 (2)}	{2, 11 {1, 12
	0.98 (4)	0.97 (4)	{1.59 (2) {0.35 (2)	8, 9 18, 19
	0.60 (4)	0.57 (4)	{0.95 (2) {0.16 (2)	4, 5 14, 15
	0.28 (4)	0.26 (4)	{0.46 (2)} {0.04 (2)}	{2, 11 {1, 12
3 (syn)	2.42 (4)	2.39 (4)	{3.64 (2) {1.06 (2)	7, 10 17, 20
	1.70 (4)	1.70 (4)	{2.32 (2)} {0.90 (2)}	{2, 11 {1, 12
	1.32 (4)	1.27 (4)	{1.91 (2) {0.60 (2)	8, 9 18, 19
	1.00 (4)	1.00 (4)	{1.43 (2) {0.55 (2)	4, 5 14, 15
	0.35 (4)	0.36 (4)	{0.50 (2)} {0.16 (2)}	{2, 11 {1, 12
4	1.56 (8)ᵇ	1.55 (8)	1.55 (8)	{2, 13 {1, 14
	1.26 (8)	1.26 (8)	1.26 (8)	{ 4, 7, 9, 12 {16, 19, 21, 24
	0.78 (8)	0.78 (8)	0.78 (8)	{ 5, 6, 10, 11 {17, 18, 22, 23

ᵃ Numbers of equivalent protons are given in parentheses. ᵇ These values agree with those reported previously.[1,2]
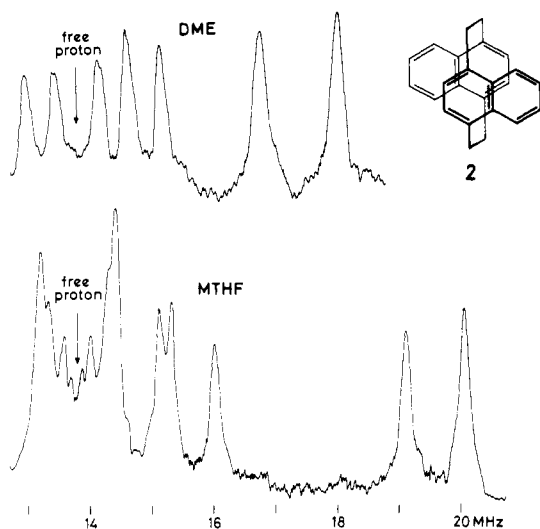
Figure 1. ENDOR spectra of 2·⁻ in DME and MTHF.
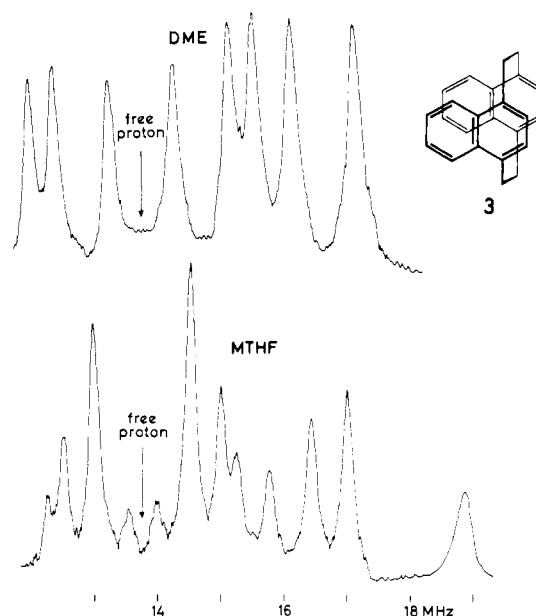
Figure 2. ENDOR spectra of 3·⁻ in DME and MTHF.

throughout. With the exception of the values published by us[1] for 1·⁻ in DME and THF, and one value estimated by Williams et al.[2] for 4·⁻ in DME, all these data are not yet available in the literature. Whereas in the latter paper[2] the spectra of 2·⁻ and 4·⁻ were presented with no analysis achieved, another author[3] erroneously attributed the spectrum of the radical anion of 1,4-dimethylnaphthalene,[4] a cleavage product of anti-[2.2](1,4)naphthalenophane (2), to 2·⁻ itself.

The proton coupling constants given in Table I allow accurate computer simulation of the complex ESR hyperfine structures. They have been derived from the positions of signals in the ENDOR spectra some of which are shown in Figures 1 and 2. Assignment is based on analogy with structurally related radical anions and is supported by the internal consistency of the data. In the case of 1·⁻ and the 1,2,13,14-protons of 4·⁻, this assignment has also been confirmed by ESR studies of deuterio derivatives.[1,2]

The intriguing question concerning the four radical an-

ions is the spin distribution between the two equivalent π systems. Ample evidence now exists[5] that such a distribution is governed by the association of the radical anion with its positively charged counterion. In the case of **1·⁻** to **4·⁻**, the symmetry of an ion pair is reduced relative to that of the corresponding unassociated species, because the cation K⁺ resides in an external position below or above the plane of either π system.[5,6] Concomitantly, the spin population is shifted to that π system which is proximate to the counterion. Since the cation migrates between the two equivalent external positions, this effect will be averaged out when such a migration is rapid on the ESR time scale. Full symmetry of the radical anion will then be apparent, along with a time-averaged spin distribution between the two π systems.

Inspection of the data in Table I reveals that, with DME as solvent, such an equal spin distribution is found in all four radical anions. Changing to THF leads to an accumulation of spin population on one benzene ring in **1·⁻**, but it has no appreciable influence on the uniform spin distribution in **2·⁻**, **3·⁻**, and **4·⁻**. A shift of spin population to one naphthalene π system in **2·⁻** and **3·⁻** is effected only by the use of MTHF, whereas in **4·⁻** even this solvent fails to bring about a measurable deviation from an equal spin distribution between the two anthracene π systems. Two factors thus determine the π-spin distribution in **1·⁻** to **4·⁻**: (1) solvent, and (2) extension of the π systems. This result illustrates once more the relevance of the association between the radical anion and its counterion, since the two factors are known to affect the stability and lifetime of such an ion pair. The spin population exhibits *more* tendency to accumulate on one π system when the association becomes *stronger*, i.e., with (1) the *decreasing* solvation of the cation in the order DME > THF > MTHF and (2) the *increasing* π-charge localization in the sequence **4·⁻** < **2·⁻** ≈ **3·⁻** < **1·⁻**.

References and Notes

(1) F. Gerson and W. B. Martin, Jr., *J. Am. Chem. Soc.*, **91**, 1883 (1969).
(2) D. J. Williams, J. M. Pearson, and M. Levy, *J. Am. Chem. Soc.*, **93**, 5483 (1971).
(3) D. H. Eargle, Jr., *J. Magn. Reson.*, **2**, 225 (1970).
(4) F. Gerson, E. Heilbronner, and B. Weidmann, *Helv. Chim. Acta*, **47**, 1951 (1964).
(5) F. Gerson, R. Gleiter, G. Moshuk, and A. S. Dreiding, *J. Am. Chem. Soc.*, **94**, 2919 (1972); F. Gerson, B. Kowert, and B. M. Peake, *ibid.*, **96**, 118 (1974); see also M. Szwarc and J. Jagur-Grodzinski, "Ion and Ion Pairs in Organic Reactions", Vol. 2, M. Szwarc, Ed., Wiley, New York, N.Y., 1974, Chapter 2.13.
(6) F. Gerson, *Chimia*, **28**, 194 (1974); F. Gerson and W. B. Martin, Jr., unpublished results.

Gas-Phase Basicities and Proton Affinities of Compounds between Water and Ammonia and Substituted Benzenes from a Continuous Ladder of Proton Transfer Equilibria Measurements

Raghavendra Yamdagni and Paul Kebarle*

Contribution from the Chemistry Department, University of Alberta, Edmonton, Alberta, Canada T6G 2E1. Received June 23, 1975

Abstract: The proton transfer equilibria $B_1H^+ + B_2 = B_1 + B_2H^+$ involving some 30 bases B with proton affinities between water and ammonia were measured with a pulsed electron beam high-pressure ion source mass spectrometer. A complete ladder of equilibria linking water to ammonia and often involving multiple cycles was obtained. Using the external standard PA(isobutene) = 193 kcal/mol (Lossing, Semeluk, and Tsang) one obtained absolute values for the proton affinities of the compounds. These include: water 169, hydrogen sulfide 172, CH_3OH 182.1, benzene 183.4, acetaldehyde 185.4, ethanol 186.8, dimethyl ether 190.1, acetone 194.6, diethyl ether 198.1, and ammonia 200.7 kcal/mol. The above values were obtained by assuming $\Delta G° = \Delta H°$. Corrections for ΔS changes due to rotational symmetry numbers are considered for some of the compounds. The basicities of benzene and some singly and multiply halo-substituted benzenes are briefly discussed.

A very large number of compounds have proton affinities which fall between those of water and ammonia. This includes organic oxygen compounds like alcohols, ethers, aldehydes, ketones, and acids as well as unsaturated and aromatic hydrocarbons.

Many previous determinations of proton affinities for compounds in this region and particularly of oxygenated compounds exist. The principal methods[1] used have been appearance potential measurements and the qualitative occurrence–nonoccurrence study of proton transfer reactions. The appearance potential method suffers from uncertainty regarding presence of excitation in the reaction products and is therefore often not reliable. The occurrence–nonoccurrence technique provides only proton affinity orders and thus requires a large number of standards, i.e., proton affinities which have been determined by other methods. Since not many reliable standards exist, this often amounts to calibration to values obtained by appearance potentials.

Not long ago the gas-phase ion equilibrium method[3] was applied to the study of proton transfer equilibria (eq 1) in ion cyclotron trapped ion sources,[4] high-pressure mass spectrometers,[5] and flowing afterglow

$$B_1H^+ + B_2 = B_1 + B_2H^+ \qquad (1)$$