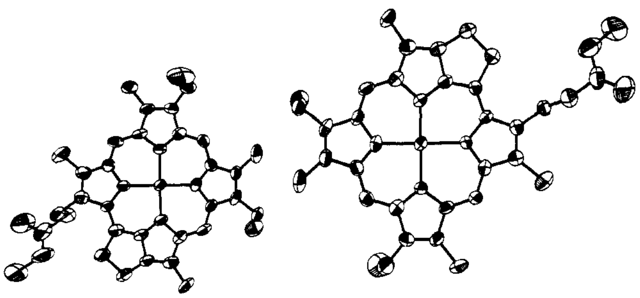

Figure 3. An ORTEP drawing of the unit cell contents projected onto the plane defined by the four nitrogen atoms of the right-hand molecule. The perspective is from a point directly above the nickel atom of the right-hand molecule and 24 in. from the plane of the paper.

Figure 3 is a computer-calculated ORTEP drawing of the unit cell contents excluding the hydrogen atoms and the solvent of crystallization.[19] The molecule on the right side was constructed using the general atomic coordinates x, y, z as given in Table III. The left-hand molecule is equivalent and has the general coordinates $-x$, $-y$, $-z$. The perspective is along the vector perpendicular to the plane of the four nitrogen atoms of the right-hand molecule and intersects this plane at the nickel atoms. Each atom is drawn as a thermal ellipsoid based on the values of the refined anisotropic thermal parameters. The size of the thermal ellipsoids is such that there is a 50% probability that random points in a distribution function describing the atom's electron density will fall within the volume of the ellipsoid. For reasons of clarity, the solvent molecule of 1,2-dichloroethane was left out of this illustration. It fills space between the layers of porphyrin molecules and is positioned on the symmetry center at $(\frac{1}{2}, 0, 0)$.

The porphyrin molecules pack in parallel layers that coincide roughly with the $2\bar{2}2$ crystallographic plane. The perpendicular spacing between the two molecules related by the center of symmetry at the origin is 4.46 Å. (This would be between the two molecules in Figure 3.) There are no intermolecular contacts, including the hydrogen atoms, which are less than 4.0 Å between these two molecules. The perpendicular spacing between the molecules related by the center of symmetry at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ is 3.47 Å. (The perpendicular separation between layers in graphite is 3.40 Å.) There are several intermolecular contacts of 4.0 Å or less for this pair of molecules and these distances are listed in Table VI along with all other distances less than 4.0 Å generated by other translational operators.

Table VI. Intermolecular Distances (Å) Less than 4.00 Å Excluding the Hydrogen Atoms

Operator x, y, z			
Cl–C(24)	3.77	C(35)–C(24)	3.89
Symmetry Operator $1 - x, 1 - y, 1 - z$			
Ni–C(21)	3.56	C(2)–C(4)	3.97
N(A)–C(1)	3.76	C(2)–C(20)	3.81
N(A)–C(2)	3.52	C(3)–C(19)	3.65
N(A)–C(21)	3.59	C(3)–C(20)	3.48
N(B)–C(21)	3.98	C(4)–C(20)	3.63
N(D)–C(22)	3.76	C(18)–C(22)	3.70
C(1)–C(1)	3.55	C(19)–C(22)	3.51
C(1)–C(2)	3.50	C(20)–C(22)	3.86
C(1)–C(3)	3.65	C(31)–Cl	3.93
C(1)–C(4)	3.78		
Translational Operator $1 + x, 1 + y, z$			
C(21)–C(25)	3.94	C(27)–C(34)	3.79
C(21)–C(26)	3.81		
Translational Operator $x, 1 + y, 1 + z$			
O(1)–C(24)	3.61	C(25)–C(33)	3.79
O(1)–C(35)	3.44	C(26)–C(33)	3.57
Translational Operator $1 + x, y, 1 + z$			
C(23)–C(33)	3.99		

Acknowledgments. I wish to thank Dr. Leroy E. Alexander for his helpful suggestions and support during the course of this work and for his critical reading of the manuscript. Thanks are due to Dr. Earl W. Baker for suggesting the problem and for supplying the compound for crystallization. I also wish to thank Dr. Robert F. Stewart for his generous help in the use of the programs on the CDC 1604A computer.

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(19) C. K. Johnson, "ORTEP, a Fortran Thermal-Ellipsoidal Plot Program for Crystal-Structure Illustrations," ORNL-3794, Oak Ridge, Tenn., 1965.

Correlation of Surface Tension between Various Liquids

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Contribution from the Martin Marietta Corporation,
Denver, Colorado 80201. *Received November 6, 1970*

Abstract: A relationship between dielectric constant or index of refraction and surface tension has been found which correlates the surface tensions of diverse dielectric liquids. This seems to be the first such relationship discovered. It may be used to estimate the surface tension of non-hydrogen-bonded polar liquids and to obtain fairly accurate values of surface tension of nonpolar liquids.

There are many relationships in the scientific literature between the surface tension of a dielectric liquid and some other property of the liquid. However, there seems to be no relationship *between* the surface tensions of diverse liquids based upon some common physical property. We have found that such

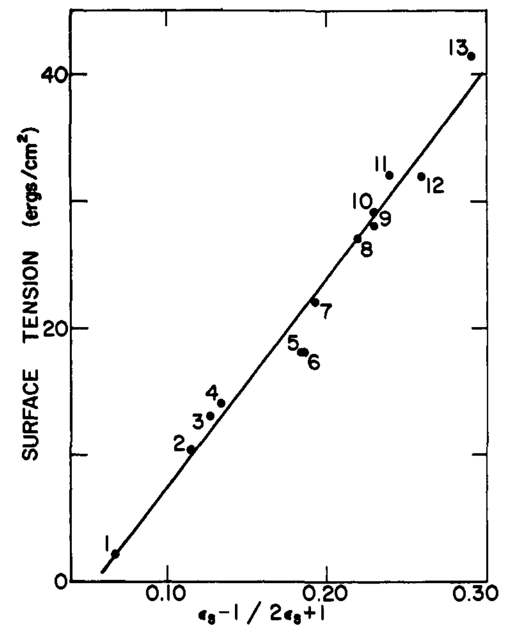

Figure 1. Correlation of surface tension of liquids of zero dipole moment: (1) H_2, (2) N_2, (3) O_2, (4) A, (5) Cl_2, (6) *n*-hexane, (7) *n*-octane, (8) CCl_4, (9) *p*-xylene, (10) benzene, (11) *p*-dichlorobenzene, (12) CS_2, (13) Br_2.

a correlation exists between surface tension and dielectric constant or index of refraction.

In Figure 1 are plotted the surface tensions of various liquids with zero dipole moment as a function of $(\epsilon_s - 1)/(2\epsilon_s + 1)$. For each liquid the surface tension and the dielectric constant were matched as closely to the same temperature as was possible from the data source,[1] and the figure represents all the liquids for which γ and ϵ_s were available from the source. The correlation is quite excellent. The equation of the line is

$$\gamma = 165[(\epsilon_s - 1)/(2\epsilon_s + 1)] - 9.1 \qquad (1)$$

where γ is in ergs per square centimeter.

For molecules with finite dipole moment there is no correlation between the surface tension and the static dielectric constant function, the plot being completely random. However, if the dipolar contribution to the dielectric constant is eliminated by using the Maxwell relation $\epsilon_s = n^2$, where n is the index of refraction, a remarkably good correlation is obtained. Figure 2 shows a plot for all the diverse liquids (such as ketones, alcohols, acids, amines, acids, etc.) for which data could be matched from the data source. The correlation could be expected to be even better if the temperature at which the index and the surface tension were obtained were better matched. Except for the strongly hydrogen-bonded liquids, an equation similar to that for the nonpolar molecules is obtained.

$$\gamma = 286[(n^2 - 1)/(2n^2 + 1)] - 28.6 \qquad (2)$$

Fowkes[2] finds the dispersion component of the surface tension of water to be about 22 ergs cm^{-2}. This

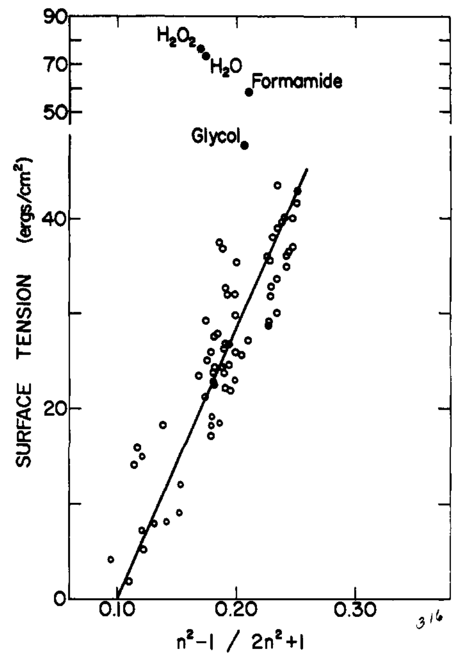

Figure 2. Correlation of surface tension of liquids with finite dipole moments (note change of scale).

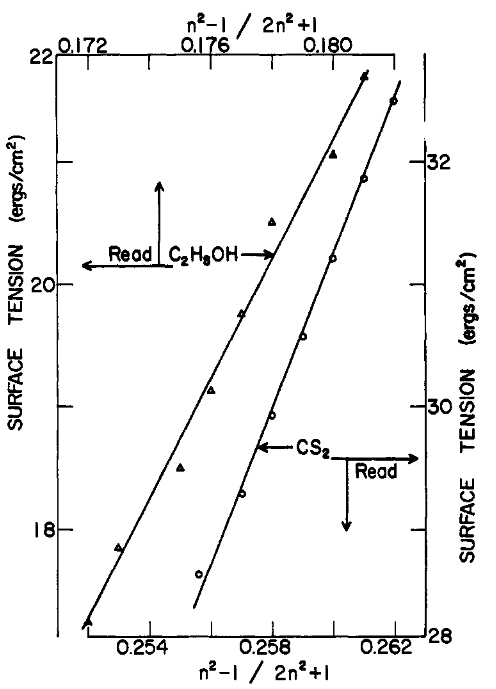

Figure 3. Surface tension as a function of index of refraction for carbon disulfide and ethyl alcohol.

value would put the datum point for water just on the line in Figure 2.

For individual liquids similar results are obtained. In Figure 3 the correlations for carbon disulfide and ethyl alcohol are presented.

Even though an equally good correlation exists simply with ϵ_s, we have attempted to justify the present correlation by the following considerations. From an elementary point of view, it is generally considered that surface tension arises from the lack of symmetry of forces about a molecule in the surface. Thus, when a nonpolar molecule is brought into the surface region

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(1) The data for all the figures were taken from the Handbook of Physics and Chemistry, 47th ed, 1966–1967, Chemical Rubber Publishing Co., Cleveland, Ohio, and from the Du Pont Technical Bulletin No. B-2, 1966.

(2) F. M. Fowkes in "Chemistry and Physics of Interfaces," American Chemical Society Publications, Washington, D. C., 1965.

from the bulk (where symmetry of forces exists), the molecule will become polarized. Frohlich[3] has considered the general case of a dielectric in a field. He consideres one molecule to be contained in a spherical volume element, V, of a dielectric which polarizes to yield a dipole $\mathbf{m} = (-e)\mathbf{r}$. There will then be an interaction between the polarized sphere and the surroundings, giving rise to an interaction free energy, $F_e = -(4\pi/3)(M^2/V)[(\epsilon_s - 1)/(2\epsilon_s + 1)]$. We suggest that the energy per unit area, γ, arises from Frohlich's F_e, the energy per molecule, created when molecules are brought into the surface and thereby polarized. This is concordant with the usual assumption of the role of London dispersion forces in surface tension. The rather remarkable result is that there is an intimate correlation between the surface tensions of such diverse dielectric liquids. These correlations may be used to estimate reasonable values of γ from n for non-hydrogen-bonded polar liquids and fairly accurate values for nonpolar liquids.

(3) H. Frohlich, "Theory of Dielectrics," Oxford University Press, London, 1958.

Electronic Structures of Substituted Aryl Cations

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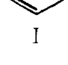
Contribution from the Division of Natural Science, University of California, Santa Cruz, California 95060. *Received February 11, 1971*

Abstract: INDO calculations of the electronic structures of the phenyl cation and the 4-aminophenyl cation indicate that the relative energies of the filled-shell singlet and open-shell triplet are strongly substituent dependent. For the case of the phenyl cation, the ground state is predicted to be a singlet σ cation with the nearest triplet being at much higher energies. In the 4-aminophenyl cation, the lowest triplet is predicted to be a π cation, while the singlet is a filled-shell σ cation. Both these states have nearly the same energy. Test calculations on the phenyl radical, the 4-aminophenyl radical, pyridine, and pyridine cation indicate that the INDO predictions are not completely reliable and therefore the results on the phenyl cation calculations are in question.

The thermal solvolysis of arenediazonium cations in acidic aqueous or alcoholic media is mechanistically complex. The exact nature or even existence of distinct intermediates in either the thermal or photochemical solvolyses of these materials is not known. Earlier work proposed the phenyl cation ($C_6H_5^+$, I) as a distinct intermediate in the solvolysis of benzenediazonium cation (II).[1,2] This is still in doubt.[3] That radical intermediates exist in the thermal acidic solvolysis of arenediazonium cations in methanol seems likely.[4]

Not only is the possible existence of distinct intermediates in doubt, but the electronic character of the transition state of arenediazonium cation thermal solvolysis is confusing. The substituent effect[1,2] on solvolysis cannot be easily analyzed within the context of a normal or an acceptably modified Hammett σ–ρ relationship.[5] The conclusions drawn for this anomaly are that either a mechanistic change occurs which is substituent dependent or there is something unusual about the electronic character of the transition state compared to those systems which give normal Hammett σ–ρ relationships. Taft argues[6] that the strong meta-substituent effects on this reaction indicate some biradical character[7] in the transition state. Such an argument does not depend on the actual kinetic existence of a phenyl or substituted-phenyl cation. However, the possible biradical character of the phenyl or substituted-phenyl cation implies that such an intermediate might undergo radical-like reaction processes in nonaqueous media.

This paper addresses itself to the theoretical acceptability of the possible biradical ground-state character of aryl cations. A preliminary qualitative analysis[8] of this problem came to the conclusion that it was likely that the corresponding singlet and triplet forms (III) of the phenyl π cation are more stable than the σ cation form I. This qualitative argument is based on the localized orbital view that the positive charge in ion I is located mainly on the carbon having the "empty" sp^2 orbital. Since the pure p orbital has a lower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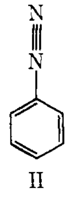
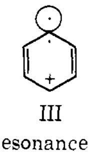


II



III
(one resonance form)

(1) J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, **49**, 273 (1949).

(2) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 1st ed, Cornell University Press, Ithaca, N. Y., 1953, pp 799–802.

(3) (a) E. S. Lewis, L. D. Hartung, and B. M. McKay, *J. Amer. Chem. Soc.*, **91**, 419 (1969); (b) E. S. Lewis and R. E. Holliday, *ibid.*, **91**, 426 (1969); (c) E. S. Lewis, R. E. Holliday, and L. D. Hartung, *ibid.*, **91**, 430 (1969), and references cited in these papers.

(4) T. J. Broxton, J. F. Bunnett, and C. H. Paik, *Chem. Commun.*, 1363 (1970).

(5) D. Schulte-Frohlinde and H. Blume, *Z. Phys. Chem. (Frankfurt am Main)*, **59**, 299 (1968). These authors obtained a rough correlation between log (solvolysis) *vs.* the sum of σ(inductive) + σ(mesomeric) for para substituents and the sum of σ(inductive) + 0.33σ(mesomeric) for meta substituents. The theoretical interpretation of even this rough correlation escapes us.

(6) R. W. Taft, *J. Amer. Chem. Soc.*, **83**, 3350 (1961).

(7) (a) R. A. Abramovitch and J. G. Saha, *Can. J. Chem.*, **43**, 3269 (1965); (b) R. A. Abramovitch and F. F. Gadallah, *J. Chem. Soc. B*, 479 (1968). Reference 7a quotes unpublished work of I. Absar and K. L. McEwen on calculations of the electronic state of the phenyl cation. No quantitative information is given.

(8) R. J. Cox, R. Bushnell, and E. M. Evleth, *Tetrahedron Lett.*, 207 (1970).