neutral or ion which is internally destablized.[12,13] The result is smaller or reversed equilibrium shifts in solution compared to the gas phase.[12,13] It will be noted for all three reactions (1–3) that $\Delta G°$(aq) values are shifted from the corresponding $\Delta G°$(g) values by ca. 4.0 kcal/mol in the direction that relieves by H–bonding solvation the NH^+ or lone pair repulsion in the 1,2-diazine or diazole system, as represented by the following structures:
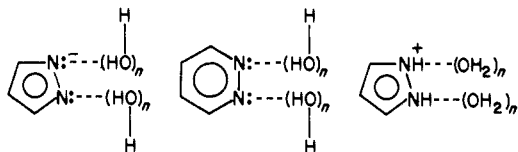

In accounting for values of $\Delta G°$(aq) for reactions 1–7, we estimate that (a) $6.5 - 4.0 = 2.5$ kcal/mol is the magnitude for the reduced electrostatic repulsion between adjacent lone pair electrons or adjacent HN^+ pairs which applies in water; (b) a reduction factor of 1.6 for the 2- and 3-aza substituent effects applies in water (giving magnitudes of 7.8 and 5.3 kcal/mol, respectively); (c) a reduction factor of 2.0 applies for the attractive lone pair/NH^+ or NH interactions (giving 1.0 and 0.5 kcal/mol, respectively, for the magnitudes of these). These structural parameters give satisfactory agreement between calculated and observed values of $\Delta G°$(aq) for reactions 1–7 as shown in Table I.

The generally good agreement btween observed and calculated values of $\Delta G°$(aq) in Table I appears to indicate that other hydration effects not considered above tend to approximately cancel between opposite sides of these equilibria.

In a later paper we will give further comparisons with theoretical calculations, ionic solvation energies obtained from a thermodynamic cycle, and further considerations of the rough quantitative assessments made in this paper. We note in closing that while the intrinsic basicity effects in reactions 1–3 may be viewed as originating largely from the effects of simple electrostatic re-

pulsions and attractions, the observed effects undoubltedly also include similar considerations as they effect the relative π electron delocalization energies. That is, for example, stabilization by π-electron delocalization in the conjugate acid of IV and in the conjugate base IV' are very likely reduced compared to that for the corresponding 1,3-diazole systems as represented in the valence bond forms:
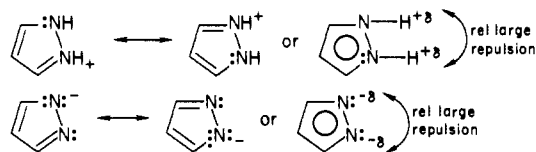
Experimental Section

Gas-phase basicities[14] and acidities[11,15] have been obtained as previously described. IV was found to be 0.5 kcal/mol more basic than $(CH_3CO)_2CH_2$ but 0.2, 0.6, and 1.0 kcal/mol less basic than 4-$CF_3C_5H_4N$, $(CH_3O)_3PO$, and $(tert\text{-}C_4H_9)_2S$, respectively. III was found to be 0.6 kcal/mol less basic than 3-$CH_3C_5H_4N$ but 0.9. and 1.8 kcal/mol more basic than *tert*-amylamine and 2-$CH_3OC_5H_4N$, respectively. IV was found to be 0.5 kcal/mol more acidic than *i*-PrSH, but less acidic by 0.6 and 1.1 kcal/mol than $m\text{-}CNC_6H_4NH_2$ and $m\text{-}NO_2C_6H_4NH_2$, respectively. III was found to be 0.2, 0.9 and 1.5 kcal/mol less acidic than $m\text{-}CH_3C_6H_4OH$, C_6H_5OH, and $p\text{-}CNC_6H_4NH_2$, respectively.

(11) Obtained in this work on the gas-phase acidity scale of: Bartmess, J. W.; Scott, J. A.; McIver, R. T., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 6046.
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On the Surface Tension of Organic Liquids

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Abstract: An earlier correlation between surface tension and dielectric constant has been modified, leading to a choice of a "best" function of dielectric constant for the correlation. This has been accomplished by a correlation between surface tension and compressibility. The relationship permits calculation of the temperature coefficient of surface tension. A rationale has been given for the relationship between surface tension and compressibility.

Some years ago the surface tension of liquids was correlated with their dielectric constants.[1] Subsequently, Holmes showed that it was difficult to choose mathematically a "best" function of dielectric constant for the correlation since the various functions he studied behaved very much like the constant itself.[2] The purpose of the present paper is to show that a best function may

be chosen through the correlation of surface tension with compressibility.

The correlation of surface tension, in the normal range, with (density/compressibility)$^{1/2}$ and the correlation with compressibility of surface tension at the triple point has been shown (ref 3 and references therein). In the present paper, surface tension (γ), in the normal range, is shown to be simply related to the

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(2) Holmes, C. F. *J. Am. Chem. Soc.* **1973**, *95*, 1014.

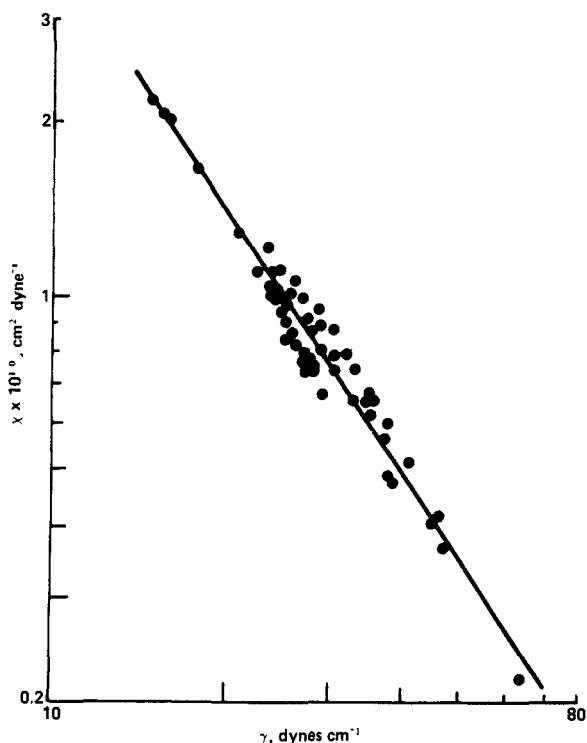(3) Sanchez, I. C. *J. Chem. Phys.*, **1983**, *79*, 405.

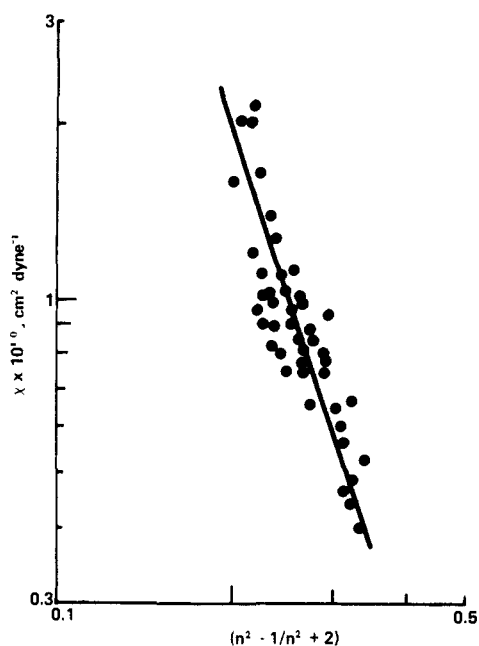**Figure 1.** Surface tension correlation with compressibility.

Figure 2. Correlation of compressibility with index of refraction.

compressibility (χ) by $\gamma \sim \chi^{-2/3}$, which then leads directly to a "best" function for the dielectric constant correlation with surface tension. The relationship has been shown to hold for liquid metals,[4] binary alloys,[4] and molten salts.[5] Thus, it appears to be a general relationship between surface tension and compressibility.

Results

Figure 1 shows the correlation of surface tension with their respective compressibilities, χ, where both were taken from ref 3. The relationship is

$$\gamma \sim \chi^{-2/3} \text{ (normal range)} \tag{1}$$

Table I. Comparison of Calculated and Observed Temperature Coefficients at 293 K

		$-d\gamma/dT$		
	γ (dyn/cm)	obsd	calcd	calcd/obsd
acetic acid	27.8	0.10	0.041	0.41
acetone	23.7	0.126	0.062	0.49
benzene	28.9	0.133	0.075	0.56
CCl_4	29.5	0.108	0.074	0.68
$CHCl_3$	27.2	0.13	0.087	0.67
CS_2	32.3	0.148	0.061	0.41
methyl alcohol	24.2	0.08	0.036	0.45

Figure 2 shows the correlation of the compressibilities with the index of refraction, where the n were taken as handbook values.[6] The relationship is

$$\chi \sim (n^2 - 1/n^2 + 2)^{-3} \tag{2}$$

Substitution of this into eq 1 yields

$$\gamma \sim (n^2 - 1/n^2 + 2)^2 \tag{3}$$

The earlier correlation[1] of surface tension with index of refraction was $\gamma \sim (n^2 - 1/2n^2 + 1)$, which Holmes[2] considered along with eq 3. The present relationship (eq 3) is concordant with the usual assumption of the role of London dispersion forces in surface tension.

From the Lorenz–Lorentz relationship $(n^2 - 1/n^2 + 2) = \alpha/r^3$, where r is an average space–filling radius and α is the polarizability, substitution into eq 3 yields

$$\gamma \sim \alpha^2/r^6 \tag{4}$$

According to London the dispersion energy of a molecular pair having random orientation and separation r is $E \sim \alpha^2/r^6$.

Equation 3 also can be developed directly from the internal pressure. It has been shown that for organic liquids, surface tension is directly proportional to the internal pressure, P_i.[7] Meeten[8] has shown that the internal pressure can be related to the dielectric constant by

$$P_i \sim (\epsilon - 1/\epsilon + 2)^2$$

From $\gamma = KP_i$, eq 3 follows directly. (It is worth noting that for liquid metals $\gamma \sim P_i$ (ref 4) and for molten salts $\gamma \sim P_i^{2/3}$ (ref 5)).

Thus, it appears that eq 3 is the most meaningful relationship for the index of refraction correlation with surface tension.[1]

Discussion

From internal pressure and bulk modulus (reciprocal of compressibility) the temperature coefficients of surface tension have been calculated for liquid metals[9] and for molten salts.[5] By using the modulus (to be consistent with the earlier work), the internal pressure relationship, and the thermal expansion relationships for organic liquids, the temperature coefficient of surface tension can be calculated in the same manner. From the internal pressure relationship for organic liquids,[7] $\gamma = KP_1$, and noting that thermodynamically $P_1 = -T\kappa\beta$, where κ is thermal expansion and $\beta = 1/\chi$, differentiation with temperature yields

$$(1/K) \, d\gamma/dT = -[T\kappa \, (d\beta/dT) + T\beta \, (d\kappa/dT) + \kappa\beta] \tag{5}$$

where β and $d\beta/dT$ can be obtained from eq 1. Table I compares such calculated values with observed temperature coefficients, for organic liquids for which thermal expansions are available.[10] The results are comparable with those calculated for liquid metals and molten alkali halides. Such calculations are, of course, dependent

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on the accuracy of the available experimental parameters.

Some comments on the $\gamma \sim \chi^{-2/3} \sim \beta^{2/3}$ relationship may be of value. For liquid metals, the surface tension was correlated[11] with the plasma frequency, ω_p, and thereby can be correlated with surface plasmons, ω_s,[14] so that

$$2\omega_s^2 = \omega_p^2 = 3Ze^2/mr^3 \qquad (6)$$

where Z is an effective valence, m is the electronic mass, and r is the size of the atom. (Equation 6 may be used also to calculate the surface tension of binary alloys.[12]) It was suggested earlier[4] that the surface tension was proportional to a surface elasticity, i.e., with $\beta^{2/3}$ dependence, the two-dimensional analogue to the three-dimensional bulk modulus. Consider the frequency of the optical branch of a one-dimensional lattice with two kinds of atoms given by[13]

$$\omega^2 = 2\mu(1/m + 1/M)$$

where μ is an elastic stiffness coefficient and m and M are the masses of the atoms. When one of these is taken as an electron this becomes

$$\omega^2 \approx 2\mu/m \qquad (7)$$

For liquid metals when $\beta^{2/3}$ is used for μ, the frequency from eq

7 is in reasonably good agreement[4] with those obtained from eq 6. This might be expected since the average of the three bulk stiffness coefficients is very nearly equal to the bulk modulus [see tables of values in ref 13]. Thus, the relationship between bulk modulus and surface tension, i.e., $\gamma \sim \beta^{2/3}$, may be considered to follow as

$$\omega_p^2 \sim \omega^2 \sim \mu \sim \beta^{2/3} \sim \gamma$$

It may, therefore, be anticipated that other liquid surface tension followed in the same manner. For a first consideration of organic liquids, it is difficult to imagine a liquid metal type of plasma oscillation. However, according to the London dispersion effect, after interaction between two oscillators, each vibrates with different frequencies, one greater than and the other less than their original frequency, ω_0, or

$$\omega^2 = \omega_0^2 \pm 2e^2/mr^3 \qquad (8)$$

where m is the electronic mass and r is the separation between oscillators.[14] For these oscillations the positive pole of the dipole moment (permanent or induced) of one oscillator will be coupled to the negative pole in an adjacent oscillator. This is analogous to the plasma frequency in a liquid metal. Indeed, when $Z = 1$ in eq 6, it becomes very nearly the dispersion effect of eq 8. This suggests that any fundamental development of surface tension must incorporate the London approach.

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Cyclopropabenzene. Geometry, Electronic Structure, Strain, Reactivity, and the Question of Bond Fixation. A Theoretical Study[†]

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Contribution from the Department of Chemistry, Technion–Israel Institute of Technology, Haifa 32000, Israel. Received July 15, 1985

Abstract: Molecular orbital calculations, both semiempirical (MINDO/3 and MNDO) and ab initio (STO-3G, 3-21G, and 3-21G*), for cyclopropabenzene (**1**) and for several 7-mono- and -disubstituted derivatives are reported. The geometry, electronic structure, strain, reactivity, and the question of bond fixation in **1** are discussed in light of the computational results. The calculated ab initio geometries are in good agreement with experiment, and the 7-substituents have a very small effect on the structure of **1**. The semiempirical methods produce erroneous geometries. In particular the fused bond is too long. The calculated bond lengths in **1** at 3-21G* are (in Å) $C_1–C_6 = 1.333$, $C_1–C_2 = 1.372$, $C_2–C_3 = 1.400$, $C_3–C_4 = 1.396$, and $C_1–C_7 = 1.495$. The bond angles around the bridge bond are severely distorted: $\angle C_6C_1C_2 = 124.7°$ and $\angle C_1C_2C_3 = 113.1°$. The reactions of **1** are rationalized by FMO theory as being controlled by the HOMO which is localized at the bridge bond, which therefore is the preferred site for reaction with electrophiles and electron-poor dienes. Both the semiempirical and the ab initio calculations reproduce well the experimental strain energy in **1** of 68 kcal·mol^{-1}. It is concluded that the concept of bond fixation provides little help in understanding either the geometry (which is not consistent with either of the conventional benzene Kekulé structures or with the π-population) or the reactions of **1**.

Strained organic molecules have always fascinated chemists and experimentalists[1] as well as theoreticians.[2] Three-membered rings have attracted special attention because of the severe enforced angle deformation,[1,2] and cyclopropabenzene (**1**) is of particular interest in this context. The fusion of the two rings in **1** is expected

1 **2** **3**
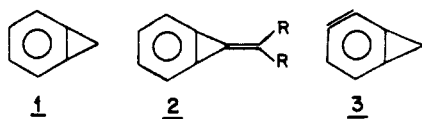
to result in considerable distortion of the benzene ring. Furthermore, its aromatic stabilization may be reduced by bond fixation.[3,4] Cyclopropabenzene and its derivatives can be now

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