tential of donor because of the decrease of the energy gap between the fluorescent state and the ground state. This circumstance may be expected from the general theory of the radiationless transitions.[16]

From the above discussions, one may expect the decrease of k_f and increase of k_{IC} as well as k_C and, accordingly, the decrease of the fluorescence yield with the decrease of the ionization potential of donor, in agreement with the observed results.

Before ending the discussions, we should make the following remark. The change of the structure of the

complex during the lifetime of the excited state, as it is assumed in the above discussions, may be observed more directly by the measurements of the absorption spectra of the excited complexes in various environmental states. This is a problem common to both the ordinary EDA complex and h.e. Such measurements may be possible if one uses the nanosecond laser photolysis method. Investigations along this line are now going on in this laboratory.

(16) S. H. Lin, *J. Chem. Phys.*, **44**, 3759 (1966); W. Siebrand, *ibid.*, **46**, 440 (1967).

Long-Range Electrostatic Effects in 4-Substituted Bicyclooctanecarboxylic Acids by CNDO/2

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Contribution from Eli Lilly and Company, Indianapolis, Indiana 46206. Received September 30, 1968

Abstract: Relative total energies, as calculated by the CNDO/2 method, successfully account for the order of dissociation constants of a number of 4-substituted bicyclooctanecarboxylic acids, provided a molecule of hydrogen-bonded water is included in the calculations on the 4-hydroxy derivative. Further solvent structuring for a number of members of the series improves the over-all correlation. The results are interpreted in terms of the electrostatic energy between the ionizable proton and the remainder of the molecule. It is further shown that the so-called "field effect" of the substituent is sufficient to account for differences in the *calculated* acidities of these compounds. This is done by comparing the CNDO/2 results to a calculation on a classical electrostatic model. The effective dielectric constant used in the latter calculation is based on representing the molecule as a dielectric material through which the charge or dipole substituent acts on the acid proton. CNDO/2 results are in good agreement with the result from electrostatic theory that such a dielectric material always increases the effect of the substituent over what it would have been in a vacuum, and that the increase is proportionally greater for a dipole than for a charged substituent.

The CNDO/2 method as originally developed by Pople, Santry, and Segal,[1] explicitly includes electrostatic interactions between all valence electrons and nuclei and contains parameters which give charge distributions in line with more exact limited basis set calculations on small molecules. The CNDO/2 method has also led to an interesting generalization concerning the distribution of charges in organic molecules, namely that atoms or groups of atoms can induce an alternation of charge density in σ systems similar but reduced in magnitude to that found in π systems.[2]

The calculation of long-range substituent effects in σ systems should be a good test of the validity of the CNDO/2 approach. Such long-range substituent effects are usually electrostatic in origin,[3-5] and should therefore be amenable to treatment by CNDO/2. Even the alteration of the long-range substituent effects due to any induced alternation of charge densities in an intervening σ system should be accountable for by CNDO/2

and might be important. As a test series, the 4-substituted bicyclooctanecarboxylic acids were chosen because of the geometric rigidity of these compounds and the availability of experimental data.

However, quantum mechanical machine calculations of expectation values pertaining to chemical systems such as these do not themselves yield a complete understanding of the chemical processes involved. While such an approach has an important predictive quality, another useful goal in quantum chemistry is to explain or interpret results in terms of familiar concepts. A question examined here is whether the field-effect concept, defined here in terms of an appropriate model, is consistent with the CNDO/2 level of approximation.

The approach chosen is to calculate total CNDO/2 energies as an approximation to total free energies of the solvated acids and bases and then to compare the energy changes in the acid–base reactions. The results are analyzed in terms of charge densities and potential energies and are then related to a field effect model of substituent effects in which the substituent acts on the acid proton through an effective dielectric constant.

Kirkwood and Westheimer[3] were the first to calculate such an effective dielectric constant by structuring the medium into two parts: a sphere or ellipsoid repre-

(1) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966); **43**, S136 (1965); J. A. Pople, D. P. Santry, and G. A. Segal, *ibid.*, **43**, S129 (1965).
(2) J. A. Pople and M. Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967).
(3) J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506 (1938); F. H. Westheimer and J. G. Kirkwood, *ibid.*, **6**, 513 (1938).
(4) N. Bjerrum, *Z. Physik. Chem.*, **106**, 219 (1923).
(5) S. Ehrenson, *Progr. Phys. Org. Chem.*, **2**, 195 (1964).

senting the entire molecule and a surrounding portion representing the solvent. After different appropriate dielectric constants were given to the two parts, an overall effective dielectric constant could be calculated.

The intention in this paper is to represent not the whole molecule but only the intervening portion between substituent and acid proton by a sphere of appropriate dielectric constant. When this is done, and the molecule is assumed to be in a vacuum, an effective dielectric constant may be calculated. The effect of the charge or dipole representing the substituent suitably modified by the effective dielectric constant can then be compared with the results calculated directly by CNDO/2.

Assumptions and Approximation in the Energy Calculation

The electronic energies for each reaction of the type

$$X-\underset{}{\bigcirc}-C\underset{O}{\overset{O-H}{\diagdown}} \rightleftharpoons$$

$$X-\underset{}{\bigcirc}-C\underset{O}{\overset{O^-}{\diagdown}} + H^+ + \Delta E_X$$
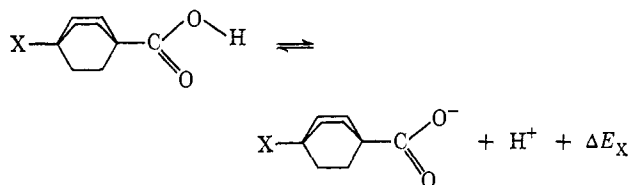
are calculated and correlated with the experimental free energies in solution. Fixed conformations are assumed and just the CNDO/2 electronic energies are calculated. Average experimental bond lengths and angles[6] are used when possible and are kept the same for both acid and negative ion. In a number of cases one or two molecules of water are assumed to be hydrogen bonded to the substituent group, and the total energies are then calculated for the entire structure.

The positions of the water molecules are assumed to be at the optimum distance for hydrogen bonding to the given substituent.[7] Where the hydrogen bond distance was unknown, the distance was found by minimizing the energy with respect to hydrogen bond length. This was done in just the two cases, X = F and X = CN. The average conformations of the hydrated species used are shown in Figure 1. The same hydrogen bond distances were used for the conjugate bases as were used for the acids. In the case of the permanently charged species X = NH_3^+, the results were compared with the experimental data[8] on X = $N(CH_3)_3^+$. Computer size limitations prevented a more complete treatment.

Results from the CNDO/2 Energy Calculation

Table I gives ΔE_X and $\Delta E_X - \Delta E_H$ for a number of acids as calculated by CNDO/2 together with the experimental log K_X/K_H in 50 wt % water–ethanol. These results are plotted in Figure 2. The calculations on the entries with the base substituents are in order except for X = OH. If this group is hydrogen bonded to water through the H atom of the group itself to the oxygen of the water molecule, then the correct order for all members is obtained for which experimental data are available.

(6) Special Publication No. 18, Supplement, The Chemical Society, London, 1965.

(7) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," Reinhold Publishing Corp., New York, N. Y., 1960, p 284.

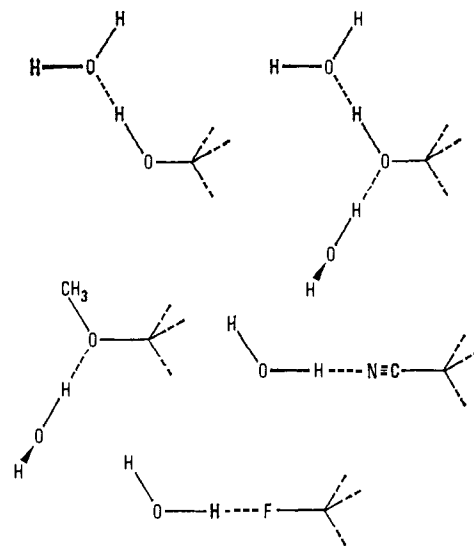(8) H. D. Holtz and L. M. Stock, *J. Amer. Chem. Soc.*, **86**, 5188 (1964).

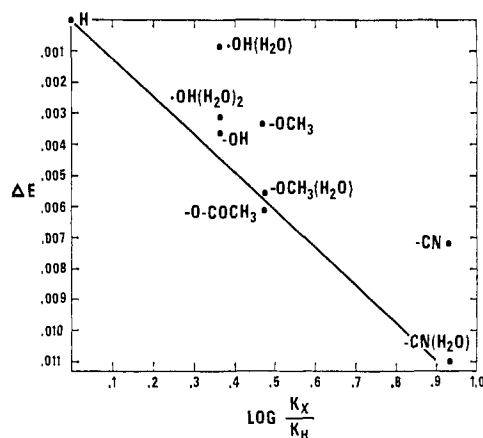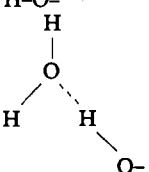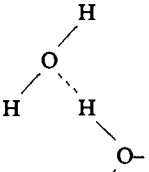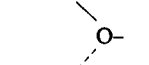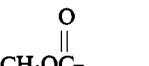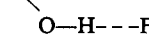Figure 1. Assumed average conformations of hydrated substituents.

Figure 2. Plot of ΔE vs. log K/K_H for the substituted bicyclooctanecarboxylic acids. ΔE here corresponds to the column $\Delta E_X - \Delta E_H$ in Table I.

An even better fit is obtained by incorporating a molecule of water, bound to the substituent through the hydrogen atom of the water molecule. The case X = $COOCH_3$ was not treated in this manner because of computer-size limitations, but a molecule of water bound in this way would be expected to bring the results considerably out of line. However, such a hydrogen-bonded $COOCH_3$ would be different from all other hydrogen-bonded substituents in that the bonded substituent atom (oxygen) does not reside on the line of center of the molecule and would be subject to rotation about the C–C bond. Less water structuring would be expected.

The energies calculated are considerably larger than the experimental quantities. In the calculation, larger energy changes are involved since a bare proton is removed and remains unsolvated. Hydrogen bonding of the proton to a water molecule for all acids would probably produce more reasonable energies, but since all derivatives would be affected in the same way, no real improvement would be expected. Finally, substituent effects, as indicated by the calculated energy differences $\Delta E_X - \Delta E_H$, are further attenuated in solution by the large dielectric constant of the solvent.

Table I. Calculated Energies and Experimental Log K/K_H for the Removal of the Proton from Bicyclooctanecarboxylic Acid with Substituent X

X	ΔE_X	$\Delta E_X - \Delta E_H$	Log K/K_H[a]
H–	−0.84446		
H–O–	−0.84085	0.00361	0.370 ± 0.044
(structure: H–O with O, H H, O–)	−0.84363	0.00083	
(structure: O, H H, O–, HO—H)	−0.84135	0.00311	
CH_3O– CH_3	−0.84109	0.00337	0.472 ± 0.032
(structure: O–, HO—H)	−0.83883	0.00563	
CH_3OC– (with O double bond)	−0.83843	0.00603	0.48[b]
F–	−0.83687	0.00759	
(structure: H, O—H- - -F–)	−0.83407	0.01039	
N≡C–	−0.83724	0.00722	0.93
(structure: H, O, H——N≡C–)	−0.83346	0.01100	
$NH_3{}^+$–	−0.72574	0.11872	1.50[c]

[a] Reference 8. [b] Value is for the ethyl ester. [c] Value is for the substituent $(CH_3)_3N^+$.

Experimental data are unavailable for the 4-fluoro compound, but from the calculation including water, this derivative should be almost as strong an acid as the 4-cyano derivative.

CNDO/2 Perturbation Energy Calculation of Base Strengths

The straightforward CNDO/2 energy calculations above give a good correlation with experiment. An analysis of contributions to the total energy from the various portions of the molecule is now necessary in order to aid in the understanding of CNDO/2 theory in terms of a field effect model. This analysis is most easily done through a recalculation of the energy by first-order perturbation theory. Both the electrostatic effects of the groups directly on the proton, and the effects of the substituent-induced changes in the hydrocarbon system on the proton should contribute to the perturbation energy. The perturbation may be either (1) the abstraction of the proton from the acid or (2) the addition of the proton to the base.

The Hamiltonian of the acid, H_A, is equal to the Hamiltonian of the base, H_B, plus the perturbation of adding a proton

$$H_A = H_B + V \tag{1}$$

$$V = \sum_{A \neq H}^A \frac{Z}{R_{AH}} - \sum \frac{1}{r_{\mu H}} \tag{2}$$

where R_{AH} is the distance between the proton and an atom A, and $r_{\mu H}$ is the distance between the proton and an electron μ. The first-order energy in the first case is found by using the wave function of the acid, ψ_A, as the zero-order wave function

$$\int \psi_A^* H_A \psi_A \, d\tau = \int \psi_A^* H_B \psi_A \, d\tau + V_A \tag{3}$$

$$V_A = \int \psi_A^* V \psi_A \cdot d\tau$$

and in the second case the zero-order wave function, ψ_B, of the base is used.

$$\int \psi_B^* H_B \psi_B \, d\tau = \int \psi_B^* H_A \psi_B \, d\tau - V_B \tag{4}$$

$$V_B = \int \psi_B^* V \psi_B \, d\tau$$

Two quantities V_A and V_B will not in general be equal because ψ_A and ψ_B are not necessarily equally appropriate as wave functions for their respective zero-order Hamiltonians, H_B and H_A. The CNDO/2 method as normally parameterized should better accommodate the acids than their conjugate bases.

An integral appears in the expression for $\int \psi_A^* V \psi_A \, d\tau$ that does not appear in CNDO/2 theory, namely the one-center nuclear attraction integral of the hydrogen atom

$$M_H = \int \chi_H \frac{1}{r_{\mu H}} \chi_H \, d\tau \tag{5}$$

We arbitrarily give this integral the calculated value −1.2 hartrees from using a 1s Slater-type orbital χ_H with orbital exponent $\zeta = 1.2$, and all other integrals appearing in either V_A or V_B are evaluated in accord with the rules of CNDO/2. The results are given in Table II.
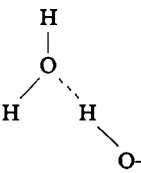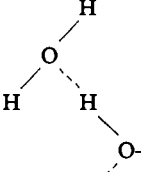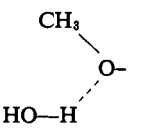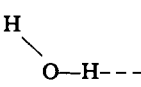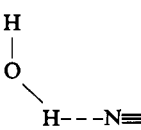
Representation of the CNDO/2 Perturbation Energy by a Classical Electrostatic Model

The difference in potential energy ΔV accompanying removal of the proton q_H from the substituted acid and the unsubstituted acid is

$$\Delta V = q_H(\phi_s - \phi_u) \tag{6}$$

where the distribution of charges representing the substituted acid and unsubstituted acid determine the electrostatic potential fields ϕ_s and ϕ_u, respectively. ΔV may thus be interpreted as the work done in transporting a charge q_H from a point in an electrostatic field with the fixed potential $(\phi_s - \phi_u)$ to infinity. ΔV is also the difference between the CNDO/2 perturbation energies V_A as calculated for the substituted and unsubstituted acids. In order to compare the perturbation energies with such a classical model of electrostatic interaction, two cases of the substituent electrostatic field in the second interpretation above are considered. In the first, where the substituent may be represented by a point charge, the difference between the energy needed to remove the proton from the sub-

Table II. Perturbation Energies for the Removal of the Proton from Bicyclooctanecarboxylic Acid with Substituent X

X	V_A	$\Delta V_A{}^a$	V_B	$\Delta V_B{}^a$
H-	−0.780238	0	−0.03403	0
H—O-	−0.77695	0.00329	−0.03103	0.00300
(H / O / H H \ O-)	−0.78055	0.00031	−0.03309	0.00094
(H / O / H H \ O- / HO—H)	−0.77768	0.00256	−0.03120	0.00283
CH₃O-	−0.77747	0.00277	−0.03070	0.00333
(CH₃ \ O- / HO—H)	−0.77549	0.00475	−0.02900	0.00503
CH₃OC- (O ‖)	−0.77567	0.00457	−0.02825	0.00578
F-	−0.77268	0.00756	−0.02822	0.00581
(H \ O—H- - -F-)	−0.77004	0.01020	−0.02583	0.00820
N≡C-	−0.77397	0.00627	−0.02768	0.00635
(H / O \ H- - -N≡C-)	−0.77042	0.00982	−0.02445	0.00958
NH₃⁺-	−0.66217	0.11806	+0.06734	0.10137

^{a} ΔV_A (ΔV_B) is the difference in perturbation energy V_A (V_B) calculated for the substituent X and V_A (V_B) calculated for the unsubstituted acid.

Figure 3. Effective dielectric constant D_E vs. b/a, the ratio of the radius of the dielectric sphere to the distance of the proton from the center of the sphere.

stituted and unsubstituted acid is[3]

$$\Delta V = q_H q_X / D_E R \qquad (7)$$

where q_X is a point charge at the position of the substituent and R is the distance between the proton and substituent. D_E is the effective dielectric constant of the medium. For a vacuum this is 1, but owing to the presence of the remainder of the molecule, it will be different from 1. For this case the representative CNDO/2 calculation is on 4-ammonobicyclooctanecarboxylic acid. In the second case, the substituent is represented by a point dipole

$$\Delta V = \frac{p_X q_H \cos \alpha}{D_E R^2} \qquad (8)$$

where p_X is the dipole moment of the substituent and $\cos \alpha$ is the angle between the direction of the dipole and the line connecting the dipole and the charge q. For this case, the representative CNDO/2 calculation is on 4-cyanobicyclooctanecarboxylic acid. It should be
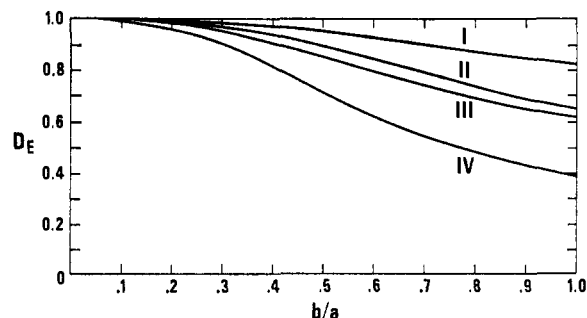
noticed that the effective dielectric constant will in general be different for charges and dipoles. The molecular model considered for each of the above cases is a dielectric sphere having a diameter smaller than the distance between the substituent and the proton. The substituent X is at a distance $R = 2a$ from the proton q_H, where R is the actual CNDO/2 distance from the proton to the nitrogen atom in the first case and from the proton to the CN carbon atom in the second case. Centered on a line joining the proton and the substituent is the sphere of dielectric constant D and radius roughly large enough to encompass half the O–H bond of the proton and half the C–X bond to the substituent. Since the CNDO/2 results rather than experimental results are under consideration here, the space surrounding the sphere represents a vacuum of dielectric constant $D_V = 1$.

Results from the Dielectric Sphere Model and Comparison with CNDO/2

The dielectric constant of the sphere is 5.0 as found by the method described in the Appendix. Using this value, the effective dielectric constant D_E is calculated in the Appendix and displayed in Figure 3. For the model in which the substituent is a point charge, the effective dielectric constant was found to be 0.729. For the other model, in which the substituent is a point dipole, $D_E = 0.463$. Since the effective dielectric constants are less than 1, this means that in both cases the above model predicts an enhancement of the influence of the substituent. Specifically, in the case where the substituent carries a point charge and its distance from the proton is 7.22 Å, then the electrostatic energy is $V = 0.1017$ hartree from eq 7 if a sphere of radius 3.0 Å and dielectric constant 5.0 is placed midway between charge and proton. The direct effect without the sphere would be considerably smaller, or 0.0732 hartree, since in such a case $D_E = 1$; thus, the inductive effect of the dielectric sphere is important in enhancing the influence of the substituent.

This is to be compared with the results of the perturbation energy calculations for 4-ammonobicyclooctanecarboxylic acid, which were 0.1180 and 0.1014 hartree for ΔV_A and ΔV_B, respectively, in rather good agreement with the dielectric sphere model. The inductive capacity of the sphere corresponds to the CNDO/2 result of a general shift of electron density toward the substituent. This induced dipolar structure can be seen by comparing the relative charge densities of the substituted and unsubstituted acids as shown in Figure 4.

Diagram A:
-.2724
O
-.0226 H——C +.0384 C -.0040 — C +.3745 H +.1677
+.0119 C——C +.0238 O -.3364
-.0064 H **Ⓐ** H -.0023

Diagram B:
+.2065 H
-.0319
+.2070 H N——C +.1109 C -.0066 — C +.3775 H +.1913
+.2070 H -.0048 C——C +.0241 O -.3064
+.0153 H **Ⓑ** H +.0269 -.2663 O

Diagram C:
+.0061
O
+.6112 H₃N——C +.0725 C -.0026 — C +.0030 H +.0236
-.0167 C——C +.0003 O +.0300
+.0217 H **Ⓒ** H +.0292

Diagram D:
-.2717
O
-.1767 +.0754 N——C +.0527 C -.0037 — C +.3751 H +.1695
+.0168 C——C +.0197 O -.3338
-.0001 H **Ⓓ** H +.0007

Diagram E:
+.0007
O
-.0787 N≡C——C -.0198 C +.0003 — C +.0006 H +.0018
+.0049 C——C -.0041 O +.0026
+.0063 H **Ⓔ** H +.0030

Diagram F:
O⁻ -.6153
-.0572 H——C +.0427 C -.02696 — C +.3279 H
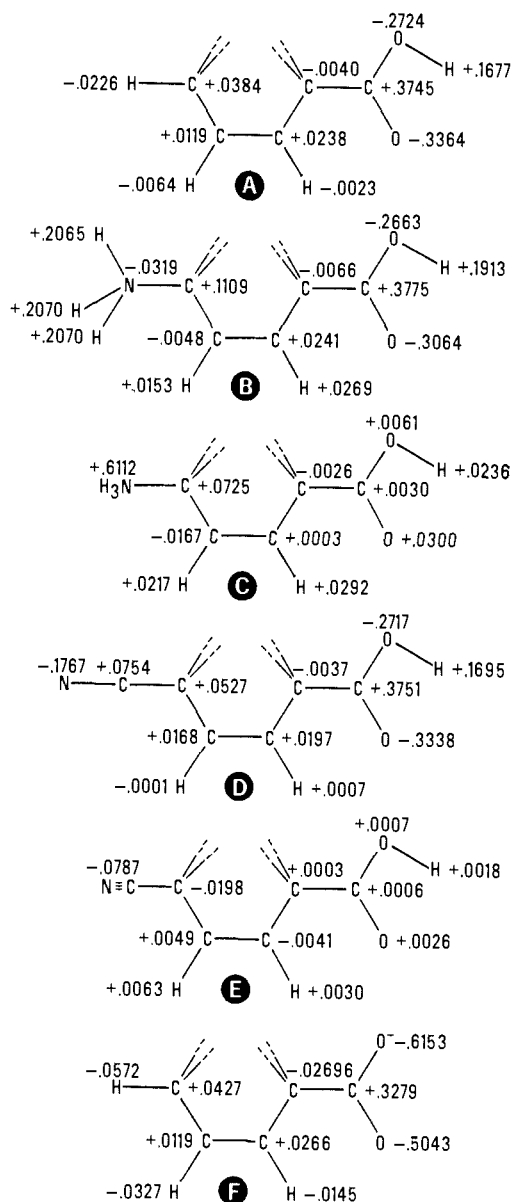+.0119 C——C +.0266 O -.5043
-.0327 H **Ⓕ** H -.0145

Figure 4. Calculated charge densities. The numbers given for the charge densities of the atoms in the bridge are the average charge densities for the several symmetrically corresponding bridge atoms not shown. Diagrams A, B, D, and F are the calculated CNDO/2 charge densities. Diagram C gives the differences between the densities of diagrams A and B. Diagram E gives the difference between A and D. In subtracting the charge densities of dissimilar groups, the entire group densities are subtracted.

The alternation effect in saturated systems pointed out by Pople[2] produces variations in atomic density from atom to atom which are comparable to average atom to atom variations induced by the substituent. Since in the CNDO/2 calculations some charge has moved from the substituent to the remainder of the molecule, the unchanged dielectric sphere model is not wholly satisfactory. In the case where the substituent may be represented by a point dipole 13.648 bohrs away from the proton, as in the 4-cyano derivative, the energy difference between the unsubstituted acid dissociation energy and that of the 4-cyano derivative is 0.00420 hartree for a cyano group dipole moment[9] of 0.36 au and D_E =

(9) This moment was calculated directly from atomic charges for HCN as given by CNDO/2 rather than some experimental value, since

0.463. This result should be compared with the two perturbation calculations of 0.00627 and 0.00635 hartree for the 4-cyanobicyclooctanecarboxylic acid.

The direct effect of the dipole on the point charge without the intervening sphere, so that the effective dielectric constant is 1, would be $V = 0.36/(13.648^2)$, or 0.00193 hartree indicating again that the substituent effect is enhanced by the intervening portion of the molecule in both CNDO/2 and the model. The inductive effect of the sphere appears as part of the over-all electrostatic effect in the model. Since this electrostatic model is the same as the so-called field effect model,[10] then CNDO/2 may be regarded as being in good agreement with a field effect model of substituent effects. In both cases the field effect model and CNDO/2 are in good agreement as to the enhancement of the substituent effect by the intervening moiety, and also as to the greater enhancement of the effect for the dipole substituent.

Computer Programs

All programs used here were written by the author except for the matrix diagonalization subroutine GIVENS which is obtainable through the Quantum Chemistry Program Exchange at Indiana University. Convergence was complete for the SCF calculations where the energy improvement was less than 0.000001 hartree. In the case of the negative ions, it was sometimes necessary to average every two successive density matrices to damp out oscillations in the beginning. The calculations were carried out on the CDC 3600 at Indiana University. As an example of a typical run time, the 4-methoxybicyclooctanecarboxylic acid took 20 min for 12 iterations.

Appendix

Estimation of D, the Dielectric Constant of the Molecule. In previous work[3,8,11] it has been customary to use a dielectric constant of about 2.0 for the volume representing the molecule, close to that of a paraffinic hydrocarbon. In the case of the sphere in this problem, this is not a good approximation, since the density of atoms within the sphere is about four times greater than the average density of atoms in bulk hydrocarbon where there is much space between molecules. Furthermore, dielectric constants usually refer to macroscopic media

a prerequisite for getting the CNDO/2 acidity would certainly be dependent on a CNDO/2 calculated dipole. Dipoles of lone pairs were not considered since these do not enter in any way into the calculation of potential energies in the CNDO/2 method.

(10) The field effect model for substituent effects consists of two parts, corresponding to the two terms in each of eq 17 and 22. The first term, which is usually called the direct effect when referring to a substituent, is a single across-empty-space function of $1/r$ for a charged substituent and $1/r^2$ for a dipole substituent. The second term, usually called an induction effect or polarization effect, represents a polarization of the sphere by the substituent. The resulting polarized sphere influences further the acid proton. A similar breakdown of the field effect was pointed out for the Westheimer–Kirkwood model by Ehrenson.[5]

(11) C. Tanford and J. G. Kirkwood, *J. Amer. Chem. Soc.*, 79, 5333, 5340 (1957); C. Tanford, *ibid.*, 79, 5348 (1957); J. D. Roberts and W. T. Moreland, Jr., *ibid.*, 75, 2167 (1953).

where there are neighboring molecules to influence the field of each individual molecule. The CNDO/2 calculations represent only a single molecule, the induced electric field of which is therefore uninfluenced by any neighboring molecules. An attempt is now made to account for these two differences. The resulting dielectric constant, while admittedly approximate, should be more accurate than one obtained from the assumption that dielectric constants of macroscopic media are directly applicable to intramolecular spacial regions.

The molecular polarizability γ_{mol} of a molecule is defined by the equation[12]

$$\mu_{mol} = \gamma_{mol}(E + E_i) \qquad (9)$$

where μ_{mol} is the average induced dipole moment of the molecule, E is the applied electric field, and E_i is the electric field at the molecule due to neighboring molecules. γ_{mol} is a molecular property independent of the presence of neighboring molecules. When E_i is not zero, as is the case for macroscopic media, the dielectric constant D is then related to γ_{mol} by the Clausius–Mossotti equation

$$\gamma_{mol} = \frac{3}{4\pi N}\left(\frac{D-1}{D+2}\right) \qquad (10)$$

where N is the number of molecules per unit volume.

In the present case, however, for the treatment of a single molecule, E_i is zero owing to the lack of neighboring molecules so that

$$\mu_{mol} = \gamma_{mol}E \qquad (11)$$

From the expression for the displacement vector and the definition of the dielectric constant in electrostatics, the relation between the dielectric constant and the molecular polarizability thus becomes

$$D = 1 + 4\pi N\gamma_{mol} \qquad (12)$$

for the sphere rather than the Clausius–Mossotti expression.[13]

In order to obtain γ_{mol} for the sphere, it is necessary to estimate the quantity $(D-1)/(D+2)$ for a medium of the molecular fragments under consideration here and packed so that it has the density d_s of the sphere. It is assumed that this may be estimated using the corresponding quantity for a similar substance such as bicyclooctanecarboxylic acid and the relative densities, since for any given substance $(D-1)/(D+2)$ should be proportional to its density.[14] Then for the case of interest here

$$\left(\frac{D-1}{D+2}\right)_S = \left(\frac{D-1}{D+2}\right)_A\frac{d_S}{d_A} \qquad (13)$$

where d is the density and the subscripts A and S refer to bicyclooctanecarboxylic acid and a medium whose density is that of the sphere, respectively. The density of the sphere is computed from its volume and its weight of enclosed atoms.

If $D = n^2$ where n is the index of refraction,[15] then $(D-1)/(D+2)$ for the acid can be found from the computed values[16] of the molar refraction, R_A, given by the equation

$$R_A = \frac{g_A}{d_A}\left(\frac{n^2-1}{n^2+2}\right) \qquad (14)$$

where g_A is the molecular weight. Then γ_{mol} for the sphere is

$$\gamma_{mol} = \frac{3}{4\pi N}\frac{d_S}{g_A}R_A \qquad (15)$$

and the dielectric constant D is

$$D = 1 + 3d_S R_A/g_A \qquad (16)$$

The molar refraction of bicyclooctanecarboxylic acid was computed to be 40.898, and the density was estimated to be 1.0.[17] For a sphere of radius 3.0 Å enclosing a portion of the molecule with molecular weight 152.186, D is found to be 5.0 for the sphere.[18]

Calculation of the Effective Dielectric Constant, D. The formula for the electrostatic potential ϕ at a point P outside a sphere of dielectric constant D, radius b, and center at $r = 0$ which is imbedded in a medium of dielectric constant D_2, and due to a charge q at point $x = a$ is[19]

$$\phi = qf$$

$$f = \frac{1}{D_2 r_2} + \left(\frac{D_2 - D}{D_2}\right)\sum_{n=0}^{\infty}\frac{n}{nD + (n+1)D_2} \times \frac{b^{2n+1}}{a^{n+1}}\frac{P_n(\cos\phi)}{r^{n+1}} \qquad (17)$$

where r_2 is the distance between q and the point r, θ, z, and the sphere is at the origin. In the special case where the point P and the point $z = a$ are equidistant from the center of the sphere and colinear with its center, and $D_2 = 1$ for a vacuum, the potential is

$$\phi = q\left\{\frac{1}{2a} + (1-D)\left(\frac{b}{a}\right)S_1\right\} \qquad (18)$$

$$S_1 = \sum_{n=0}^{\infty}\frac{n}{nD + n + 1}\left(\frac{b}{a}\right)^{2n}(-1)^n$$

since $P_n(\cos\theta) = (-1)^n$ for $\theta = 180°$.

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(12) J. D. Jackson, "Classical Electrodynamics," John Wiley and Sons, Inc., New York, N. Y., 1962, pp 108, 116–119.

(13) This treatment neglects the permanent dipole moment μ of the sphere since the Debye equation for the molar polarization P is

$$P = \frac{g}{d}\left(\frac{D-1}{D+2}\right) + \frac{4\pi N_0}{9kT}\mu^2$$

The molecular polarizability is related to the molar polarization by $\gamma_{mol} = P/N_0$. The second term in the Debye equation is based on the assumption that the permanent dipoles are free to move in an applied field. For the sphere of the problem here, the dipole is fixed with respect to the field of the substituent, and the contribution due to the second term is therefore zero for the sphere.

(14) Reference 12, p 119. It is assumed that this should be true here because the sphere and the acid differ only by two hydrogen atoms.

(15) The dielectric constant D is equal to n^2 for light of infinite wavelength. Measurements of n are customarily made at the sodium D-line. Refraction equivalents used in computing the molar refraction were referred to the D-line.

(16) S. Glasstone, "The Elements of Physical Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1946, p 158.

(17) For nonanoic acid $d = 0.906$, while for cyclohexanecarboxylic acid $d = 1.049$. Because of its greater compactness the density of bicyclooctanecarboxylic acid should be greater than nonanoic acid. Since the hydrocarbon moiety forms a larger percentage of its total weight compared to cyclohexanecarboxylic acid, it is probably less dense than this compound. The estimate of $d = 1.0$ is probably accurate to 5%.

(18) This result is similar to bulk diamond where $D = 5.5$. This might be expected, even disregarding the correction for lack of neighboring molecules, because the density of atoms in the sphere is more like bulk diamond than like bulk hydrocarbon.

(19) J. A. Stratton, "Electromagnetic Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p 204.

If the ϕ of eq 18 is identified with the quantity $(\phi_s - \phi_u)$, then from eq 6, 7, and 18 the formula for the effective dielectric constant is

$$D_E = \left[1 + 2(1 - D)\left(\frac{b}{a}\right)S_1 \right]^{-1} \quad (19)$$

The effective dielectric constant is plotted in Figure 3. D_E is plotted for the ratio b/a for $D = 2.0$ (curve I) and $D = 5.0$ (curve II). In the case where $b = 3.0$ Å and $a = 3.61$, D_E is 0.729 for $D = 5.0$.[20]

For a dipole substituent of finite length l with charges $+q$ and $-q$ at the end points a_1 and a_2 on the z axis, the potential at the proton, also on the z axis is

$$\phi = qf_1 - qf_2 = p(f_1 - f_2)/l \quad (20)$$

$$p = ql$$

where p is the dipole moment of the charge distribution. If q is increased and at the same time l goes to zero in such a manner that the product p remains constant, there is obtained for the potential due to the point dipole

$$\phi = p \lim_{l \to 0}(f_1 - f_2)/l = p\nabla f \quad (21)$$

(20) The most arbitrary quantity leading to the above results is the radius of the sphere. If the size of the sphere is varied but its weight is held constant, D will vary. However, under such circumstances the ratio b/a also varies, but in such a manner that D_E remains relatively constant. Thus, the value of D_E is not extremely dependent on the size of the sphere chosen. For example, in the case of the potential due to the point charge, when the radius of the sphere is 2.8, $b/a = 0.7756$, $D = 7.0934$, and $D_E = 0.725$. When the radius of the sphere is 3.5, $b/a = 0.9695$, $D = 2.597$, and $D_E = 0.771$.

where the derivative ∇f is to be evaluated at the location of the point dipole.

In the special case where the point r, θ and the dipole are equidistant from the center of the sphere and colinear with it and the direction of the dipole is toward the center of the sphere, from eq 17 and 21

$$\phi = \frac{p}{(2a)^2}\left\{ 1 + 4(1 - D)\frac{b}{a} \sum_{n=0}^{\infty} \frac{n(n + 1)}{nD + n + 1}\left(\frac{b}{a}\right)^{2n} \times (-1)^n \right\} \quad (22)$$

If the potential ϕ of eq 22 is now identified with $(\phi_s - \phi_u)$, then in this case D_E becomes, from (6), (8), and (22)

$$D_E = \left[1 + 4(1 - D)\frac{b}{a}S_2 \right]^{-1} \quad (23)$$

$$S_2 = \sum_{n=0}^{\infty} \frac{n(n + 1)}{nD + n + 1}\left(\frac{b}{a}\right)^{2n}(-1)^n$$

since $\cos \alpha$ is 1.

In this paper the substituent is treated as a point dipole so that the above expression for an effective dielectric constant may be used. Curves III and IV of Figure 3 then give D_E for the ratio b/a for the two values of D of 2.0 and 5.0, respectively. For the case $a = 3.6$ and $b = 3.0$, D_E is 0.463 for $D = 5.0$.[20] The sums S_1 and S_2 were evaluated by a direct summation of terms and are accurate to at least eight decimal places after 100 terms.

Infrared Spectra and Molecular Orbital Model for Carbon Monoxide Adsorbed on Metals

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Abstract: Infrared spectra are presented in the CO stretching region for CO adsorbed on V, Cr, Mn, and Co. Band maxima for the two main bands of each metal are located at V, 1940 and 1890 cm^{-1}; Cr, 1940 and 1880 cm^{-1} (sh); Mn, 1950 and 1890 cm^{-1}; and Co, 2000 and 1880 cm^{-1}. These data together with previously presented data for Fe, Ni, and Cu allow comparisons across the first transition series from V to Cu. A molecular orbital model for the π-electron system of CO adsorbed on a cluster of metal atoms successfully accounts for the shifts in position of the two principal bands as the metal is varied across the series.

The structures of species adsorbed on metal surfaces have been partially determined in a number of cases by using infrared spectroscopy. These studies have usually considered only one metal at a time, with each metal being treated as an isolated case. In the case of CO, which is one of the most studied adsorbates in infrared work, C–O stretching frequencies have been reported over a considerable spectral range, about 300 cm^{-1}. While a few authors have discussed possible relationships between infrared band positions and the structure of chemisorbed CO, no previous attempts have been made to explain variations in band position from

one metal to another based on the electronic properties of the metal.

It was first suggested that infrared bands above 2000 cm^{-1} represented a linear M–C–O structure, while bands somewhat below 2000 cm^{-1} were due to a bridging CO group in which the carbon atom was bonded to two metal atoms.[1] Kavtaradze and coworkers have surveyed many metal carbonyl complexes, but no substituted metal carbonyls, and concluded that for chemisorbed CO bands in the 2000–2200-cm^{-1} region

(1) R. P. Eischens, S. A. Francis, and W. A. Pliskin, *J. Phys. Chem.*, **60**, 194 (1956).