TABLE V.

Atom	δ	Bond	η
=N—	0, 4	C=N—	1
—N̈— $\mid$	1	C—N— $\mid$	0, 9
=N— $\mid$+	2ᵃ	C=N— $\mid$+	1
=O	1, 2	C=O	2
—Ö—	2	C—Ö—	0, 9
=S	0	C=S	1, 2
—S̈—	0	C—S̈—	0, 6
C_{arom}—C_{aliph}≡H₃	C_{arom} = —0.1	C—C	0, 1
	C_{aliph} = —0.2	C≡H₃	2

ᵃ In this case there are also δ's=0.3 on the C atoms adjacent to =N—.
$\mid$+

tically in their very beginnings. The results obtained so far seem greatly encouraging. It is hoped that a better understanding of this relation may lead to a rational approach to chemotherapy in place of the purely empirical present one. In the field of chemical carcinogens, the success of the theory was such that it led to the creation of more powerful carcinogens than the previously known ones. It is hoped that one day the same might be done in the field of cancer chemotherapy.

CONCLUSIONS

We have chosen two subjects among those which are presently being studied in our Laboratory in the field of electronic biochemistry. Among other important problems on which work is far advanced but which, cannot be described here are, e.g., studies on the electronic structure of the energy-rich phosphates, on the mechanism of action of hydrolytic enzymes, on the mechanism of action of decarboxylating enzymes, on the electronic structure of the bile pigments, on the electronic structure and biochemical role of porphyrins, etc. We are also continuing our work on the relation between electronic structure and carcinogenic activity, especially in the field of the aromatic amines and the aza-compounds.

Electronic biochemistry appears as a most thrilling development of theoretical chemistry and also is a wide-open gateway to submolecular biology through which a fundamentally better understanding of the secrets of life should be reached.

APPENDIX

The energies of the Coulomb and the exchange integrals involving heteratoms being of the type

$$\alpha_r = \alpha_c + \delta\beta_{c=c}$$

and

$$\beta_{r-c} = \eta\beta_{c=c},$$

the set of δ's and η's in Table V has been used in the calculations referred to in this paper.

Semiempirical Theory of Vibronic Interactions in Some Simple Conjugated Hydrocarbons*

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FOR most problems in the theory of molecular structure, the electronic and nuclear motions may be viewed separately. However, for the comprehension of the appearance of certain weak electronic absorption bands and of the geometrical instability of particular molecular conformations of degenerate electronic systems, this is no longer possible. To see this let us first consider the variation of the electronic energy of $C_6H_6^+$ with nuclear displacements. The charge density functions are as pictured in Fig. 1 and a few selected permissible nuclear displacements are shown in Fig. 2.

If the nuclei composing the $C_6H_6^+$ molecule are

* Presented at the William E. Moffitt Memorial Session.

displaced, the Coulombic potential energy V changes; and the magnitude of this change, for small displacements, is given by the first few terms in the Taylor series expansion

$$V_{\text{displaced}} = V^0 + \sum_j S_j V_j' + \tfrac{1}{2}\sum_{j>k} S_j S_k V_{jk}'' + \cdots, \quad (1)$$

or

$$V_{\text{displaced}} - V^0 = \Delta V = \sum_j S_j V_j' + \tfrac{1}{2}\sum_{j>k} S_j S_k V_{jk}'' + \cdots. \quad (2)$$

As the change in the electronic energy engendered by this change in the Coulombic potential energy ΔV is given by the summation of the charge density times the

increment of Coulombic potential energy ΔV, we have that the terms

$$\Delta V_x = \int \Theta_x{}^2 \Delta V d\tau, \quad \Delta V_y = \int \Theta_y{}^2 \Delta V d\tau,$$

$$\Delta V_{xy} = \int \Theta_x \Theta_y \Delta V d\tau, \tag{3}$$

describe the change in the electronic energy, $\Delta E = E - E^0$. If the coupling term ΔV_{xy} vanishes, the new energies are simply $\Delta E_x = \Delta V_x$ and $\Delta E_y = \Delta V_y$, as is readily apparent. However, if this term does not vanish, we see that a new charge density function, $\psi = A\Theta_x + B\Theta_y$, is more appropriate. The amount of mixing is determined by the minimum energy principle, which leads to the secular equation

$$\begin{vmatrix} \Delta V_x - \Delta E & \Delta V_{xy} \\ \Delta V_{xy} & \Delta V_y - \Delta E \end{vmatrix} = 0, \tag{4}$$

so that the change in the electronic energy ΔE is given by

$$\Delta E = \tfrac{1}{2}(\Delta V_x + \Delta V_y) \pm \tfrac{1}{2}[(\Delta V_x - \Delta V_y)^2 + (2\Delta V_{xy})^2]^{\frac{1}{2}}. \tag{5}$$

Let us now examine the form of the various ΔV terms. Their structure is easily determined by squaring or multiplying together the charge density functions Θ_x and Θ_y, and superimposing the displacements of Fig. 2 upon them. For example, consider ΔV_x. The coefficients of the linear terms in the displacements are given by the sum of the individual derivatives (all equal), at each atom, of the Coulomb potential, as given in Fig. 2, times the relative charge density at each atom, as given in Fig. 1. Thus,

$$(\Delta V_x)_{\text{linear}} = S_{8a} \cdot (\text{const}) \cdot [c^2 \cdot \tfrac{1}{2}(7/3)^{\frac{1}{2}} + c^2 \cdot \tfrac{1}{2}(7/3)^{\frac{1}{2}}$$
$$+ c^2 \cdot \tfrac{1}{2}(7/3)^{\frac{1}{2}} + c^2 \cdot \tfrac{1}{2}(7/3)^{\frac{1}{2}}] + S_{8b} \cdot (\text{const})$$
$$\cdot [c^2(-\tfrac{1}{2}) + c^2(\tfrac{1}{2}) + c^2(-\tfrac{1}{2}) + c^2(\tfrac{1}{2})],$$
or

$$(\Delta V_x)_{\text{linear}} + k_1 S_{8a}. \tag{6}$$

Only the term S_{8a} may here appear linearly as all other *bond stretching* displacements (there also exists a non-vanishing carbon-carbon angle bond contribution and two contributions due to carbon-hydrogen displacements) give mutually canceling sums of interaction
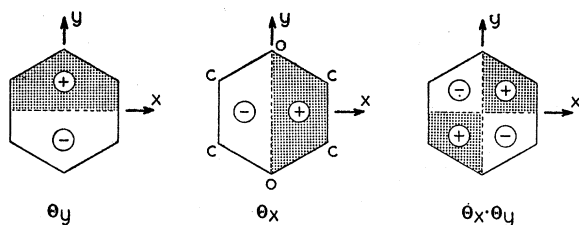

FIG. 1. Component charge density functions (in D_{2h}) Θ_x and Θ_y of the benzene plus one ion ($C_6H_6^+$) ground electronic state $^2E_{1g}$ (in D_{6h}).
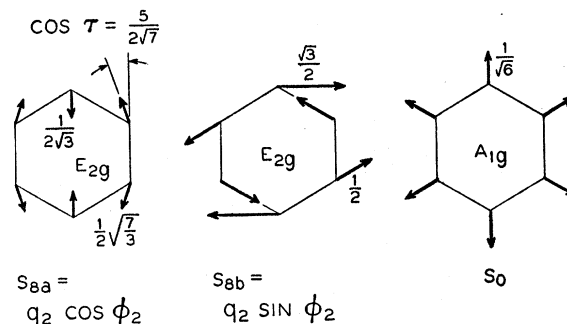

FIG. 2. E_{2g} and A_{1g} bond stretching symmetry displacements of $C_6H_6^+$

terms, as is evident from Figs. 1 and 2. We have not included a term linear in the totally symmetric "breathing" displacement A_{1g} since we have assumed that we have started with a configuration which is stable with respect to all symmetric displacements.

All the displacements yield quadratic contributions to the energy ΔV_x. But since it is only the terms which contribute *both* linearly and quadratically which are, in general, physically significant, we here determine only the form of the terms quadratic in S_{8a} and S_{8b}. *Multiplying the displacement patterns of Fig. 2 together yields the second-order Coulombic potential correction to ΔV*; their magnitude is determined by the individual second-order derivatives. Hence, from Figs. 1 and 2 we again have $(a \neq b)$

$$(\Delta V_x)_{\text{quadratic}} = \tfrac{1}{2}\{aS_{8a}{}^2 + bS_{8b}{}^2\} = \tfrac{1}{2}(a+b)(S_{8a}{}^2 + S_{8b}{}^2)$$
$$+ \tfrac{1}{2}(a-b)(S_{8a}{}^2 - S_{8b}{}^2). \tag{7}$$

The term $S_{8a}{}^2 + S_{8b}{}^2$ is the usual isotropic contribution to the $C_6H_6^+$ force constant and so may be surpressed; the term in $S_{8a}{}^2 - S_{8b}{}^2$ is a term characteristic of the Jahn-Teller theorem. Since the charge density sum $\Theta_x{}^2 + \Theta_y{}^2$ is totally symmetric, we must have that the asymmetric terms of $\int \Theta_x{}^2 \Delta V d\tau$ and $\int \Theta_y{}^2 \Delta V d\tau$ must vanish when added together. If we let $k_2 = \tfrac{1}{2}(a-b)$, we then have that

$$\Delta V_x = k_1 S_{8a} + k_2(S_{8a}{}^2 - S_{8b}{}^2) \tag{8}$$

implies that

$$\Delta V_y = -k_1 S_{8a} - k_2(S_{8a}{}^2 - S_{8b}{}^2). \tag{9}$$

The use of Figs. 1 and 2 for the evaluation of the energy term ΔV_{xy} shows that it must be of the form

$$\Delta V_{xy} = k_3 S_{8b} + k_4 S_{8a} S_{8b}. \tag{10}$$

To connect the constants k_3 and k_4 with those previously defined, k_1 and k_2, we note that a rotation of the coordinate system by $120°$ about the z axis cannot change the validity of Eqs. (3) and (10). Such a rotation sends Θ_x into $\tfrac{1}{2}\Theta_x - \tfrac{1}{2}\sqrt{3}\Theta_y$ and Θ_y into $\tfrac{1}{2}\sqrt{3}\Theta_x + \tfrac{1}{2}\Theta_y$. At the same time it sends S_{8a} into $-\tfrac{1}{2}S_{8a} - \tfrac{1}{2}\sqrt{3}S_{8b}$ and S_{8b} into $\tfrac{1}{2}\sqrt{3}S_{8a} - \tfrac{1}{2}S_{8b}$. Hence Eqs. (3) and (10) become
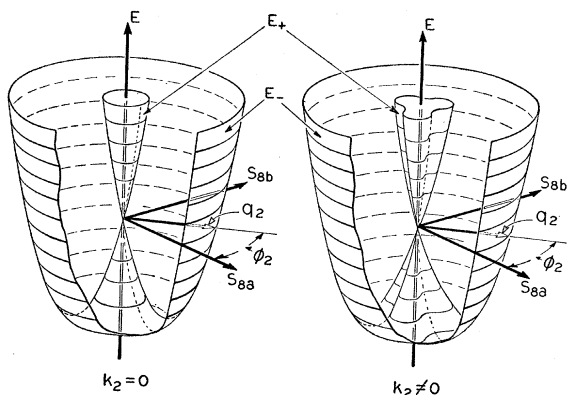
FIG. 3. Two possible electronic energy surfaces for $C_6H_6^+$. The case $k_2 \neq 0$ shows minima, on the bottom surface, at $\varphi_2 = 0°$, $120°$, $240°$, and saddles at $\varphi_2 = 60°$, $180°$, $300°$. In Fig. 4 the corresponding (many-centered) potential surfaces are drawn in *physical* (that is, *real*) space.

[from (3)]

$$(\Delta V_{xy})_{\text{rotated}} = \left(\int \Theta_x \Theta_y \Delta V d\tau \right)_{\text{rotated}}$$

$$= \tfrac{1}{4}\sqrt{3}(\Delta V_x - \Delta V_y) - \tfrac{1}{2}\Delta V_{xy}, \quad (11)$$

and [from (10)]

$$(\Delta V_{xy})_{\text{rotated}} = k_3[\tfrac{1}{2}\sqrt{3}S_{8a} - \tfrac{1}{2}S_{8b}]$$

$$+ k_4[-\tfrac{1}{4}\sqrt{3}(S_{8a}^2 - S_{8b}^2) - \tfrac{1}{2}S_{8a}S_{8b}]. \quad (12)$$

The substitution of Eqs. (8) and (9) into (11) gives the more useful final relation

$$(\Delta V_{xy})_{\text{rotated}} = \tfrac{1}{2}\sqrt{3}k_1 S_{8a} + \tfrac{1}{2}\sqrt{3}k_2(S_{8a}^2 - S_{8b}^2)$$

$$- \tfrac{1}{2}k_3 S_{8b} - \tfrac{1}{2}k_4 S_{8a}S_{8b}. \quad (13)$$

Direct comparison of Eqs. (12) and (13) then yields $k_1 = k_3$ and $k_2 = -\tfrac{1}{2}k_4$. Thus we may write our results as

$$\tfrac{1}{2}(\Delta V_x + \Delta V_y) = 0,$$

$$(\Delta V_x - \Delta V_y) = 2k_1 S_{8a} + 2k_2(S_{8a}^2 - S_{8b}^2), \quad (14)$$

$$2\Delta V_{xy} = 2k_1 S_{8b} - 4k_2(S_{8a}S_{8b}).$$

The placement of Eq. (14) into Eq. (5) then produces the desired energy surfaces

$$\Delta E = \tfrac{1}{2}k_0(S_{8a}^2 + S_{8b}^2) \pm [k_1^2(S_{8a}^2 + S_{8b}^2)$$

$$+ k_2^2(S_{8a}^2 + S_{8b}^2)^2 + 2k_1 k_2(S_{8a}^3 - 3S_{8a}S_{8b}^2)]^{\frac{1}{2}}, \quad (15)$$

where we have now explicitly added in the isotropic force constant contribution. If we introduce the polar coordinates $q_2 \cos\varphi_2 = S_{8a}$ and $q_2 \sin\varphi_2 = S_{8b}$, we may simplify Eq. (15) as follows:

$$\Delta E = \tfrac{1}{2}k_0 q_2^2 \pm q_2(k_1^2 + k_2^2 q_2^2 + 2k_1 k_2 q_2 \cos3\varphi_2)^{\frac{1}{2}}. \quad (16)$$

The corresponding charge density functions ψ_{1+} and ψ_{1-} are obtained by substitution of Eq. (16) into (4). If k_2 is zero, these are given by

$$\psi_{1+} = \cos\tfrac{1}{2}\varphi_2 \; \Theta_x + \sin\tfrac{1}{2}\varphi_2 \; \Theta_y,$$

$$\psi_{1-} = \sin\tfrac{1}{2}\varphi_2 \; \Theta_x - \cos\tfrac{1}{2}\varphi_2 \; \Theta_y. \quad (17)$$

The total energy, $E^0 + \Delta E$, is plotted in Fig. 3 for the case k_2 equals zero. For $k_2 \neq 0$ we obtain bumps on the bottom and top energy surfaces corresponding to maxima and minima every $120°$ due to the $\cos3\varphi_2$ in Eq. (16). If the energy separation from the origin to the bottom of the trough is large, the Born-Oppenheimer separation still applies and the system remains entirely on the bottom energy surface. The behavior of the charge density function ψ_{1-} corresponding to the lower surface then varies, in a semiclassical sense, periodically in the time, as $\tfrac{1}{2}\varphi_2$ has the classical significance of a frequency times the time, $\tfrac{1}{2}\varphi_2 = \omega t$ (note: this implies the charge density varies in time as $\psi_{1-}^2 = \sin^2\omega t \Theta_x^2 - \sin2\omega t \Theta_x \Theta_y + \cos^2\omega t \Theta_y^2$). If this energy separation is not large, one must solve the vibrational and electronic problems simultaneously, and one can no longer speak of motion on an electronic potential energy surface. A complete discussion of these latter points is given in the papers by Longuet-Higgins, Öpik, Pryce, and Sack, and Moffitt, Thorson, and myself. We give here a qualitative picture of this complicated problem and refer to these papers for the quantitative solution. Before passing to the qualitative dynamical discussion, it should be noted that if it were not for the linear S_{8b} term of ΔV_{xy}, the system would always be one of three possible D_{2h} distorted hexagonal configurations, and that it is this term which causes "tunneling" amongst these latter configurations (see Fig. 4).
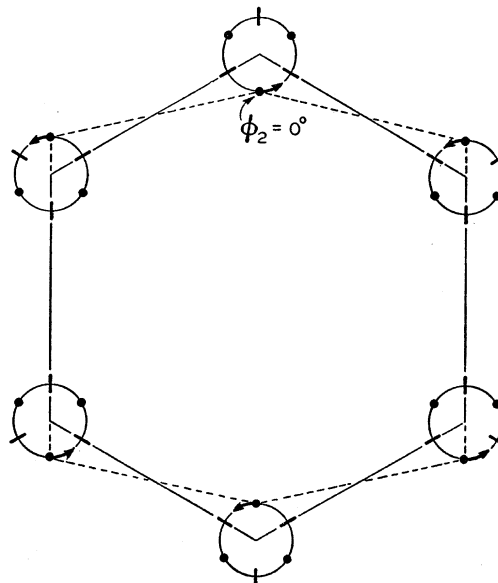
Let us consider our system to be specified as being

FIG. 4. Pictorial representation of the permissible E_{2g} nuclear displacements of the benzene plus one ion. Small darkened circles indicate the three equivalent (distorted) static equilibrium conformations, and the heavy lines represent the saddle points which separate these. The equilibrium (D_{2h}) configuration corresponding to $\varphi_2 = 0$ is given by the dotted trace, and the path along which it interconverts (see also Fig. 3, case $k_2 \neq 0$) is indicated by the heavy arrows.

in the state

$$\Theta_x \cdot \prod_{vk,k'} N_{vk}(S_{8a})N_{vk'}(S_{8b})$$

at time zero. Then according to time-dependent perturbation theory it has the probability

$$P(t)_{x \to y} = 4 |\Delta V_{xy}|^2 \sin^2\tfrac{1}{2}\omega t/\hbar^2\omega^2 \qquad (18)$$

of being in the state

$$\Theta_y \cdot \prod_{vk,k'} N_{vk}(S_{8a})N_{vk'\pm 1}(S_{8b})$$

at time t, where ω is the frequency of the vibration corresponding to the symmetry coordinates $S_{8a,b}$ and ΔV_{xy} is as before. This is the probability that the electrons are scattered from the state Θ_x to the state Θ_y by the emission or absorption of a phonon of energy $\hbar\omega$. Hence it is impossible to confine our system to the electronic state Θ_x. The true state of the system, after statistical equilibrium has been reached consists of a superposition of states of Θ_x and Θ_y which differ from each other by one unit of vibrational energy of the displacements $S_{8a,b}$. We can therefore no longer speak of an electronic or vibrational state of the system, but can talk only of the "vibronic" configuration of the molecule.

A similar picture may be presented to describe the appearance of vibronically allowed absorption bands. Here we have to compound two probabilities, (1) the probability that our initial state, l say, has acquired allowed electronic character due to a vibronic perturbation ΔV_{jl}, and (2) the probability that it absorbs or radiates whilst possessing this allowed character. With such a physical picture of the intensity "borrowing" mechanism, it is easy to see that as the total intensity depends upon the total probability of an electron being scattered into a different electronic spatial distribution, and hence upon the integrated scattering cross section, it is relatively insensitive to the nature of the perturbing or scattering potential ΔV; but that the detailed distribution of intensity amongst the various vibrational levels, which corresponds, in our analogy, to the angular dependence of the scattering process, is highly dependent upon the exact nature of the scattering mechanism ΔV. Detailed

calculations have shown these expectations to be only too true.

With the aid of the Lennard-Jones approximation for the variation of the aromatic resonance integral β with nuclear displacements, I have been able to estimate the constants k_1 and k_2 which particularize the Jahn-Teller effect in $C_6H_6^+$ and its analogs, and to compute the probabilities required for the prediction of vibronically allowed intensities in benzenelike systems. The agreement with existent experimental data is fair, and thus tenders the fond hope that this simple method of estimating vibronic constants might be quite generally useful.

In closing I should like to point out that it was the late Professor William E. Moffitt who first realized the true import of the vanishing of the Jahn-Teller constant k_2 (see Fig. 3, case $k_2=0$, which is due to him). And it was he who also first obtained an analytical solution of the $C_6H_6^+$ static and dynamic Jahn-Teller problem. My indebtedness to him as a teacher and friend is inestimable: I miss him sorely. I sincerely hope that my poor efforts here today will serve as a fitting memorial to this truly wonderful human being.

I should also like very much to acknowledge that the electron-phonon scattering analogy for the benzene intensity problem was kindly brought to my attention by Dr. Philip W. Anderson during my employment interview at the Bell Telephone Laboratories in 1956. I am extremely grateful to him for this kindness.

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