1,1-Dibromoethylene and 1,1-Difluoroethylene. A partial normal coordinate calculation is available for both molecules;[66] we have repeated the calculations so as to include the out of plane vibrations. The observed frequencies of ref 67 were used (Tables XXXI and XXXII).

Acetylene. Valence force constants were obtained for this molecule by fitting to the observed fundamentals for C_2H_2, C_2HD, and C_2D_2 reported by Herzberg[13] (Table XXXIII).

Monohaloacetylenes. Valence force constants for the monohaloacetylenes have been calculated from the frequency data of ref 15. For monofluoroacetylene a second set of force constants was evaluated, fitting to the slightly different assignments of ref 14; see main text (Tables XXXIV–XXXVI).

Methane. We have taken the observed frequencies of ref 68 to obtain a set of force constants (Table XXXVII).

Fluoroform. We have used the relevant force constants reported in ref 69 as starting values in our least-squares fitting (Table XXXVIII).

Chloroform and Bromoform. Although a good Urey-Bradley force field is available for both molecules,[70] we have repeated the calculations in terms of valence force fields, using the same types of interaction force constants that were used for fluoroform. All fittings converged well except for the A_1 block of bromoform, which would not converge. We have chosen the set of force constants for this symmetry block which gives the closest agreement between observed and calculated frequencies (Tables XXXIX and XL).

(66) J. R. Scherer and J. Overend, *J. Chem. Phys.*, 32, 1720 (1960).

(67) S. Brodersen and A. Langseth, *J. Mol. Spectrosc.*, 3, 114 (1959).

(68) I. M. Mills, *Spectrochim. Acta*, 16, 35 (1960).

(69) D. A. Long, R. B. Gravenor, and D. T. L. Jones, *Trans. Faraday Soc.*, 60, 1509 (1964).

(70) T. Shimanouchi and I. Suzuki, *J. Mol. Spectrosc.*, 6, 277 (1961)

Vibrationally Induced Stabilization of the Vertically Excited States of Benzene

Alain Devaquet*

Contribution No. 44 of the Photochemistry Unit,
Department of Chemistry, University of Western Ontario,
London, Ontario, Canada. *Received March 3, 1972*

Abstract: This paper examines the vibrationally induced stabilization of the lowest singlet and triplet vertically excited states of the benzene molecule. The nuclear motions which lead to a favorable (at least initially) stabilizing path are selected both qualitatively and quantitatively. The resulting potential energy surfaces of the excited states are discussed in relation to the spectroscopical and photochemical behavior of the benzene molecule.

In 1944 Lewis and Kasha[1] concluded after an investigation of the benzene phosphorescence spectrum that the molecule in its triplet state was contracted along the 1.4 axis. Even though it appeared later that the study of the phosphorescence intensity alone was not a very sensitive way of determining such distortions,[2] and, indeed, Shull[3] has shown that the phosphorescence spectrum can be interpreted in terms of a hexagonal D_{6h} configuration, more convincing experimental results are now available which support a very slight distortion away from hexagonal symmetry.[4] They indicate that the lowest triplet state, $^3B_{1u}$, is distorted into a nonplanar structure with two long bonds and four short ones. It is very important to note that these results have been obtained for the C_6H_6 molecule in a crystalline environment (usually in a C_6D_6 crystal). Therefore the nuclear displacements may result from the crystal field itself rather than being intrinsic properties of the free single molecule. Notwithstanding it is shown in this paper, by using a second-order perturbation method, that the nuclear motions which might stabilize the vertically excited triplet state $^3B_{1u}$ of the free molecule are precisely those which distort the triplet molecule in the crystal.

I. Qualitative Selection of the Stabilizing Vibrations

The problem we are looking at here is the selection of the nuclear motions which may be particularly efficient in the process of stabilizing a vertically excited species. One approach to this problem is the Herzberg–Teller expansion of the Hamiltonian in a Taylor series in normal coordinates of the ground electronic state.[5] If this development is restricted to only one coordinate, Q, we may write the correct Hamiltonian to second order in nuclear displacements

$$H = H_0 + (\partial H/\partial Q)_0 Q + {}^1\!/_2(\partial^2 H/\partial Q^2)_0 Q^2 + 0(Q^3) \quad (1)$$

---

* On leave from the Laboratoire de Chimie Théorique, Centre Scientifique d'Orsay, Université de Paris—Sud, 91 Orsay, France.

(1) G. N. Lewis and M. Kasha, *J. Amer. Chem. Soc.*, 66, 2100 (1944).

(2) G. C. Nieman, *J. Chem. Phys.*, 50, 1660, 1674 (1969).

(3) H. Shull, *ibid.*, 17, 295 (1949).

(4) (a) G. C. Nieman and D. S. Tinti, *ibid.*, 46, 1432 (1967); (b) D. M. Burland, G. Castro, and G. W. Robinson, *ibid.*, 52, 4100 (1970); (c) J. H. van der Waals, A. M. D. Berghuis, and M. S. de Groot, *Mol. Phys.*, 13, 301 (1967); (d) A. M. Ponte-Goncalves and C. A. Hutchison Jr., *J. Chem. Phys.*, 49, 4235 (1968).

(5) This set of normal coordinates is well adapted to the study of vibronic problems in *absorption* where the originating state is the ground state; in *emission* problems it is more appropriate to use the normal coordinates of the excited electronic state from whose equilibrium nuclear configuration emission takes place. In the problem at hand neither one is perfect; it would be better to simply use a set of symmetry coordinates. In the benzene case, however, some matrix elements are readily evaluated in terms of the ground state's normal coordinates. It is hoped that such a convenient choice entails only slight impairment of our description.

where H_0 is the electronic Hamiltonian under the zeroth-order Born–Oppenheimer approximation. The eigenfunctions and eigenvalues of H_0 being respectively christened $|n\rangle$ and E_n^0, the second-order energy E_n of $|n\rangle$ is[6]

$$E_n = E_n^0 + Q\langle n|\left(\frac{\partial H}{\partial Q}\right)_0|n\rangle + {}^1\!/_2 Q^2\left\{\langle n|\left(\frac{\partial^2 H}{\partial Q^2}\right)_0|n\rangle - 2\sum_{k\neq n}\frac{\left|\langle k|\left(\frac{\partial H}{\partial Q}\right)_0|n\rangle\right|^2}{E_k^0 - E_n^0}\right\} \tag{2}$$

In this expansion k runs over all states $|k\rangle$ which have the same multiplicity as $|n\rangle$. Such a development has been extensively used as the starting point in all studies of vibrationally induced perturbations in molecular *ground-state* electronic distributions.[7] In the present excited state case the interpretation of the various terms remains. Following Salem[8] the second and third terms in (2) represent "the energy change due to the nuclear motion within a fixed electronic density" whereas the fourth one can be called the "relaxability" of the molecule along the coordinate Q and represents "the energy change due to the rearrangement of the electronic density induced by the nuclear displacements." In order to analyze (2) using group theory arguments we dub $\Gamma(S)$ the irreducible representation to which the species S belongs. Since the Hamiltonian H is invariant under the operations R of the group of the molecule, $(\partial H/\partial Q)_0$ has the same symmetry properties in electron space that Q has in the nuclear space. Therefore $(\partial H/\partial Q)_0$ belongs to $\Gamma(Q)$ and $(\partial^2 H/\partial Q^2)_0$ to the direct product $\Gamma(Q) \times \Gamma(Q)$. The first-order diagonal term (second term in (2)) vanishes unless the direct product $\Gamma(n) \times \Gamma(n)$ contains $\Gamma(Q)$. If $\Gamma(n)$ is a *nondegenerate* irreducible representation (and this will be the case for the lowest triplet, B_{1u}, and the lowest singlet, B_{2u}, of benzene), the first-order term is nonzero only if Q is a totally symmetric vibration. Q therefore corresponds to a "breathing" motion of the whole molecule. (It is well known that in the excited states of benzene the ring gets slightly bigger.) The second-order diagonal term (third term in (2)) will always be nonzero, since, whatever the degree of degeneracy of $\Gamma(n)$ or $\Gamma(Q)$, the direct products $\Gamma(n) \times \Gamma(n)$ and $\Gamma(Q) \times \Gamma(Q)$ both contain the totally symmetric irreducible representation Γ_1. This term, however, may be accidentally very small since its magnitude depends upon the overlap, *i.e.*, the relative localization in the molecule, of the electronic density $\langle n||n\rangle$ and the nuclear displacements involved in Q. In our qualitative analysis these two diagonal terms will not be further considered. (For more details see ref 9.) The off-diagonal second-order term (fourth term in (2)) is always a stabilizing term. This statement is unambiguous in the case of the *lowest triplet* state of a molecule (since the denominator $E_k^0 - E_n^0$ always has a positive value) and is roughly true in the case of the *lowest excited singlet* state.[10]

The first step in the analysis of this off-diagonal matrix element, term 3, is to consider the difference of

$$-\sum_{k\neq n}\frac{\left|\langle k|\left(\frac{\partial H}{\partial Q}\right)_0|n\rangle\right|^2}{E_k^0 - E_n^0} \tag{3}$$

eigenenergies appearing in the denominator. For the stabilizing contribution to be important $E_k^0 - E_n^0$ has to be small (in the limits permitted by the perturbation theory framework). Therefore, if $|n\rangle$ is the lowest excited state of a given multiplicity, the sum over all excited states $|k\rangle$ of the same multiplicity may be truncated and restricted to the three or four states $|k\rangle$ that follow $|n\rangle$ in order of increasing vertical excitation energies.[11] In the case of benzene, Table I[12] shows that, in the study of the lowest B_{1u} *triplet* state, the important $|k\rangle$ states are ${}^3E_{1u}$ and, to a lesser extent, ${}^3B_{2u}$, ${}^3A_{2u}$, and ${}^3E_{2g}$. For the study of the lowest B_{2u} *singlet* state we should take into account $|k\rangle = {}^1B_{1u}$, ${}^1E_{1u}$, ${}^1E_{2g}$ and, eventually, ${}^1A_{2u}$. For a particular excited state $|k\rangle$, selected as described on energetic grounds, the matrix element of the numerator in (3) vanishes unless the direct product $\Gamma(n) \times \Gamma(k)$ contains $\Gamma(Q)$. This second selection rule then determines, for each $|k\rangle$, the irreducible representation(s) to which a vibration Q must belong in order to stabilize $|n\rangle$ by mixing $|n\rangle$ and $|k\rangle$. The vibrations Q which might eventually stabilize the vertically excited ${}^3B_{1u}$ state of benzene are listed in Table II.[13]

Table I. *Ab Initio* SCF Vertical Excitation Energies of the Triplet and Singlet Excited States of Benzene (Energies in eV)

Triplet states		Singlet states	
${}^3B_{1u}$	3.66	${}^1B_{2u}$	4.89
${}^3E_{1u}$	4.69	${}^1B_{1u}$	6.14
${}^3A_{2u}$	>4.7 (assumed value)	${}^1E_{1u}$	6.75
${}^3B_{2u}$	5.76	${}^1E_{2g\delta}$	8.18
${}^3E_{2g}$	5.96	${}^1E_{2g\gamma}$	8.89
${}^3E_{2g}$	8.36	${}^1A_{2u}$	?

The third step is finally to select the most efficient vibration(s) among those belonging to the same irreducible representation (among the four e_{2g} vibrations, for example). As already pointed out, the matrix ele-

---

[6] It must be remembered that, for (2) to be strictly true, the wave function $|n\rangle$ has to fulfill some conditions. Let us for example consider the first order term. The relation $\partial E_n/\partial Q = \langle n|(\partial H/\partial Q)_0|n\rangle$ is true only if $\langle \delta n|H_0 - E_n^0|n\rangle + \langle n|H_0 - E_n^0|\delta n\rangle = 0$ (δn denoting the small change of $|n\rangle$ produced by dQ) or more precisely if (a) $|n\rangle$ is the *exact* solution of the eigenvalue equation $(H_0 - E_n^0)|n\rangle = 0$ or (b) $|n\rangle$ is determined variationally. For our particular benzene case the eigenfunctions $|n\rangle$ are "virtual orbital" wave functions in which the molecular orbitals are assumed to have their ground state forms. Such particular eigenfunctions do not obey (a) or (b) and (2) is only approximately true (even though this approximation is probably a reasonable one).

[7] (a) R. F. W. Bader and A. D. Brandrauk, *J. Chem. Phys.*, **49**, 1666 (1968); (b) R. F. W. Bader, *Can. J. Chem.*, 40, 1164 (1962); (c) R. G. Pearson, *J. Amer. Chem. Soc.*, **91**, 4947 (1969); *Accounts Chem. Res.*, 4, 152 (1971); (d) L. Salem, *Chem. Phys. Lett.*, **3**, 99 (1969); (e) J. Burdett, *J. Chem. Phys.*, **52**, 2983 (1970); *Appl. Spectrosc. Rev.*, 4, 43 (1970).

[8] L. Salem, *J. Chem. Phys.*, **38**, 1227 (1963).

[9] A. Devaquet, *J. Amer. Chem. Soc.*, **94**, 5626 (1972).

[10] If this lowest singlet state $|n\rangle$ results from the promotion of an electron from ψ_i to ψ_j, it may be shown[9] that the destabilizing contribution of the ground state $|0\rangle$ $(E_0^0 - E_n^0 < 0)$ is roughly cancelled by the stabilization provided by the corresponding doubly excited state $|m\rangle = \psi_i\bar{\psi}_i \rightarrow \psi_j\bar{\psi}_j$ $(E_m^0 - E_n^0 > 0)$.

[11] As pointed out by one of the referees, this approach is customary but not rigorous. Since the perturbation involves the motion of atoms, the perturbation treatment must describe the displacements of the cups of the atomic orbitals. This would require a summation not only over the discrete $|k\rangle$ excited states, but also over the continuum functions.

[12] R. J. Buenker, J. L. Whitten, and J. D. Petke, *J. Chem. Phys.*, **49**, 2261 (1968).

[13] These vibrations are represented in Figure 50, G. Herzberg, "Infrared and Raman Spectra," Van Nostrand, Princeton, N. J., 1968, p 118.

Table II. Possible Stabilizing Vibrations of the $^3B_{1u}$ State of Benzene[a]

Triplet state $\|k\rangle$	$\Gamma(Q) = \Gamma(n) \times \Gamma(k)$ with $\|n\rangle = {}^3B_{1u}$	Nature of Q	
$^3E_{1u}$	e_{2g}	ν_{15},7	CH stretching
		ν_{16},8	CC stretching
		ν_{17},9	CH || bending
		ν_{18},6	CCC || bending
$^3B_{2u}$	a_{2g}	ν_3,3	CH || bending
$^3E_{2g}$	e_{1u}	$\nu_{,2}$,18	CH stretching
		ν_{13},19	CC stretching
		ν_{14},20	CH || bending
$^3A_{2u}$	b_{2g}	ν_7,5	CH ⊥ bending
		ν_8,4	CCC ⊥ bending

[a] The numbering and the description of the normal vibrations of benzene used here are those of G. Herzberg ("Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N. J., p 363). However, for convenience, the numbering of Wilson (E. B. Wilson Jr., *Phys. Rev.*, **45**, 706 (1934)) has been added.

ment depends upon the overlap between the electronic transition density $\langle n| \; |k\rangle$ and the nuclear displacements Q. For the matrix element not to be too small these two parts have to be localized in the same regions of the molecule. In the *triplet* B_{1u} *case* all the transition densities involve π,π^* excited states, the only exception being the $^3B_{1u}$,$^3A_{2u}$ transition density, and are therefore mainly located on the hexagonal ring. Vibrations involving the CH bonds provide a poor coupling between these π,π^* states and, when competing with CC vibrations, may be ignored. For this reason the e_{2g} ν_{15},7 and ν_{17},9 and the e_{1u} ν_{12},18 and ν_{14},20 CH vibrations may be neglected (at least according to the descriptions in Table II) since they compete respectively with the e_{2g} ν_{16},8 and ν_{18},6 and the e_{1u} ν_{13},19 very active[14] CC vibrations. On the other hand the a_{2g} ν_3,3 vibration is the *only* vibration coupling the $^3B_{1u}$ and $^3B_{2u}$ states. Even though ν_3,3 is a CH bending vibration it has to be considered as a possible active vibration. If we finally consider the $^3B_{1u}(\pi,\pi^*)$,$^3A_{2u}(\sigma,\pi^*)$ transition density it is clear that the two interesting vibrations ν_7,5 and ν_8,4 involve roughly the same carbon atoms displacements. They differ by the fact that the hydrogen and the carbon atoms move "in phase" (ν_8) or "out of phase" (ν_7).[13] It seems difficult to make a choice between them either qualitatively or quantitatively (since our calculations—see next section—are restricted to the carbon framework and to π,π^* states); it appears therefore safe to keep them in mind as they might eventually intervene in the interpretation of the experimental results. In conclusion the only remaining choice is between the ν_{16},8 and ν_{18},6, e_{2g} vibrations; this choice cannot be made without the evaluation of the corresponding matrix elements. These calculations will now be carried out, not only for this peculiar case but also for all e_{1u} and e_{2g} motions in order to check our qualitative arguments.

II. Quantitative Selection of the Active e_{1u} and e_{2g} Vibrations

The calculation of the off-diagonal matrix element

$$h_{kn}(Q) = h_{kn}(Q) = \langle k|\left(\frac{\partial H}{\partial Q}\right)_0|n\rangle \tag{4}$$

follows a three-step procedure: (a) the reduction of all the necessary integrals to a small number (1 or 2) of basic matrix elements between *state* wave functions; (b) the development of these basic integrals in matrix elements between *atomic* wave functions; and (c) the determination of the necessary atomic integrals. The first two steps have been developed by Albrecht[15] and the third one by Liehr.[16] In this paragraph we simply outline the general framework of the method (mainly (a)) and complete Albrecht's results by some additions which were necessary in our particular problem. The *practical* rules involved in steps b and c are summarized in various appendices.

The only nuclear coordinate dependent part of H which has to be taken into account in (4) is the nuclear–electron attraction potential.

$$\left(\frac{\partial H}{\partial Q}\right)_0 = \left\{\frac{\partial}{\partial Q}\sum_{l=1}^{m}\sum_{\sigma=1}^{N} H_{l\sigma}\right\}_0, \quad H_{l\sigma} = -\frac{Z_\sigma e^2}{r_{l\sigma}} \tag{5}$$

The innocuous looking expression 5, in which l runs over the electrons and σ over the nuclei, is transformed into the potent eq 6 by inserting in the derivative a system of local coordinates $\xi_\sigma{}^f$ (f = 1, 2, 3) defined on the σ atom.

$$\left(\frac{\partial H}{\partial Q}\right)_0 = \sum_l\sum_\sigma\left(\frac{\partial H_{l\sigma}}{\partial r_{l\sigma}}\right)_0\left\{\sum_{f=1}^{3}\left(\frac{\partial r_{l\sigma}}{\partial \xi_\sigma{}^f}\right)_0\left(\frac{\partial \xi_\sigma{}^f}{\partial Q}\right)_0\right\} \tag{6}$$

In the benzene case the in-plane local cartesian set on atom σ is composed of a radial coordinate $\xi_\sigma{}^1 = R$ (positive outward) and a tangential coordinate $\xi_\sigma{}^2 = U$ (positive clockwise); the out-of-plane coordinate is $\xi_\sigma{}^3 = Z$. In (6) the factor $(\partial r_{l\sigma}/\partial\xi_\sigma{}^f)_0$ is the direction cosine of the vector $\mathbf{r}_{l\sigma}$ with respect to the local displacement $\xi_\sigma{}^f$; the factor $(\partial\xi_\sigma{}^f/\partial Q)_0$ is an element of the matrix which transforms the normal coordinate Q into the local cartesian system. This second factor must be obtained from a normal coordinate analysis which, in the benzene case, has been done by Albrecht.[17] Because $(\partial H/\partial Q)_0$ is a sum of monoelectronic operators, we can perform the integration over all but one (p) electron in (6) and sum over the m indistinguishable electrons. By introducing the one-electron transition densities $\rho_{nk}(p)$[18]

$$\rho_{nk}(p) = m\int \psi_n(x',p)\psi_k(x',p)\mathrm{d}x' \tag{7}$$

we can rewrite (4) in a form (8) which is the starting point of our analysis, or more simply, christening the

$$h_{nk}(Q) = \sum_{f=1}^{3}\sum_{\sigma=1}^{N}\left(\frac{\partial \xi_\sigma{}^f}{\partial Q}\right)_0\int \rho_{nk}(p)\left(\frac{\partial H_{p\sigma}}{\partial r_{p\sigma}}\right)_0\left(\frac{\partial r_{p\sigma}}{\partial \xi_\sigma{}^f}\right)_0 \mathrm{d}p \tag{8}$$

coefficient by $\xi_\sigma{}^f(Q)$ and the integral by $I_\sigma{}^f(n,k,Q)$.

$$h_{nk}(Q) = \sum_f\sum_\sigma \xi_\sigma{}^f(Q) I_\sigma{}^f(n,k,Q) \tag{9}$$

---

(14) It has to be borne in mind that the third term in (2) is not considered here. By "active" we refer to terms in (3) which are negative and not too small. This does not insure that the overall second-order contribution is itself negative and stabilizing.

(15) (a) A. C. Albrecht, *J. Chem. Phys.*, **33**, 156 (1960); (b) *ibid.*, **33**, 169 (1960).

(16) (a) A. D. Liehr, *Z. Naturforsch. A*, **13**, 311 (1958); (b) *ibid.*, **13**, 429 (1958).

(17) A. C. Albrecht, *J. Mol. Spectrosc.*, **5**, 236 (1960).

(18) J. N. Murrell and J. A. Pople, *Proc. Phys. Soc., London, Sect. A*, **69**, 245 (1956).

Considering a reference carbon atom σ^* and the associated local coordinate f^* it is possible to create group theoretically all parent local coordinates $\xi_\sigma{}^f$ which belong to a given irreducible representation.[19] In other words $\xi_\sigma{}^f$ and $\xi_{\sigma^*}{}^{f^*}$ are related by an expression such as

$$\xi_\sigma{}^f(Q) = \eta_{\sigma,f}(\sigma^*,f^*,Q)\xi_{\sigma^*}{}^{f^*}(Q) \qquad (10)$$

Furthermore it has been demonstrated[20] that the same relation holds among the corresponding integrals I.

$$I_\sigma{}^f(n,k,Q) = \eta_{\sigma,f}(\sigma^*,f^*,Q)I_{\sigma^*}{}^{f^*}(n,k,Q) \qquad (11)$$

The matrix element may therefore be rewritten

$$h_{nk}(Q) = \sum_{\sigma^*f^*}\xi_{\sigma^*}{}^{f^*}(Q)I_{\sigma^*}{}^{f^*}(n,k,Q)\sum_{\sigma,f}\eta_{\sigma,f}{}^2(\sigma^*,f^*,Q) \qquad (12)$$

where the sum over σ^* and f^* goes over a minimum number of atomic centers and corresponding local cartesian coordinates. In addition, the analysis of $I_{\sigma^*}{}^{f^*}$ shows that this integral vanishes unless the triple direct product $\Gamma(n) \times \Gamma(k) \times \Gamma(\xi^f)$ contains Γ_1 and also that the number of nonvanishing integrals $I_{\sigma^*}{}^{f^*}$ is given by the number of times Γ_1 appears in the triple direct product (the application of these rules and of (12) is shown in Appendix A where a particular example is detailed). The determination of the basic integrals $I_{\sigma^*}{}^{f^*}$ is based on the fact that whenever the state wavefunctions $|n\rangle$ and $|k\rangle$ are ultimately based on LCAO molecular orbitals it will be possible to express the one-electron transition density $\rho_{nk}(p)$ as a linear combination of basic transition densities $\rho_i(p)$ built on *atomic* orbitals.

$$\rho_{nk}(p) = \sum_i \alpha_{nk}(i)\rho_i(p) \qquad (13)$$

The components $\rho_i(p)$ are completely determined by both the nature of the atomic basis set (in the benzene case, we will consider six equivalent $2p_z$ atomic orbitals ϕ_i, $i = 1\ldots6$, located at the six equivalent carbon atoms of a hexagonal ring) and the symmetry properties of the molecule (D_{6h} point group in the benzene case). The coefficients $\alpha_{nk}(i)$ depend on the actual forms of the LCAO expansion (the molecular orbitals of benzene are given in Table III) and of the state wavefunctions, with or without configuration interaction (the usual state wavefunctions of benzene are given in Table IV).

Table III. LCAO Molecular Orbitals of Benzene[a]

$$\begin{aligned}
\psi_1 &= 0.3238(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6)\\
\psi_2 &= 0.2637(2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6)\\
\psi_3 &= 0.4567(\phi_2 + \phi_3 - \phi_5 - \phi_6)\\
\psi_4 &= 0.5855(-\phi_2 + \phi_3 - \phi_5 + \phi_6)\\
\psi_5 &= 0.3381(2\phi_1 - \phi_2 - \phi_3 + 2\phi_4 - \phi_5 - \phi_6)\\
\psi_6 &= 0.5485(\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6)
\end{aligned}$$

[a] These MO's have been normalized including overlap (since the terms $\phi_1\phi_2$, $\phi_1\phi_3$, $\phi_1\phi_4$ as well as the terms $\phi_1{}^2$ have been considered in our atomic one-electron densities ρ_i).

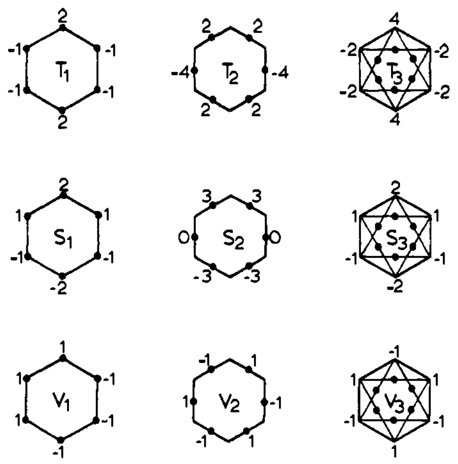


Figure 1. The nine component transition densities arising when the electronic functions are based on six equivalent $2p_z$ atomic orbitals (each dot is located midway between a pair of atomic orbitals whose overlap constitutes a contribution to the transition density). All numbers are expressed in the unit $^1/_6\,e$ where e is the charge of the electron. The symmetries of the components are respectively $E_{2ga}(T_1,T_2,T_3)$, $E_{1ua}(S_1,S_2,S_3)$, $B_{1u}(V_1,V_3)$, $B_{2u}(V_2)$.

Table IV. State Functions for Benzene[a]

State function	Symmetry
$2^{-1/2}(\chi_3{}^4 + \chi_2{}^5)$	B_{1u}
$2^{-1/2}(\chi_3{}^5 - \chi_2{}^4)$	B_{2u}
$2^{-1/2}(\chi_3{}^5 + \chi_2{}^4)$	E_{1ua}
$2^{-1/2}(\chi_3{}^4 - \chi_2{}^5)$	E_{1ub}
$2^{-1/2}(\chi_1{}^5 - \chi_2{}^6)$	$E_{2ga\gamma}$
$2^{-1/2}(\chi_1{}^4 - \chi_3{}^6)$	$E_{2gb\gamma}$
$2^{-1/2}(\chi_1{}^5 + \chi_2{}^6)$	$E_{2ga\delta}$
$2^{-1/2}(\chi_1{}^4 + \chi_3{}^6)$	$E_{2gb\delta}$

[a] $\chi_i{}^j$ means a configuration with an electron in j and a hole in i.

A basic (state) integral may therefore be expressed as

$$I_{\sigma^*}{}^{f^*} = \sum_i \alpha_{nk}(i)\int \rho_i(p)\left(\frac{\partial H}{\partial r_{p\sigma^*}}\right)_0\left(\frac{\partial r_{p\sigma^*}}{\partial \xi_{\sigma^*}{}^{f^*}}\right)_0 \mathrm{d}p = \sum_i \alpha_{nk}(i)I_{\sigma^*}{}^{f^*}(i) \qquad (14)$$

The components ρ_i which belong to the irreducible representation $\Gamma(a)$ are simply obtained by the action of the operator given in ref 19 on $\phi_1{}^2$, $\phi_1\phi_2$, $\phi_1\phi_3$, and $\phi_1\phi_4$, successively. If we ignore the A_{1g} components which are not of great interest in our problem and if we choose the a component of the degenerate irreducible representations E_{2g} and E_{1u},[21] nine densities are obtained ($3E_{2g}$, $3E_{1u}$, $2B_{1u}$, B_{2u}) which are depicted in Figure 1. For each of the components ρ_i we have to calculate the atomic integrals $I_{\sigma^*}{}^{f^*}(i)$. The rules to be used in these evaluations and the various results are given in Appendix B. The last step in the practical determination of the integrals $I_{\sigma^*}{}^{f^*}$ is to develop the transition densities between states (see Table IV) in terms of the components ρ_i. These expansions[22]

---

(19) The proper linear combination of the $\xi_\sigma{}^f$ belonging to a given irreducible representation $\Gamma(a)$ is obtained by forming the expression

$$\Sigma_R \chi^a(R)R\xi_{\sigma^*}{}^{f^*}$$

i.e., by applying successively all the operations R of the molecular point group to the reference local coordinate $\xi_{\sigma^*}{}^{f^*}$ and by weighting each term by the character of R in $\Gamma(a)$.

(20) This theorem is proved by A. C. Albrecht in the Appendix A of ref 15a using a method previously outlined by E. P. Wigner (see E. P. Wigner, "Group Theory," Academic Press, New York, N. Y., 1959, Chapters 11 and 12).

(21) Interaction with the degenerate component a is only considered since the contribution from the b component is identical.

(22) The matrix elements between the χ's may be developed in terms of the ψ's (and then in terms of the ϕ's) using the rules given by L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, New York, N. Y., 1966, p 530.

Table V. Transition Densities $\rho_{nk}(p)$ in Terms of the Components $\rho(i)$ and Value of the Corresponding Integrals I_1^R and I_2^U (in eV/Å)

State $\|n\rangle$	State $\|k\rangle$	Transition density $\rho_{nk}(p)$	I_1^R	I_2^U
B_{1u}	E_{1ub}	$-0.2686(T_1 + T_3) + 1.1028T_2$	1.1030	3.1700
B_{2u}	E_{1ua}	$1.1028(T_1 + T_3) - 0.2686T_2$	−1.1784	2.2837
B_{1u}	$E_{2ga\delta}$	$0.3003(S_l + S_3) - 0.8121S_2$	−1.1992	−0.8622
B_{2u}	$E_{2gb\delta}$	$-0.8121(S_1 + S_3) + 0.3003S_2$	0.0903	−2.4824
$\sqrt{2}E_{1ua}$	$E_{2gb\delta}$	$0.4243(S_1 + S_3) - 1.1490S_2$	−1.6967	−1.2212

are shown in Table V together with the values of the integrals $I_{\sigma*}{}^{f*}$. Knowing the integrals $I_{\sigma*}{}^{f*}$ we are in a position to apply eq 12 to the couples of states $|n\rangle$, $|k\rangle$ and the vibrations Q of interest (see for example eq A6 in Appendix A). Table VI shows fo rvarious $|n\rangle$, $|k\rangle$, and Q the values of the *square* of the matrix element $h_{nk}(Q)$ which appears in the numerator of (3). In addition, this table gives the values of the complete expression 3 (without the −1 factor) using the state energies of Table I.[23]

Table VI. Value of the Expressions $|\langle k|(\partial H/\partial Q)_0|n\rangle|^2/(E_k{}^0 - E_n{}^0)$ Involved in the Study of the B_{1u}, B_{2u}, and E_{1u} Excited States of Benzene

Couple ($\|n\rangle$, $\|k\rangle$)	Vibration Q	$h_{nk}{}^2(Q)$, eV^2 Å^{-2}	$h_{nk}{}^2(Q)/E_k{}^0 - E_n{}^0$, eV Å^{-2}
$\|n\rangle = {}^3B_{1u}$	ν_{18},6	0.250	0.242
$\|k\rangle = {}^3E_{1u}$	ν_{15},7	0.060	0.058
	ν_{16},8	3.157	3.065
	ν_{17},9	0.183	0.177
$\|n\rangle = {}^3E_{1u}$	ν_{18},6	1.307	1.221
$\|k\rangle = {}^3B_{2u}$	ν_{15},7	0.017	0.016
	ν_{16},8	0.759	0.709
	ν_{17},9	~0	~0
$\|n\rangle = {}^3B_{1u}$	ν_{12},18	0.039	0.017
$\|k\rangle = {}^3E_{2g\delta}$	ν_{13},19	0.289	0.126
	ν_{14},20	0.274	0.119
$\|n\rangle = {}^1B_{2u}$	ν_{12},18	~0	~0
$\|k\rangle = {}^1E_{2g\delta}$	ν_{13},19	0.757	0.230
	ν_{14},20	0.288	0.087
$\|n\rangle = \sqrt{2}\,{}^3E_{1u}$	ν_{12},18	0.078	0.061
$\|k\rangle = {}^3E_{2g\delta}$	ν_{13},19	0.579	0.456
	ν_{14},20	0.549	0.432

Using the results displayed in Table VI we may first check the validity of the third selection rule (the so-called "spatial localization" rule). As expected the e_{2g} vibrations 7 and 9 (using Wilson's numbering) give almost negligible matrix elements in the coupling of the states ${}^3B_{1u}$ and ${}^3E_{1u}$ on one hand, ${}^3B_{2u}$ and ${}^3E_{1u}$ on the other. In these two cases the active vibrations are e_{2g} 6 and 8. In the three other coupling schemes, however, the e_{1u} vibrations 19 and 20 give comparable matrix elements. This result disagrees with the expected predominance of the vibration e_{1u} 19. Although the two vibrations 19 and 20 are assigned different descriptions (Table II), it turns out that the carbon atom displacements in each actually do not differ greatly (see Table III, *f*, ref 17) so their similar importance is not surprising.

Our results also remove the ambiguity between the two vibrations 6 and 8. The most efficient vibration in the process of stabilizing the ${}^3B_{1u}$ vertically excited state is undoubtedly the 1595-cm^{-1} CC stretching vibration 8 whereas the ${}^3B_{2u}$ triplet state is predominantly mixed with the ${}^3E_{1u}$ state *via* vibration 6. In his paper on the electronic structure of cyclic polyenes having the general formula $C_{4n+2}H_{4n+2}$ Moffitt[24] defined even and odd perturbations respectively as those which connect atomic orbital basis functions on carbon atoms whose numbering differs by even (including zero) and odd integers. A CC stretching vibration (e_{2g} 8, for example) is "odd" whereas a carbon bending vibration (e_{2g} 6) is a smaller odd-type perturbation which contains even terms as well. Table V shows that the predominant term in the transition density B_{1u},E_{1u} is T_2, which involves "odd" interactions between neighboring carbon atoms. This perfect match between the odd ν_8 vibration and the (mainly) odd B_{1u},E_{1u} transition density[25] explains the very active role of the e_{2g} 8 vibration in the stabilization of the lowest triplet state ${}^3B_{1u}$. Table V shows also that the transition density B_{2u},E_{1u} is mainly even (T_1,T_3). The interaction of these dominant transition densities with the small "even" part of the bending vibration 6 and of the (smaller) odd transition density T_2 with the small odd part of the bending vibration explains the fact that e_{2g} 6 is the most active vibration in the B_{2u} case (though much less than e_{2g} is in the B_{1u} case).

The only remaining problem to be investigated is the influence of the degeneracy of the e_{2g} vibration 8 on the potential energy surface E of the lowest triplet state (${}^3B_{1u}$). If the two components of the vibration are called Q_a and Q_b, what are the characteristics of the surface $E(Q_a,Q_b)$ in the vicinity of the vertically excited point?

III. Potential Energy Surface $E(Q_a,Q_b)$ of the ${}^3B_{1u}$ State of Benzene

The e_{2g} 8 vibration renders the doubly degenerated ${}^3E_{1u}$ state Jahn–Teller unstable and, in addition, couples the ${}^3E_{1u}$ states with the ${}^3B_{1u}$ state which lies 1 eV below. The effect of the E_{1u} Jahn–Teller instability on the B_{1u} state may be studied by perturbation theory,[26] but we shall use here the method of Longuet-Higgins.[27] We may adopt for the wavefunction of B_{1u} a real form ψ_0 (energy E_0) and for those of E_{1u} the two complex conjugate forms ψ_1 and ψ_2 (energy E_1). These functions are supposed to be orthogonal. In the same

---

[23] Alternately, one could use the state energies given by D. R. Kearns, *J. Chem. Phys.*, 36, 1608 (1962), but the *relative* magnitude of the various terms would not change appreciably.

[24] W. Moffitt, *ibid.*, 22, 320 (1954).

[25] More precisely, the integrals I_1^R and I_2^U associated with T_2 have the same sign and this fact remains after inclusion of the contributions of T_1 and T_3 (see Table V). On the other hand, the coefficients $\xi_1{}^R(8)$ and $\xi_2{}^U(8)$ also have the same sign (eq A5 of Appendix A). The two contributions add together to give a large matrix element $h_{B_{1u},E_{1u}}(8)$.

[26] G. Fisher and G. S. Small, *J. Chem. Phys.*, 56, 5934 (1970).

[27] H. C. Longuet-Higgins, *Advan. Spectrosc.*, 2, 249 (1961). The method used here is an extension of the method outlined in paragraph IX of this paper. The perturbation treatment 26 has been used to verify our results.

way we define the two "complex" vibrations

$$Q_1 = Q_a + iQ_b = \rho e^{i\phi} \qquad (15)$$

$$Q_2 = Q_a - iQ_b = \rho e^{-i\phi} \qquad (16)$$

Since the double degeneracy of the E irreducible representations in benzene is basically due to the C_3 axis (simply called C here) we suppose that the ψ and Q have the property that ($\omega = \exp(2\pi i/3)$)

$$C\psi_0 = \psi_0;\ C\psi_1 = \omega\psi_1;\ C\psi_2 = \omega^*\psi_2 \qquad (17)$$

$$CQ_1 = \omega Q_1;\ CQ_2 = \omega^* Q_2 \qquad (18)$$

Denoting by H' the Hamiltonian of the molecule including distortions, we may express its wavefunctions as linear combinations of the ψ_i (i = 0, 1, 2). By the variational principle the required coefficients and the associated electronic potentials E would then be the eigenvectors and eigenvalues of the matrix

$$\begin{vmatrix} H'_{00} & H'_{01} & H'_{02} \\ H'_{10} & H'_{11} & H'_{12} \\ H'_{20} & H'_{21} & H'_{22} \end{vmatrix} \qquad (19)$$

The matrix elements $H'_{ij} = \int \psi_i H' \psi_j \mathrm{d}g$ (i, j = 0, 1, 2; dg represents the integration over the electronic coordinates) are expanded in powers of the normal coordinates Q_1 and Q_2.

$$H'_{ij} = E_i\delta_{ij} + \sum_{\nu} Q_\nu \alpha_{ij} + {}^1/_2\sum_{\mu\nu} Q_\nu Q_\mu \beta_{ij} + \cdots \quad (\nu, \mu = 1, 2) \qquad (20)$$

The electronic potential E of the B_{1u} state will be calculated through the third order in ρ. That is, the diagonal elements in (19) have to be evaluated to the third order whereas the off-diagonal elements need only to be determined to the second order. On the other hand, both sides of eq 20 must behave the same way under C. The diagonal matrix elements are invariant under C; we may therefore write, taking, for example, $i = j = 0$

$$H'_{00} = E_0 + \beta_{00}Q_1Q_2 + {}^1/_6\gamma_{00}(Q_1^3 + Q_2^3) = E_0 + \beta_{00}\rho^2 + {}^1/_3\gamma_{00}\rho^3 \cos 3\phi \qquad (21)$$

If we now consider, for example, the off-diagonal matrix element H'_{01} ($i = 0\ j, = 1$) the left-hand side of (20) is multiplied by ω under C and so has to be the right side.

$$H'_{01} = \alpha_{01}Q_1 + {}^1/_2\beta_{01}Q_2^2 = \alpha_{01}\rho e^{i\phi} + {}^1/_2\beta_{01}\rho^2 e^{-2i\phi} \qquad (22)$$

Using these expressions, the three eigenvalues of (19) are given by

$$E_0(B_{1u}) = E_0 + A\rho^2 + B\rho^3 \cos 3\phi \qquad (23)$$

$$E_1(E_{1u}) = E_1 - C\rho + D\rho^2(1 - F\cos 3\phi) \qquad (24)$$

$$E_2(E_{1u}) = E_1 + C\rho + D\rho^2(1 + F\cos 3\phi) \qquad (25)$$

when the A, B, C, D and F are functions of the parameters α, β, and γ. One has to remember that these expressions are only valid for *small* values of ρ, the value ρ = 0 corresponding to the vertically excited state.

The ${}^3B_{1u}$ potential energy surface displays two characteristics. In the first place the coefficient A is given by (26) where β_{00} corresponds to the second-order

$$A = \beta_{00} - 2\alpha_{01}^2/(E_1 - E_0) \qquad (26)$$

diagonal element $\langle n|(\partial^2 H/\partial Q^2)_0|n\rangle$ (see formula 2) which has not been considered in our analysis and α_{01} to the *large* off-diagonal element $h_{kn}(Q)$ with n = ${}^3B_{1u}$, k = ${}^3E_{1u}$, and Q = e_{2g} 8 (see Table VI). A is certainly negative and, therefore, the B_{1u} vertically excited state is stabilized by the vibrationally induced mixing with the E_{1u} states. In the second place, the stabilization is not uniform. This is due to the third order term which readily shows that the steepest stabilization paths arise when ϕ = 0, $2\pi/3$ and $4\pi/3$ if B is negative, when $\phi = \pi/3$, π, $5\pi/3$ if B is positive.[28] The values $\phi = 2m\pi/3$ (m = 0, 1, 2) correspond to "elongated" geometries of benzene (two long and four short bonds) whereas the values $\phi = (2m + 1)\pi/3$ (m = 0, 1, 2) correspond to "compressed" structures (two short and four long bonds).[29,30] The alternation of "elongated" and "compressed" structures when ϕ varies from 0 to 2π is represented in Figure 5, ref 29. This alternation has also been studied by semiempirical methods. These methods require the knowledge of the bond length dependence of π-electron energies. Two approximate formulas are available (a) the Lennard-Jones (LJ) or harmonic approximation[31] and (b) the exponential dependence of Longuet-Higgins and Salem (LHS).[32] The nature of the energetically lowest configuration depends upon the sign of the second derivative $\beta''(r)$ of the π-electron resonance energy $\beta(r)$ with distance.[33] In the LJ approximation $\beta''(r)$ is positive and *nonquinoidal* structures are favored. Indeed Liehr, using the LJ approximation, found that the nonquinoidal structure (two long bonds in the 1,2 and 4,5 positions, our "elongated" benzene) is 505 cm^{-1} more stable than the "compressed" quinoidal structure (two short bonds in 1,2 and 4,5).[29] In the LHS approximation $\beta''(r)$ is negative and the *quinoidal* structures are favored. de Groot and van der Waals,[34] using the LHS approximation and assuming D_{2h} distortions, found that the quinoidal form is 520 cm^{-1} more stable than the nonquinoidal structure. At the present time it is therefore impossible to decide if the B_{1u} state is quinoidal (compressed) or nonquinoidal (elongated).

In conclusion we may classify the "active" vibrations for the B_{1u} triplet state of benzene in two groups: (a) the doubly degenerate e_{2g} 8 vibration which is probably a stabilizing vibration distorting the hexagonal free molecule into a D_{2h} "elongated" or compressed" structure and (b) the e_{1u} (19, 20), a_{2g} (3) and b_{2g} (4, 5) which, depending upon the corresponding diagonal second-order term, might slightly stabilize the vertically excited species, but more certainly are simply associated with flat parabolic energy curves. Due to this soft energy variation these vibrations are particularly well

---

(28) The coefficient B is made up of three contributions and its sign cannot be predicted easily.

(29) A. D. Liehr, *Z. Naturforsch. A*, **16**, 641 (1961).

(30) L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, New York, N. Y., 1966, p 473.

(31) J. E. Lennard-Jones, *Proc. Roy. Soc., Ser. A*, **158**, 280 (1937).

(32) H. C. Longuet-Higgins and L. Salem *ibid.*, **251**, 172 (1959).

(33) W. D. Hobey and A. D. McLachlan, *J. Chem. Phys.*, **33**, 1695 (1960).

(34) M. S. de Groot and J. H. van der Waals, *Mol. Phys.*, **6**, 545 (1963).

adapted to accommodate extrinsic perturbations such as the small steric constraints at a crystalline site.

IV. Comparison with the Experimental Results

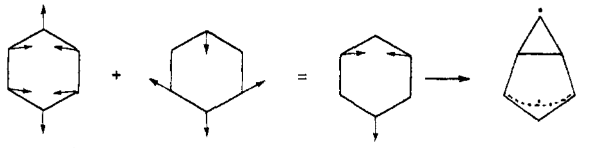
Most of our knowledge concerning the distortions in the $^3B_{1u}$ and $^1B_{2u}$ excited states of benzene comes from solid state experiments where the benzene molecule (or isotopic benzene) is diluted in a host crystal. In such an environment, the ground-state molecule itself displays slight deviations from the high D_{6h} symmetry. X-Ray studies[35a] show that the difference in the magnitude of the interatomic CC distances amounts to 0.005 Å (0.4%) and in the angles to 1° 14′ (0.8%).[35b] The carbon atoms are not coplanar, their out-of-plane shift being 0.0013 Å. These intermolecular perturbations on the molecular force field of the *ground state* also shift nondegenerate vibrations in the infrared spectrum of isotopic modifications of benzene having lower than D_{3h} symmetry.[36]

The crucial question of the intrinsic or extrinsic nature of the excited state distortions is carefully detailed in the very interesting paper of Nieman and Tinti. This question is not yet solved and we will simply recall some prominent experimental facts which are directly related to the results obtained in the preceding sections of this paper.

The conspicuous role of the e_{2g} 8 vibration in the properties of the lowest B_{1u} triplet is clearly indicated by the absorption and emission spectra. The ground state e_{2g} 8 mode at 1596 cm^{-1} is shifted to 250 cm^{-1} in the singlet triplet absorption spectrum.[4b] van der Waals, *et al.*, have indeed shown that this mode, which is involved in the vibronic coupling with the E_{1u} states, may decrease in frequency to as much as a third of its value in the absence of coupling. (Inclusion of higher order terms would further reduce the frequency.[4c]) In the emission spectra at low temperatures, where only ground-state vibrations appear, the most active vibration in the phosphorescence spectrum of C_6H_6 is also the e_{2g} 8 mode at 1596 cm^{-1}.[4a] If we now consider the equilibrium geometry of the $^3B_{1u}$ state, the endor experiments[4d] show that, in a crystalline environment, the only symmetry possessed by this triplet state is a center, in agreement with the C_i site symmetry of the crystal. The molecule also has two long bonds and therefore a nonquinoidal "elongated" structure. (This corresponds to a negative value of B; see section III.) Furthermore, (1) the nonplanarity of the molecule is obvious and (2) the detection of three proton endor lines shows that the six protons occur in three measurably inequivalent pairs of equivalent hydrogen atoms. These two facts may be related, the first one to b_{2g} (4, 5) and the second to a_{2g} (3) distortions, distortions which have been shown to be the best candidates in accommodating extrinsic perturbations. Shortly speaking, one might consider the e_{2g} 8 distortion as an intrinsic distortion of the triplet state modified—magnified or even demagnified—by the crystalline environment and the other b_{2g} (4, 5) and a_{2g} (3) displacements as arising from extrinsic perturbations. The intrinsic character of the e_{2g} 8 distortion seems to be confirmed by the fact that the B_{1u} singlet state (S_2) of benzene can isomerize directly into Dewar benzene.[37] An "elongated" structure of this singlet (see Figure 5 in ref 29) would make this symmetry-allowed process easier. Basically, the appearance of this isomerization in the second excited singlet is due to the fact that the internal conversion efficiency from upper electronic states to S_1 (which is normally unity for most organic molecules) is significantly lower than one for benzene and methylbenzenes.[38]

If we turn our attention towards the lowest excited *singlet* state $^1B_{2u}$ we see that now the prominent role is played by the e_{2g} 6 vibration, in agreement with the results of section II. This mode (606 cm^{-1}) is the most active fluorescence vibration but the absorption experiments[39] show that its frequency is only shifted to 521 cm^{-1} in the $^1B_{2u}$ state (whereas the e_{2g} 8 mode is shifted from 1596 to 1470 cm^{-1}), a small displacement compared to the shift of e_{2g} 8 in $^3B_{1u}$. On the other hand, the splittings in the fluorescence spectrum due to isotopic substitution of benzene are only about one-eight as large as those in the phosphorescence implying that the distortion in the $^3B_{1u}$ state is larger than that in the $^1B_{2u}$ state,[4a] but here again, it does not seem possible to decide if the distortion is intrinsic or extrinsic. Table VI indicates in addition that the e_{1u} 19 vibration which couples the $^1B_{2u}$ state with the $^1E_{2g}$ states might be important. It is interesting to point out that the superposition of the 6 and 19 vibrations may readily give the "biradical" (I) which is considered to be the precursor[40] in the formation of 1,3 adducts in the photoaddition of monoolefins to benzene[41] or in the formation of benzvalene in the irradiation of 1,2,4- or 1,3,5-tri-*tert*-butylbenzenes.[42]

Scheme I



I

If we now briefly consider the *second triplet state* E_{1u} it appears that, in addition to its interaction with the $^3B_{1u}$ state, this state interacts with the doubly degenerate $^3E_{2g\delta}$ state. (The symbol δ means the (+) combination of the wavefunctions χ; see Table IV. This (+) combination is slightly lower in energy than the (−) combination γ.[43]) The symmetry-adapted transition densities ρ_{nk} ($|n\rangle$ = $^3E_{1u}$, $|k\rangle$ = $^3E_{2g}$) are

$$(1/\sqrt{2}\{{}^3E_{1ua}{}^3E_{2ga\delta} \pm {}^3E_{1ub}{}^3E_{2gb\delta}\} \qquad (27a)$$

$$(1/\sqrt{2})\{{}^3E_{1ua}{}^3E_{2gb\delta} \pm {}^3E_{1ub}{}^3E_{2ga\delta}\} \qquad (27b)$$

---

(35) (a) E. G. Cox, D. W. J. Cruickshank, and J. A. S. Smith, *Proc. Roy. Soc., Ser. A*, 247, 1 (1958); (b) V. L. Broude and M. J. Onoprienko, *Opt. Spectrosc.* (*USSR*), 10, 332 (1961).

(36) E. R. Bernstein and G. W. Robinson, private communication to G. C. Nieman and D. S. Tinti; see ref 4a.

(37) D. Bryce-Smith, A. Gilbert, and D. A. Robinson, *Angew. Chem., Int. Ed. Engl.*, 10, 745 (1971).

(38) C. L. Braun, S. Kato, and S. Lipsky, *J. Chem. Phys.*, 39, 1645 (1963).

(39) F. M. Garforth, C. K. Ingold, and H. G. Poole, *J. Chem. Soc.*, 491 (1948).

(40) D. Bryce-Smith and H. C. Longuet-Higgins, *Chem. Commun.*, 593 (1966).

(41) (a) K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, 88, 2066 (1966); (b) D. Bryce-Smith, A. Gilbert, and B. H. Orger, *Chem. Commun.*, 512 (1966).

(42) K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, 87, 4004 (1965).

(43) J. N. Murrell and K. L. McEwen, *J. Chem. Phys.*, 25, 1143 (1956).

Due to our choice of $^3E_{1u}$ and $^3E_{2g}$ wavefunctions (see Table IV) the transition densities corresponding to b_{1u} and b_{2u} ($E_{1u} \times E_{2g} = B_{1u} + B_{2u} + E_{1u}$) vibrations vanish whereas, for example, the (+) combination in eq 27a is simply

$$\sqrt{2}\,{}^3E_{1ua}\,{}^3E_{2ga\delta} \qquad (28)$$

Table VI shows that the two e_{1u} (19,20) vibrations significantly couple the two states $^3E_{1u}$ and $^3E_{2g\delta}$ and might possibly provide a further stabilization of the $^3E_{1u}$ states.

V. Conclusion

The aim of this paper was mainly to propose a set of *qualitative* rules which would be of some use in selecting the vibrations which might possibly stabilize a vertically excited species. Such rules may be helpful for the purpose of rapidly determining the geometry and the reactivity of an excited species but also as a guide in the choice of the distortions worthy of consideration in an *ab initio* SCF calculation. In addition, we have given the sequence of steps to be followed in the *quantitative* evaluation of the off-diagonal second order terms. Even though this sequence may seem rather awkward its practical use is straightforward.

The limitations of our treatment of the $^3B_{1u}$ state of benzene are (a) the neglect of the diagonal second-order term and (b) the nature of the wavefunctions we used. More generally, the study of excited states is very often done using the virtual orbitals from the ground-state calculation. The field terms in the Hamiltonian for a virtual orbital are due to all N electrons while the appropriate field for the excited state orbital ψ_j contains only interactions with $N - 1$ electrons. (The simplest possible way to take this into account would be for example to take ψ_j to be the solution of

$$(h + 2J_c - K_c + J_i \pm K_i)\psi_j = \epsilon_j\psi_j \qquad (29)$$

where (+) is for the singlet state and (−) for the triplet state and where the orbitals in J_c and K_c (the closed-shell Coulomb and exchange operators) and J_i and K_i are assumed to have their ground-state forms. This is called the frozen core[44] or IVO[45] approximation and corresponds to variationally adjusting ψ_j in the open-shell Hartree–Fock wavefunction for the excited state.) On the other hand, the *state* wavefunctions have to include the necessary configuration interactions (this is particularly important for example in the case of the E_{2g}, E_{1u} coupling[15b] where the b_{1u} and b_{2u} vibrations could then be activated). However, such a mixing of ASMO wavefunctions does not restrict the treatment since, ultimately, all transition densities may always be developed in terms of the components $\rho(i)$.

Acknowledgments. The author wishes to express his sincere gratitude to Professors J. C. D. Brand and N. C. Baird for their kind interest in this work and for numerous stimulating discussions.

Appendix A

The reducible representations $\Gamma(\xi^f) = \Gamma(R)$, $\Gamma(U)$, $\Gamma(Z)$, are first decomposed in terms of the irreducible representations of the D_{6h} point group.

$$\begin{aligned}\Gamma(R) &= A_{1g} + E_{2g} + B_{1u} + E_{1u}\\ \Gamma(U) &= A_{2g} + E_{2g} + B_{2u} + E_{1u} \qquad (A1)\\ \Gamma(Z) &= B_{2g} + E_{1g} + A_{2u} + E_{2u}\end{aligned}$$

Let us now consider, for example, the matrix element $h_{nk}(Q)$ with $|n\rangle = {}^3B_{1u}$, $|k\rangle = {}^3E_{1u}$ and $Q = \nu_{16},8$ (the 1595 cm^{-1} vibration of benzene). Since $\Gamma(B_{1u}) \times \Gamma(E_{1u}) = \Gamma(E_{2g})$ it is clear that both triple products $\Gamma(B_{1u}) \times \Gamma(E_{1u}) \times \Gamma(R)$ and $\Gamma(B_{1u}) \times \Gamma(E_{1u}) \times \Gamma(U)$ contain Γ_1 only one time. Therefore $h_{B1u,E1u}(8)$ may be ultimately expressed in terms of two basic integrals $I_{\sigma^*}{}^R$ and $I_{\sigma^*}{}^U$, respectively located for convenience at the atoms $\sigma^* = 1$ and 2, and simply dubbed $I_1{}^R$ and $I_2{}^U$.

To obtain the complete expansion of h we first determine the quantities η^2, using for this purpose Table VII, ref 17. Considering the R displacements and the component a of the doubly degenerate irreducible representation e_{2g}, we have

$$\xi_1{}^R(e_{2ga}) = x,\ \xi_2{}^R(e_{2ga}) = -x/2 \qquad (A2)$$

and therefore $\eta_{2.R}(1,R,e_{2ga}) = -{}^1/_2$. It is straightforward to obtain

$$\sum_{\sigma=1}^{6} \eta_{\sigma.R}{}^2(1,R,e_{2ga}) = 3 \qquad (A3)$$

and following an identical procedure for the U displacements

$$\sum_{\sigma=1}^{6} \eta_{\sigma,U}{}^2(2,U,e_{2ga}) = 4 \qquad (A4)$$

The last step is now to simply read the coefficient $\xi_{\sigma^*}{}^{f^*}(e_{2ga}, 8)$ in Table IIIe, ref 17.

$$\begin{aligned}\xi_1{}^R(8) &= -0.06905\\ \xi_2{}^U(8) &= -0.12221\end{aligned} \qquad (A5)$$

We are now in position to apply (12), leaving $I_1{}^R$ and $I_2{}^U$ as parameters to be determined.

$$h_{B1u.E1u}(8) = (-0.06905) \times 3 \times I_1{}^R + (-0.12221) \times 4 \times I_2{}^U \qquad (A6)$$

Appendix B

When the component density $\rho(i)$ is ultimately developed in atomic terms (such as $\phi_1{}^2$, $\phi_1\phi_2$, . . .) as illustrated in Figure 1 it appears that $I_{\sigma^*}{}^{f^*}(i)$ is made of terms whose basic structure is

$$\langle\phi_i|h(R_1) \text{ or } h(U_2)|\phi_j\rangle \qquad (B1)$$

The detailed expression of the operators h is not necessary here (for further details see ref 16b.) They come from the development of the derivatives in (14). Except for the vanishing integrals $\langle\phi_1|h(R_1)$ or $h(U_1)|\phi_1\rangle$ the quantities (B1) may be expressed as

$$\langle\phi_i|h(R_1) \text{ or } h(U_2)|\phi_j\rangle = \cos(d, R_1 \text{ or } U_2) \times I(d) \times S \qquad (B2)$$

In this expression d and cos (d, R_1 or U_2) are respectively the length and the direction cosine (with respect to R_1 or U_2) of a vector **d** whose definition in the various cases is given in Table VII. The integral $I(d)$ may be I_0 or I_1 depending on the cases (see Table VII). The overlap integral S is called I_2 by Liehr. These three

---

[44] H. Lefebvre-Brion, C. Moser, and R. Nesbet, *J. Mol. Spectrosc.*, 13, 418 (1964).

[45] W. J. Hunt and W. A. Goddard III, *Chem. Phys. Lett.*, 3, 414 (1969).

Table VII. Definition of the Vector **d** and of the Integrals $I(d)$ and S for the Various Cases Encountered in the Evaluation of the Integrals $I_{\sigma^*}{}^{f^*}(i)$.

Integral	**d**	$I(d)$	S
$\langle\phi_i\|h_1\|\phi_i\rangle$ $i \neq 1$	Joins atoms 1 and i	$I_0(d)$	1
$\langle\phi_i\|h_1\|\phi_1\rangle$	Joins atoms 1 and i	$I_1(d)$	1
$\langle\phi_i\|h_1\|\phi_j\rangle$ $i, j \neq 1$	Joins atom 1 to the center of the transition density $\phi_i\phi_j$ (midway point between i and j)	$I_0(d)$	$I_2(d')$, d' being the distance between atoms i and j

basic integrals I_i ($i = 0, 1, 2$) have been tabulated for various distances d and are independent of the particular benzene problem.[16b]

Table VIII. Integrals $I_1{}^R$ and $I_2{}^U$ for the Nine Transition Densities $\rho(i)$ (Values are Given in eV/Å)

	T_1	T_2	T_3
$I_1{}^R$	−1.3681	0.7867	0.4912
$I_2{}^U$	2.8290	3.5924	0.1171
	S_1	S_2	S_3
$I_1{}^R$	0.1396	1.6629	0.3640
$I_2{}^U$	3.8926	2.5394	0.1033
	V_1	V_2	V_3
$I_1{}^R$	−0.9490	0	0.1060
$I_2{}^U$	0	0.7908	0

The integrals $I_{\sigma^*}{}^{f^*}(i)$ for the nine transition densities $\rho(i)$ are summarized in Table VIII.

Mechanism of the Chemiluminescent Reaction of Certain Alkyl Halides with Electrogenerated Aromatic Hydrocarbon Radical Anions[1,2]

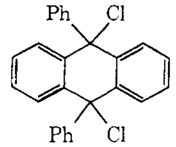
Theodore M. Siegel and Harry B. Mark, Jr.*

Contribution from the Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221.

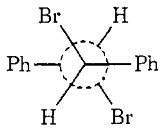
Received May 10, 1972

Abstract: The electroreduction of a variety of polycyclic, aromatic hydrocarbons (R) in the presence of either 9,10-dichloro-9,10-dihydro-9,10-diphenylanthracene ($DPACl_2$) or 1,2-dibromo-1,2-diphenylethane ($DPEBr_2$) was found to result in intense luminescence. In each instance the spectrum of this electrochemiluminescence (ecl) was virtually identical with the singlet emission spectrum of the aromatic hydrocarbon. In general, the efficiency of this luminescence was found to be greater than that of the normal radical anion–radical cation ecl of the same hydrocarbon. It was also found that when two or more aromatic hydrocarbons were present in the same solution only the emission spectrum of the lower singlet energy species could be observed regardless of which aromatic radical anion was being generated at the electrode. Experiments with mixed systems containing fluoranthene, which did not exhibit ecl by itself with $DPEBr_2$, and several aromatic hydrocarbons which have lower triplet energies than fluoranthene, resulted in only fluoranthene singlet emission. These experiments indicated the excited singlet is generated directly upon electron transfer from $R\cdot^-$ rather than through a triplet–triplet annihilation reaction. The following general mechanism was found consistent with the observed experimental results: $R + e \rightleftarrows R\cdot^-$ (1), $R\cdot^- + AX_2 \rightleftarrows R + AX_2\cdot^-$ (2), $AX_2\cdot^- \rightarrow AX\cdot + X^-$ (3), $R\cdot^- + AX\cdot \rightleftarrows {}^1R^* + AX^-$ (4), $R + AX\cdot \rightleftarrows R\cdot^+ + AX^-$ (5), $AX^- \rightarrow A + X^-$ (6), $R\cdot^- + R\cdot^+ \rightarrow {}^1R^* + R$ (7), ${}^1R^* \rightarrow R + h\nu$ (8). (AX_2 represents the alkyl halide.) The efficiency of the $DPACl_2$ systems and the behavior of the fluoranthene mixed systems indicate that the excited singlet can arise by both reaction 4 and reactions 5 plus 7.

Recently, preliminary observations concerning the electrochemiluminescence, ecl, obtained upon the reaction of electrogenerated aromatic hydrocarbon radical anions, $R\cdot^-$, of a variety of aromatic hydrocarbons (in various nonaqueous solvents) with either 9,10-dichloro-9,10-dihydro-9,10-diphenylanthracene ($DPACl_2$) or 1,2-dibromo-1,2-diphenylethane ($DPEBr_2$) have been reported.[2] For the $DPACl_2$ system it was found that the intensity of the observed emission of the aromatic hydrocarbon, DPA, was unexpectedly about two orders of magnitude greater than that observed for the more commonly reported ecl obtained upon the annihilation of the electrogenerated radical anions and radical cations of 9,10-diphenylanthracene (DPA).[3] Also, it was reported that for solutions con-



$DPACl_2$



meso-$DPEBr_2$

---

[1] This research was supported by a grant from the National Science Foundation, No. GP-27216.

[2] A preliminary communication concerning this phenomenon has been published: T. M. Siegel and H. B. Mark, Jr., *J. Amer. Chem. Soc.*, **93**, 6281 (1971).

[3] (a) The intensity of the 9,10-diphenylanthracene (DPA) singlet emission obtained for the reaction of $DPACl_2$ with electrogenerated $DPA\cdot^-$ was compared with $DPA\cdot^-/DPA\cdot^+$ annihilation ecl using the same solvent-supporting electrolyte system. Square wave voltages (−0.1 to −2.0 V for the $DPACl_2$ case, +1.4 to −2.0 V for the DPA case) of the same frequency were employed and integrated light intensities during negative pulses were compared. (b) For detailed discussion of radical cation–radical anion annihilation ecl, see A. J. Bard, K. S. V. Santhanam, S. A. Cruser, and L. R. Faulkner in "Fluorescence," G. G. Guibault, Ed., Marcel Dekker, New York, N. Y., 1967, pp 627–651; D. M. Hercules in "Physical Methods of Organic Chemistry," 4th ed., Part II, A. Weissberger and B. Rossiter, Ed., Academic Press, New York, N. Y., 1971; A. Zweig, *Advan. Photochem.*, 6, 425 (1968).