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PI-ELECTRON FORCES BETWEEN CONJUGATED DOUBLE BOND MOLECULES*

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ABSTRACT

The long-range forces between large conjugated double bond molecules are highly directional and anomalously strong. This is due to pi-electrons moving freely from one end of the conjugated double bond system to the other, making the molecule behave like an extended oscillator. All three types of dispersion forces: $\sigma\sigma$ $\sigma\pi$ and $\pi\pi$ are calculated for ethylene, acetylene, and the higher polyenes. In addition the $\pi\pi$ interaction energy is calculated for benzene. The free electron molecular orbitals are used for the π electrons and products of these orbitals are approximated by "transition monopoles". Our treatment of the σ electrons and the use of the transition monopoles were suggested by London[1]. The resulting energies are easy to calculate and easy to interpret. The $\pi\pi$ energy is proportional to the square of the energy of interaction of two real transition dipoles (real in the sense of the monopoles being separated by a finite distance). Previously, Coulson and Davies[2] calculated the $\pi\pi$ interaction energy using LCAO orbitals and evaluating all integrals accurately; however, because of the complicated nature of their calculations it was not possible for them to obtain a simple understanding of the variation of the energy with the orientations of the molecules. The values we obtain for the $\pi\pi$ energy agree with those of Coulson and Davies except for a scale factor, our results being uniformly 3/5 smaller. Such a scale factor corresponds to an adjustable parameter in either the Coulson and Davies treatment or ours. The $\sigma\pi$ interaction energy has never previously been considered. For long polyenes, for which a simplified treatment is given, the $\pi\pi$ energy is larger than the $\sigma\pi$ which is larger than that of the $\sigma\sigma$. In the appendix, the free electron model is used to calculate the pi-electron contribution to the polarizability and excellent agreement is obtained with the LCAO calculations of Davies[3].

1. F. London, J. Chem. Phys. 46, 305 (1942)
2. C. A. Coulson and P. L. Davies, Trans. Faraday Soc. 48, 777 (1952)
3. P. L. Davies, Doctor's Dissertation, King's College, University of London (1949)

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I. Introduction.

The long-range dispersion forces between large conjugated double bond molecules are highly directional and very strong. This is due to pi-electrons moving freely from one end of the conjugate double bond system to the other, making the molecule behave like an extended oscillator. These forces may help to explain some of the anomalous effects of steroids and other conjugated double bond molecules of biological importance. Also the pi-bond forces are important in the interaction between aromatic molecules and are partially responsible for the non-zero angles between the planes of neighboring molecules in an aromatic crystal. In this paper, a simple treatment is developed for calculating and explaining these forces.

In contrast to the pi-electrons, molecules contain sigma-electrons which are localized in specific chemical bonds or within the inner shells of the atoms. Corresponding to the two types of electrons, the dispersion energy can be divided into three terms:

$$E^{(dis)} = E_{\sigma\sigma} + E_{\sigma\pi} + E_{\pi\pi} \qquad (1.1)$$

Here $E_{\sigma\sigma}$ is that part which arises from the interaction between the σ- electrons of the two molecules; $E_{\pi\pi}$ corresponds to the interaction between the π-electrons of the two molecules; and $E_{\sigma\pi}$ gives the energy of interaction of the σ- electrons of one molecule with the π- electrons of the other molecule and vice versa. London[1] developed an excellent method for calculating the $E_{\sigma\sigma}$. It is the purpose of the present paper to describe a simple method for calculating $E_{\sigma\pi}$ and $E_{\pi\pi}$.

We use free electron molecular orbitals for the pi-electrons and approximate products of these orbitals by "transition monopoles". The resulting

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1. F. London, J. Chem. Phys. 46, 305 (1942)

values of $E_{\sigma\pi}$ and $E_{\pi\pi}$ are easy to calculate and easy to interpret. For example, to a good approximation in most cases, the values of $E_{\pi\pi}$ are proportional to the square of the energy of interaction of two real transition dipoles (real in the sense that the monopoles are separated by a finite distance). We are indebted to London[1] for the notion of transition monopoles and their use in connection with dispersion energy. Our results for $E_{\pi\pi}$ are to be compared with the calculations of Coulson and Davies[2] who used LCAO orbitals and evaluated all of the integrals accurately without using the monopole approximation. Because of the complications of their calculations it was not possible for them to obtain a simple understanding of the variation of the interaction energy with the orientations of the molecules. However, our values of $E_{\pi\pi}$ agree with those of Coulson and Davies except for a scale factor (our values being uniformly 3/5 of the Coulson and Davies numbers). Such a scale factor corresponds to an adjustable parameter in either treatment. Prior to the present paper, there were no evaluations of $E_{\sigma\pi}$. For long polyenes $E_{\sigma\pi}$ is by no means negligible and as a matter of fact: $E_{\pi\pi} > E_{\sigma\pi} > E_{\sigma\sigma}$. For ethylene, acetylene, and the lower polyenes: $E_{\sigma\sigma} > E_{\sigma\pi} > E_{\pi\pi}$. In the case of ethylene and acetylene where the complete dispersion energy is compared with experimental data, the agreement is satisfactory in the sense that it is quite comparable with the ratio of theoretical to observed values for simple molecules in which there are no complications due to pi-electrons.

In the appendix, the free electron molecular orbitals are used to calculate the contributions of the pi-electrons to the polarizability of polyenes. Excellent agreement is obtained with the LCAO calculations of Davies[3] and the results seem to be consistent with experimental data. This agreement serves as a check on the accuracy of the free electron molecular orbitals as used in the present paper.

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2. C. A. Coulson and P. L. Davies, Trans. Faraday Soc. 48, 777 (1952).
3. P. L. Davies, Doctor's Dissertation, King's College, University of London (1949).

In retrospect we feel that the simple free electron molecular orbitals, as used here, give roughly the right values for $E_{\sigma\pi}$ and $E_{\pi\pi}$. However, the fact that the orbitals have been taken as one-dimensional rather than as three-dimensional has its limitations. For example, consider the interaction of two ethylene molecules in which the C=C axes of the two molecules are parallel. With the present free electron orbitals, the value of $E_{\pi\pi}$ is independent of the orientation of the planes containing the hydrogen atoms. Such a result is obviously erroneous. An obvious improvement would result by replacing our present one-dimensional molecular orbital, $\phi_n(x)$, (see Eq. 2.29) by three-dimensional free electron molecular orbitals such as

$$\Phi_n = y\,\phi_n(x)\exp\left(-\alpha\sqrt{y^2+z^2}\right) \tag{1.2}$$

Here x is the cartesian coordinate along the axis of the conjugated double bond system and y and z are coordinates perpendicular to this axis. The parameter α, would of course be adjustable. The use of three-dimensional free-electron orbitals would not appreciably increase the amount of work required and at the same time it should improve the comparison of the dispersion energy for different orientations of the molecules.

II. Method.

In dealing with dispersion forces, the molecules are sufficiently separated to make a perturbation calculation correct. Furthermore, it is not necessary to antisymmetrize the wave function for the two molecule system, since we may assume that there is no overlapping between the wave functions of different molecules. We may then employ a simple product of the electronic wave functions of the individual molecules as our zero order wave function for the system and treat the potential energy of interaction as the perturbation. Actually, the only part of the potential energy of interaction which affects the dispersion energy are the electron-electron interaction terms[1]

$$\varphi_e = \sum_{a=1}^{n_a} \sum_{b=1}^{n_b} \frac{e^2}{r_{ab}} \tag{2.1}$$

Here the n_a electrons designated by the subscript "a" are in molecule "A" and the n_b electrons designated by the subscript "b" are in molecule "B". Furthermore r_{ab} is the instantaneous separation between electrons "a" and "b". If Ψ_o^A and Ψ_i^A are the electronic wave functions of molecule A in its ground state and i-th excited state respectively; if Ψ_o^B and Ψ_j^B are the wave functions of molecule B in its ground state and j-th excited state respectively; and if E_o^A, E_i^A, E_o^B, and E_j^B are the energies of these molecular states respectively, the usual second order perturbation theory gives the energy of dispersion:

$$E^{(dis)} = -\sum_{l,k}{}' \frac{\left(\int \Psi_o^A \Psi_o^B \varphi_e \Psi_l^A \Psi_k^B d\tau^A d\tau^B\right)^2}{E_l^A + E_k^B - E_o^A - E_o^B} \tag{2.2}$$

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1. The matrix components which give the greatest contribution to the dispersion energy correspond to one electron in each of the two molecules making a transition. For such two electron transitions, only the electron-electron terms in the perturbation potential as given by Eq. (2.1) lead to non-vanishing matrix components. However, it should be pointed out that one electron transitions do give small but finite contributions to the dispersion energy. For one electron transitions, it is the electron-other-nucleus terms in the perturbation potential which are important. In the present paper we ignore the small contributions from one electron transitions.

Here the prime over the summation sign indicates that those states with either ℓ or k equal zero are excluded. The conjugate complex of the wave function does not appear in Eq. (2.2) since the wave functions in the following development are taken to be real. Furthermore, for present purposes it is convenient to suppose that the wave function for each of the molecules can be taken as a Slater determinant made up of molecular orbitals, ϕ^A and ϕ^B. The orbitals are numbered by a subscript according to their energy, ϵ. Thus ϕ_1 is the orbital of lowest energy, ϵ_1; ϕ_2 has the next higher energy, ϵ_2; etc. the molecules which we shall consider have an even number of electrons $n = 2N$, and their ground state is a singlet. To the approximation of the present treatment, there are no singlet-triplet transitions so that the only excited states which need be considered are themselves singlets. Thus the wave function for the ground state of a molecule is a Slater determinant with two electrons in each of the molecular orbitals: ϕ_1, ϕ_2; ...., ϕ_i, ..., ϕ_N. The wave functions of the excited states which we consider are the same as the wave function of the ground state except that one of the two electrons in the i-th molecular orbital has been promoted to the j-th molecular orbital. Such a transition is denoted by the symbol (i, j). In terms of these orbitals the ground state of the molecule A is the Slater determinant,

$$\Psi_0^A = \frac{1}{\sqrt{(2N_A)!}} \begin{pmatrix} \phi_i^A & \phi_i^A & \phi_1^A & \phi_1^A & \cdots & \phi_{i-1}^A & \phi_{i-1}^A & \phi_{i+1}^A & \phi_{i+1}^A & \cdots & \phi_{N_A}^A & \phi_{N_A}^A \\ \alpha & \beta & \alpha & \beta & \cdots & \alpha & \beta & \alpha & \beta & \cdots & \alpha & \beta \end{pmatrix} \quad (2,3)$$

Here the i-th orbitals are moved from their normal positions in the determinant in order to facilitate the algebraic manipulations which follow. Similarly the excited state ℓ of the molecule corresponding to the transition (i, j) has as its wave function the difference of two Slater determinants,

$$\Psi_\ell^A = \frac{1}{\sqrt{2(2N_A)!}} \left[\begin{pmatrix} \phi_j^A & \phi_i^A & \phi_1^A & \phi_1^A & \cdots & \phi_{i-1}^A & \phi_{i-1}^A & \phi_{i+1}^A & \phi_{i+1}^A & \cdots & \phi_{N_A}^A & \phi_{N_A}^A \\ \alpha & \beta & \alpha & \beta & \cdots & \alpha & \beta & \alpha & \beta & \cdots & \alpha & \beta \end{pmatrix} + \begin{pmatrix} \phi_i^A & \phi_j^A & \phi_1^A & \phi_1^A & \cdots & \phi_{i-1}^A & \phi_{i-1}^A & \phi_{i+1}^A & \phi_{i+1}^A & \cdots & \phi_{N_A}^A & \phi_{N_A}^A \\ \alpha & \beta & \alpha & \beta & \cdots & \alpha & \beta & \alpha & \beta & \cdots & \alpha & \beta \end{pmatrix} \right] \quad (2,4)$$

Now integrating the product of Ψ_0^A and Ψ_ℓ^A over all of the coordinate and spin space for electrons 1, 2, ... (a-1), (a+1), ... $2N_A$ leads to the result,

$$\int \Psi_0^A \Psi_\ell^A \, d\tau_1 d\tau_2 \cdots d\tau_{a-1} d\tau_{a+1} \cdots d\tau_{2N_A} =$$

$$\frac{1}{\sqrt{2}\, n_A} \phi_i^A(a) \phi_j^A(a) \left(\alpha(a)\alpha(a) + \beta(a)\beta(a) \right) \tag{2.5}$$

Since all of the electrons are equivalent, substitution of Eqs. (2.1) and (2.5) into Eq. (2.2) leads to the following expression for the dispersion energy in terms of the molecular orbitals.

$$E^{(dis)} = -\sum_{i=1}^{N_A} \sum_{j=N_A+1}^{\infty} \sum_{i'=1}^{N_B} \sum_{j'=N_B+1}^{\infty} \frac{\left(i i' \middle| \frac{2e^2}{r_{ab}} \middle| j j' \right)^2}{(\epsilon_j^A - \epsilon_i^A) + (\epsilon_{j'}^B - \epsilon_{i'}^B)} \tag{2.6}$$

Here

$$\left(i i' \middle| \frac{2e^2}{r_{ab}} \middle| j j' \right) = \int \int \phi_i^A(a) \phi_j^A(a) \frac{2e^2}{r_{ab}} \phi_{i'}^B(b) \phi_{j'}^B(b) \, d\tau_a \, d\tau_b \tag{2.7}$$

where the integrations are taken over the coordinate space of electrons a and b.

In a molecule containing conjugate double bonds there are two kinds of molecular orbitals. First, there are the pi-orbitals in which the electron is not localized in either a particular bond or on a particular atom but rather, the pi-electron is free to roam over the length of the conjugate double bond system. The other electrons in the molecules, which we shall loosely refer to as σ - electrons, are localized in either individual atoms or chemical bonds. The usual treatment of dispersion energy applies to interactions between the sigma type electrons in one molecule and the sigma electrons of the second molecule, $E_{\sigma\sigma}$. In calculating $E_{\sigma\sigma}$, the terms e^2/r_{ab} are expanded in inverse powers of R, the separation between the molecules. This expansion converges rapidly provided that the linear dimensions of the electron orbitals are small compared to the separation between the molecules. For pi-electrons, the size of the orbitals are comparable with the size of the molecules, so that this type of expansion would not converge rapidly when the molecules are separated by one or two molecular diameters. Thus a somewhat different treatment is required in the calculation of the interaction of the pi-electrons of one molecule with either the pi-electrons of the other molecule, $E_{\pi\pi}$, or the sigma electrons of the other molecule, $E_{\sigma\pi}$.

The London Approximation

F. London[2] suggested a method for approximating the matrix elements of Eq. (27) corresponding to either pi-pi or sigma-pi electron interactions in which cases the usual treatment (expansion of e^2/r_{ab} in inverse powers of R)

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2. F. London, J. Chem. Phys. 46, 305 (1942)

does not apply for the values of the intermolecular separation which have the greatest physical interest. First, he considered the matrix element to be electrostatic energy of interaction between two electrical charge distributions:

$$\rho^A_{ij}(a) = \sqrt{2}\, e\, \phi^A_i(a)\, \phi^A_j(a)$$

$$\rho^B_{i'j'}(b) = \sqrt{2}\, e\, \phi^B_{i'}(b)\, \phi^B_{j'}(b) \tag{2.8}$$

The matrix component can then be written:

$$\left(i'i' \middle| \frac{e^2}{r_{ab}} \middle| jj'\right) = \iint \rho^A_{ij}(a) \frac{1}{r_{ab}} \rho^B_{i'j'}(b)\, d\tau_a\, d\tau_b \tag{2.9}$$

These charge distributions are negative in some regions of space and positive in others, depending upon the signs of the molecular orbitals. Thus the nodal surfaces of $\rho^A(ij)$ divides all space into a number of cells or zones k. Similarly the nodal surfaces of $\rho^B(i'j')$ divides space into a set of cells or zones labelled k'. The matrix component can then be written in the form:

$$\left(i i' \middle| \frac{2e^2}{r_{ab}} \middle| jj'\right) = \sum_k \sum_{k'} \int_{(k)} \int_{(k')} \rho^A_{ij}(a) \frac{1}{r_{ab}} \rho^B_{i'j'}(b)\, d\tau_a\, d\tau_b \tag{2.10}$$

Throughout each cell, the charge distribution maintains either a positive or negative sign. London now defines a set of monopoles corresponding to the charge distributions. The charges on the monopoles are

$$g^A_{ij}(k) = \int_{(k)} \rho^A_{ij}(a)\, d\tau_a$$

$$g^B_{i'j'}(k') = \int_{(k')} \rho^B_{i'j'}(b)\, d\tau_b \tag{2.11}$$

The monopoles are considered to be located at the points $\underline{R^A_{ij}}(k)$ and $\underline{R^B_{i'j'}}(k')$ given by the first moments of the charge distributions within their

respective zone,

$$\underline{R}^{A}_{ij}(k) = \int_{(k)} \underline{r}_a \, \rho^{A}_{ij}(a) \, d\tau_a \Big/ g^{A}_{ij}(k)$$

$$\underline{R}^{B}_{i'j'}(k') = \int_{(k')} \underline{r}_b \, \rho^{B}_{i'j'}(b) \, d\tau_b \Big/ g^{B}_{i'j'}(k') \tag{2.12}$$

The London approximation then consists of replacing the individual integrals of Eq. (2.1) by the electrostatic interaction of the corresponding monopoles,

$$\left(ii' \middle| \frac{2e^2}{r_{ab}} \middle| jj' \right) = \sum_{k} \sum_{k'} g^{A}_{ij}(k) \, g^{B}_{i'j'}(k') \frac{1}{\left| \underline{R}^{A}_{ij}(k) - \underline{R}^{B}_{i'j'}(k') \right|} \tag{2.13}$$

Since the London approximation forms the basis for the present calculations, it is important to examine its validity. Let us consider one of the integrals of Eq. (2.10)

Take $R^{A}_{ij}(k)$ to be the center of the coordinate system for electron "a" and $R^{B}_{i'j'}(k')$ be the center of the coordinate system for electron "b". Let the Z-axis for both coordinate systems point in the line from $\underline{R}^{A}_{ij}(k)$ towards $\underline{R}^{B}_{i'j'}(k')$. Then (r, θ, ϕ) are the spherical coordinates of electron "a" and (r', θ', ϕ') are the spherical coordinates of electron "b" in the two separate reference frames. Then we can expand $1/r_{ab}$ in a bipolar expansion:[3]

$$\frac{1}{r_{ab}} = \sum_{n=0}^{\infty} \sum_{n'=0}^{\infty} \sum_{m=-n_<}^{+n_<} B^{|m|}_{n,n'}(r, r'; \mathcal{R}) \, P^{|m|}_{n}(\cos\theta) \, P^{|m|}_{n'}(\cos\theta') \, e^{im(\phi - \phi')} \tag{2.14}$$

Here the $B^{m}_{n,n'}$ are the bipolar expansion coefficients, and $\mathcal{R} = \left| \underline{R}^{A}_{ij}(k) - \underline{R}^{B}_{i'j'}(k') \right|$.

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3. See "Molecular Theory of Gases and Liquids" by J.O. Hirschfelder, C.F. Curtiss, and R.B. Bird (John Wiley, 1954), p. 834, Eq. (12.1-28).

If the k-th zone of molecule A and the k'-th zone of molecule B do not overlap or if $r = r' < \mathcal{R}$, the bipolar expansion coefficients have the very simple form,

$$B^{|m|}_{n,n'}(r, r'; \mathcal{R}) = \frac{(-1)^{n'+m} \cdot (n+n')!}{(n+|m|)!\,(n'+|m|)!} \frac{r^n r'^{n'}}{\mathcal{R}^{n+n'+1}} \tag{2.15}$$

In this case, the integral of Eq. (2.10) becomes:

$$\int_{(k)}\int_{(k')} \rho^A_{ij}(a) \frac{1}{r_{ab}} \rho^B_{i'j'}(b)\, d\tau_a\, d\tau_b = \sum_{\ell=0}^{\infty} \frac{\ell!}{\mathcal{R}^{\ell+1}} K_\ell \tag{2.16}$$

where the K_ℓ are a set of constants given by

$$K_\ell = \sum_{n=0}^{\ell} S_n S'_{\ell-n} \tag{2.17}$$

$$+ \sum_{m=1}^{\ell/2 \text{ or } (\ell-1)/2} 2(-1)^m \sum_{n=m}^{\ell-m} \left[L_{nm} L'_{(\ell-n),m} + W_{nm} W'_{(\ell-n),m} \right]$$

The summation going to $\ell/2$ or $(\ell-1)/2$ means to take whichever of the two is an integer. The constants in this equation are the integrals,

$$S_n = \frac{1}{n!} \int_{(k)} r^n P_n(\cos\theta)\, \rho^A_{ij}(k)\, d\tau_a \tag{2.18}$$

$$S'_{\ell-n} = \frac{(-1)^{\ell-n}}{(\ell-n)!} \int_{(k')} r'^{(\ell-n)} P_{(\ell-n)}(\cos\theta')\, \rho^B_{i'j'}(k')\, d\tau_b \tag{2.19}$$

$$L_{nm} = \frac{1}{(n+m)!} \int_{(k)} r^n P^m_n(\cos\theta) \cos m\phi\, \rho^A_{ij}(k)\, d\tau_a \tag{2.20}$$

$$L'_{\ell-n} = \frac{(-1)^{(\ell-n)}}{(\ell-n+m)!} \int_{(k')} r'^{(\ell-n)} P^m_{(\ell-n)}(\cos\theta')\cos m\phi' \rho^B_{i'j'}(k')\, d\tau_b \tag{2.21}$$

$$W_{n,m} = \frac{1}{(n+m)!} \int_{(k)} r^n P^m_n(\cos\theta) \sin m\phi\, \rho^A_{ij}(k)\, d\tau_a \tag{2.22}$$

$$W'_{\ell-n,m} = \frac{(-1)^{\ell-n}}{(\ell-n+m)!} \int_{(k')} r'^{(\ell-n)} P^m_{(\ell-n)}(\cos\theta')\sin m\phi' \rho^B_{i'j'}(k')\, d\tau_b \tag{2.23}$$

Thus $S_o = q^A_{ij}(k)$, $S'_o = q^B_{i'j'}(k')$ and because of the location of the origins of the two coordinate systems, $S_1 = S'_1 = L_{11} = L'_{11} = W_{11} = W'_{11} = 0$. As a result the leading terms of Eq. (2.13) are

$$\iint_{(k)(k')} \rho^A_{ij}(a) \frac{1}{r_{ab}} \rho^B_{i'j'}(b)\, d\tau_a\, d\tau_b$$

$$= \frac{q^A_{ij}(k)\, q^B_{i'j'}(k')}{R} + \frac{0}{R^2} + \frac{2\left[q^A_{ij}(k)\, S'_2 + q^B_{i'j'}(k') S_2\right]}{R^3} + \cdots \tag{2.24}$$

The London approximation therefore consists of taking the first term of this infinite series. The second term in the series vanishes because of the location of the monopoles. The third term, which gives the first corrections to the London approximation depends on the second moment of the charge distributions. The series converges rapidly and the London approximation is accurate provided that R is large compared to the sum of the effective radii of the two charge distributions in the particular zones being considered.

The Coulson-Davies Method.

Instead of using the London approximation, Coulson and Davies[4] expressed the molecular orbitals for pi-electrons as linear combinations of the 2p atomic orbitals,

$$\chi_\alpha(a) = \sqrt{\frac{c^5}{\pi}}\; Z_a \exp(-c r_{\alpha a}) \tag{2.25}$$

Here $r_{\alpha a}$ is the distance of the "a"-th electron from the α-th atom (carbon atoms in the problems considered here); the Z-axis is taken perpendicular to the axis of the molecule so that Z_a is the coordinate of the a-th electron in this direction; and "c" is a constant which for carbon has the value $1.625/a_o$ where a_o is the first Bohr radius. In a linear conjugated polyene with 2N carbon atoms, there are 2N molecular orbitals that can be formed by linear combinations of the above atomic orbitals:

$$\phi_j(a) = \sum_{\alpha=1}^{2N} \sqrt{\frac{2}{2+1}}\; \sin\left(\frac{j\alpha\pi}{2N+1}\right) \chi_\alpha(a) \tag{2.26}$$

$$j = 1, 2, \ldots, 2N$$

The one electron energies associated with these orbitals are

$$\epsilon_j = 2\gamma \cos\left(\frac{j\pi}{2N+1}\right) \qquad j = 1, 2, \ldots, 2N \tag{2.27}$$

Here γ is the "resonance integral" which Coulson estimated empirically to have the value -40 kcal/mole.

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4. C.A.Coulson (Proc.Roy.Soc. 169A, 413 (1939)) developed the molecular orbitals given in Eqs. (2.22) and (2.23) and C.A.Coulson and P.L.Davies (Tr. Faraday Soc. 48, 777 (1952)) applied them to problems involving pi-bond intermolecular forces.

Using the molecular orbitals of Eq. (2.26) the matrix elements of Eq. (2.7) which occur in the dispersion energy become linear combinations of integrals of the type,

$$\iint \chi^{A}_{\alpha}(a)\,\chi^{B}_{\beta}(b)\,\frac{2e^{2}}{r_{ab}}\,\chi^{A}_{\alpha'}(a)\,\chi^{B}_{\beta'}(b)\,d\tau_a\,d\tau_b \qquad (2.28)$$

Because of the exponential decrease of the atomic orbitals with distance, the only integrals which have appreciable size correspond to α' and β' either coinciding with or being next door neighbors to α and β respectively. Furthermore, since the size of the atomic ortibals is small compared to the separation, R, between the molecules, it is possible to evaluate integrals of the type of Eq. (2.[illegible]) in the same manner as is usually done for the matrix elements of Eq. (2.7) in the case of sigma-sigma electron interactions.

The FEM orbitals

Recently a different type of molecular orbital has been introduced which is more satisfactory for the calculations that follow because of its greater simplicity. Moreover, it is in no way inferior for predicting the energies of excited states and contains no constants which require empirical determination.

This approach is known as the free electron model approximation. The delocalization of the pi-electrons is taken literally and they are regarded as free to move in a one dimensional box which extends along the skeleton of the conjugated carbon atoms. Thus the skeleton for a benzene molecule is essentially a circle around the benzene ring and for a linear polyene it is a line along the carbon network. Whenever there is a free endpoint such as the terminal carbon atom of a linear polyene, the "box" is extended an additional bond length, or the carbon-carbon distance.

For linear polyenes with N conjugated double bonds, the free electron model molecular orbitals are given by:

$$\phi_n = \sqrt{\frac{2}{\ell}}\,\sin\frac{n\pi x}{\ell}, \quad n = 1, 2, \cdots 2N \qquad (2.29)$$

with the energies:

$$\epsilon_n = \frac{n^2 h^2}{8 m \ell^2} \quad , \quad n = 1, 2, \cdots, 2N \tag{2.30}$$

Here ℓ is the length of the one dimensional box and is equal to $(2N + 1)D$, where D is the carbon-carbon bond length, which we take to be 1.4 Å , x is the distance along the electron path measured from one end and m is the mass of the electron.

Because of the simplicity of the free-electron orbitals it is possible to substitute them directly into the matrix components of Eq. (2.7) and evaluate the resulting integrals directly. However, these integrals can be expressed in a simple closed mathematical form only if the conjugate double bond molecules are parallel and colinear. For any other orientation, the resulting answers can only be expressed in numerical form. Thus, it is desirable to use the London approximation which leads to very simple results with very simple interpretations.

The total energy of dispersion is the sum of contributions from the sigma-sigma, pi-pi, and sigma-pi electron interactions:

$$E = E_{\sigma\sigma} + E_{\pi\pi} + E_{\sigma\pi} \tag{2.31}$$

The treatment of these three types of interactions are quite distinct.

Determination of $E_{\sigma\sigma}$

A satisfactory treatment of $E_{\sigma\sigma}$ has been given independently by

London and by de Boer[5] in terms of the polarizabilities of the chemical bonds, in the parallel and perpendicular directions, $\alpha_{\parallel}$ and $\alpha_{\perp}$ respectively. The mean bond polarizability is $\alpha = (\alpha_{\parallel} + 2\alpha_{\perp})/3$ and $\delta = (\alpha_{\parallel} - \alpha_{\perp})/\alpha$ is a measure of the electrical assymetry of the bond. In the London or de Boer treatment, the energy of the principal transition ($h\nu_{\parallel}$ or $h\nu_{\perp}$ depending whether the perturbation is parallel or perpendicular to the bond) plays an important role. We assume that this energy is equal to the bond ionization potential, I. Thus $I = h\nu_{\parallel} = h\nu_{\perp}$. For calculational purposes we assume that $I = 100{,}000\ \mathrm{cm}^{-1} = 12.4$ e.v. With these assumptions, the London or de Boer treatment gives:

$$E_{\sigma\sigma} = -\frac{I}{8}\sum_{k_A,\ell_B}\frac{\alpha_{k_A}\alpha_{\ell_B}}{R_{AB}^{6}}\left[\begin{array}{l} 6 \\ +\delta_{k_A}\left[3\cos^2\theta_{k_A}-1\right] \\ +\delta_{\ell_B}\left[3\cos^2\theta_{\ell_B}-1\right] \\ +\delta_{k_A}\delta_{\ell_B}\left[\begin{array}{l}\left(\sin\theta_{k_A}\sin\theta_{\ell_B}\cos(\phi_{k_A}-\phi_{\ell_B})\right)^2 \\ -2\cos\theta_{k_A}\cos\theta_{\ell_B} \\ -\cos^2\theta_{k_A}-\cos^2\theta_{\ell_B}\end{array}\right]\end{array}\right] \tag{2.32}$$

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5. F. London, J. Phys. Chem. 46, 305 (1942); J. de Boer, Physica 9, 363 (1942); also J.O. Hirschfelder, C.F. Curtiss, and R.B. Bird, "Molecular Theory of Gases and Liquids", (John Wiley, 1954), p. 969.

Here the k_A and ℓ_B signify the chemical bonds in molecules A and B respectively and the summation is to be taken over all of the chemical bonds. The angles θ_{k_A} and θ_{ℓ_B} are the angles which the bonds make with a radius vector joining the centers of the two molecules. The ϕ_{k_A} and ϕ_{ℓ_B} are the angles which the projection of these bonds make with a plane passing through the radius vector. Values of the bond polarizabilities have been estimated by Denbigh[6]. For the aliphatic C-C bond and for the C-H bond:

	α 10^{25} cm^3	δ
$(C\text{-}C)_{aliph}$	6.4	2.90
(C-H)	6.5	0.32

(2.33)

If the two molecules are held at a fixed separation between their centers and rotated through all orientations, we obtain for the averaged value of $E_{\sigma\sigma}$,

$$\bar{E}_{\sigma\sigma} = -\frac{3}{4}\frac{I}{R^6}\sum_{k_A,\ell_B}\alpha_{k_A}\alpha_{\ell_B} \tag{2.34}$$

The values of the $E_{\sigma\sigma}$ as calculated by Eq. (2.12) are probably not accurate to within a factor of two but it is difficult to see how substantial improvements can be made in the formulation without making detailed calculations using accurate wave functions for each of the molecular species. This short summary of the treatment of the $E_{\sigma\sigma}$ is included here since we need to know values of the $E_{\sigma\sigma}$ in order to compare the calculated with the experimental values for the dispersion energy.

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6. K. G. Denbigh, Trans. Faraday Soc. 36, 936 (1940)

Determination of $E_{\pi\pi}$

In seeking the simplest determination of $E_{\pi\pi}$, we used the "free-electron" model for the molecular orbitals in Eq. (2.4). Then, we used the London method of approximating the resulting integrals. The combination of the two approximations lead to comparatively simple expressions for $E_{\pi\pi}$ which are easy to interpret. Our results are to be compared with the more accurate calculations of Coulson and Davies[4] who used good molecular orbitals and accurately evaluated their integrals.

Determination of $E_{\sigma\pi}$

The sigma-pi electron interactions have not been considered by previous investigators as a source of intermolecular energy. It is therefore necessary to develop a new approach. Consider the interaction between the sigma electrons in molecule A and the pi-electrons in molecule B. The sigma electrons are localized in chemical bonds. For the pi-electrons we use the London notion of monopoles. The matrix components of Eq. (2.7) then become the sum of interaction integrals between the n_p sigma electrons in the p-th chemical bond of molecule A with the k-th monopole in molecule B. The matrix components of Eq. (2.7) then become:

$$\left(ii' \middle| \frac{2e^2}{r_{ab}} \middle| jj'\right) = \sum_{\substack{p \\ \text{chemical bonds in A}}} \sum_{\substack{k \\ \text{monopoles in B}}} \sqrt{2}\, e \int \left[\phi_i^A(a)\, \phi_j^A(a)\right]_p \frac{q^B_{i'j'}(k)}{\left|\underline{r}_a - \underline{R}^B_{i'j'}(k)\right|} \qquad (2.35)$$

If the size of the chemical bond is small compared to the distance, R_{pk}, from the center of the p-th chemical bond of molecule A to the k-th monopole of molecule B, then $1/\left|\underline{r}_a - \underline{R}^B_{i'j'}(k)\right|$ can be expanded in inverse powers of R_{pk}. Let the z axis be the axis

of the chemical bond and let the center of the bond be the origin. Then the spherical coordinates of the electron "a" are (r_a, θ_a, ϕ_a). Similarly the spherical coordinates of the monopole are $(R_{pk}, \theta_{pk}, \phi_{pk})$ Then[7]

$$\frac{1}{|\underline{r}_a - \underline{R}^B_{ij}(k)|} = \frac{1}{R_{pk}} \sum_{n=0}^{\infty} \sum_{m=-n}^{n} \frac{(n-|m|)!}{(n+|m|)!} \left(\frac{r_a}{R_{pk}}\right)^n P_n^{|m|}(\cos\theta_a) P_n^{|m|}(\cos\theta_{pk}) e^{im(\phi_a - \phi_{pk})} \tag{2.36}$$

The leading terms of this expansion are:

$$\frac{1}{|\underline{r}_a - \underline{R}^B_{ij}(k)|} \tag{2.37}$$

$$= \frac{1}{R_{pk}} + \frac{r_a}{R^2_{pk}} \left[\cos\theta_a \cos\theta_{pk} + \sin\theta_a \sin\theta_{pk} \sin\phi_a \sin\phi_{pk} + \sin\theta \sin\theta_{pk} \cos\phi_a \cos\phi_{pk} \right] + \cdots$$

$$= \frac{1}{R_{pk}} + \frac{x_a X_{pk} + y_a Y_{pk} + z_a Z_{pk}}{R^3_{pk}} + \cdots$$

Since $\phi^A_i(a)$ is orthogonal to $\phi^A_j(a)$ when we substitute this expansion, Eq. (2.37), into Eq. (2.35), the term $1/R_{pk}$ does not contribute. However, the next term does not lead to vanishing integrals and it plays the leading role in the sigma-pi dispersion forces. Thus to a good approximation,

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7. "Molecular Theory of Gases and Liquids", Eq. (12.1-25), p. 842.

$$\left(ii' \middle| \frac{2e^2}{r_{ab}} \middle| jj'\right)$$

$$= \sum_{p,k} \frac{\sqrt{2}\, e\, g^{B}_{i'j'}(k)}{R^3_{pk}} \int \phi^A_i(a)\, \phi^A_j(a) \left[x_a X_{pk} + y_a Y_{pk} + z_a Z_{pk}\right] d\tau_a \tag{2.38}$$

Now the transition (i,j) is associated with a particular chemical bond p so that the x component of the transition dipole moment of the chemical bond is given by

$$(\mu_x(p))_{ij} = e \int \Psi^A_0 \Psi^A_\ell \left(\sum_{k=1}^{2N_A} x_k \right) d\tau_1 \cdots d\tau_N \tag{2.39}$$

Then making use of the equivalence of the electrons and Eq. (2.5) it follows that

$$(\mu_x(p))_{ij} = \sqrt{2}e \int \phi^A_i(a)\, \phi^A_j(a)\, x_a\, d\tau_a \tag{2.40}$$

The matrix components can therefore be written

$$\left(ii' \middle| \frac{2e^2}{r_{ab}} \middle| jj'\right)$$

$$= \sum_{p,k} \frac{g^{B}_{i'j'}(k)}{R^3_{pk}} \left[X_{pk} (\mu_x(p))_{ij} + Y_{pk} (\mu_y(p))_{ij} + Z_{pk} (\mu_z(p))_{ij} \right] \tag{2.41}$$

Now we must make use of the special properties of bond functions before substituting Eq. (2.41) back into Eq. (2.6). These properties are:

(1) Each transition $i \rightarrow j$ occurs in a particular chemical bond so that the summation over p in Eq. (2.41) is redundant.

(2) If a particular transition $i \rightarrow j$ has a transition dipole moment in the z-direction parallel to the bond, it cannot have a transition dipole moment in a direction perpendicular to the bond; and vice versa.

(3) The symbols i and j denote the sets of quantum numbers defining the state of the one electron bond orbital. These quantum numbers are quite

analogous to the set of four (n, ℓ, m, σ) defining the state of an electron in an atom. Here now the energy of the state depends on the quantum numbers corresponding to $n, \ell, |m|$.

Making use of these properties Eq. (2.5) becomes:

$$E_{\sigma_A \pi_B} = -\sum_{\substack{i,j \\ p}} \sum_{i',j'} \frac{\left[\sum_k \frac{g^B_{i'j'}(k)}{R^3_{pk}}\left[(\mu_x(p))_{ij} X_{pk} + (\mu_y(p))_{ij} Y_{pk}\right]\right]^2 + (\mu_z(p))^2_{ij}\left[\sum_k \frac{g^B_{i'j'}(k) Z_{pk}}{R^3_{pk}}\right]^2}{(\epsilon^A_j - \epsilon^A_i) + (\epsilon^B_{j'} - \epsilon^B_{i'})} \tag{2.42}$$

To reduce this summation still further, we note that[8] the cross-term $(\mu_x(p))_{ij}\,(\mu_y(p))_{ij}$ is proportional to $[\delta_{m_i, m_j+1} - \delta_{m_i, m_j-1}]$. Furthermore the denominator of Eq. (2.40) depends only on the absolute value of m_i and of m_j and in the summation both m_i and $-m_i$ as well as m_j and $-m_j$. On these accounts it follows that the cross-terms vanish and so

$$E_{\sigma\pi} = -\sum_{\substack{i,j \\ p}} \sum_{i',j'} \frac{\left(\sum_k \frac{g^B_{i'j'}(k)}{R^3_{pk}} X_{pk}\right)^2 (\mu_x(p))^2_{ij} + \left(\sum_k \frac{g^B_{i'j'}(k)}{R^3_{pk}(k)} Y_{pk}\right)^2 (\mu_y(p))^2_{ij}}{(\epsilon^A_j - \epsilon^A_i) + (\epsilon^B_{j'} - \epsilon^B_{i'})}$$

$$+ \left(\sum_k \frac{g^B_{i'j'}(k)}{R^3_{pk}(k)} Z_{pk}\right)^2 (\mu_z(p))^2_{ij} \tag{2.42}$$

Now let us assume that in molecule A there is only one principal transition in each chemical bond and that the energy of this transition is $\epsilon^A_j - \epsilon^A_i = I$, the ionization potential or roughly 100,000 cm^{-1} or 12.4 e.v. Also the parallel and perpendicular bond polarizabilities are[9]

8. H. Margenau, Rev. Mod. Phys. 11, 1 (1939), see discussion on p. 20.
9. See "Molecular Theory of Gases and Liquids", p. 889, Eq. (12.6-16a).

$$\alpha_{\perp}^{A}(p) = \frac{2(\mu_x(p))_{ij}^2}{I} = \frac{2(\mu_y(p))_{ij}^2}{I}$$

$$\alpha_{\parallel}^{A}(p) = \frac{2(\mu_z(p))_{ij}^2}{I} \tag{2.43}$$

Then, the dispersion forces between the sigma electrons of molecule A and the pi electrons of molecule B can be written in the form,

$$\sum_{\sigma_A \pi_B} = -\sum_{p}\sum_{i'j'} \frac{\left[\alpha_{\perp}\left\{\left[\sum_k \frac{q_{i'j'}^{B}(k)}{R_{pk}^3} X_{pk}\right]^2 + \left[\sum_k \frac{q_{i'j'}^{B}(k)}{R_{pk}^5} Y_{pk}\right]^2\right\} + \alpha_{\parallel}\left[\sum_k \frac{q_{i'j'}^{B}(k)}{R_{pk}^3} Z_{pk}\right]^2\right]}{2\left[1 + \frac{(\epsilon_{j'}^{B} - \epsilon_{i'}^{B})}{I}\right]} \tag{2.44}$$

The total sigma-pi interaction energy between the two molecules is then the sum of $E_{\sigma_A \pi_B}$ and $E_{\sigma_B \pi_A}$.

Monopoles for Linear Polyenes

The calculation of the monopoles for linear polyenes is easily carried out using the FEM orbitals of Eq. (2.24), assuming that the polyenes are truly linear and that all carbon-carbon bonds have the same length, 1.4 Å. For linear polyenes the charge density of the monopoles is given by Eq. (2.8)

$$\rho_{ij} = \frac{2^{3/2} e}{\ell} \sin\frac{i\pi x}{\ell} \sin\frac{j\pi x}{\ell} \tag{2.45}$$

This has nodes whenever x is either a multiple of ℓ/i or a multiple of ℓ/j. Thus the first monopole lies between $x = 0$ and $x = \ell/j$ and each of the other monopoles lie between successive nodes. If y_k is the x coordinate of the k-th node, then the strength of the k-th monopole is

$$q_{ij}(k) = \int_{y_{k-1}}^{y_k} \rho_{ij}\, dx \tag{2.46}$$

$$= \frac{\sqrt{2}\,\epsilon}{\pi} \left[\begin{array}{l} \frac{1}{(j-i)} \left[\sin\left(\frac{(j-i)\pi y_k}{\ell}\right) - \sin\left(\frac{(j-i)\pi y_{k-1}}{\ell}\right)\right] \\ - \frac{1}{(j+i)} \left[\sin\left(\frac{(j+i)\pi y_k}{\ell}\right) - \sin\left(\frac{(j+i)\pi y_{k-1}}{\ell}\right)\right] \end{array} \right]$$

And the location of the centroid of the k-th monopole $X_{ij}(k)$ is given by

$$X_{ij}(k)\, q_{ij}(k) = \frac{\sqrt{2}\,e}{\pi} \left[\begin{array}{l} \frac{\ell}{\pi(j-i)^2} \left[\cos\left(\frac{(j-i)\pi y_k}{\ell}\right) - \cos\left(\frac{(j-i)\pi y_{k-1}}{\ell}\right)\right] \\ - \frac{\ell}{\pi(j+i)^2} \left[\cos\left(\frac{(j+i)\pi y_k}{\ell}\right) - \cos\left(\frac{(j+i)\pi y_{k-1}}{\ell}\right)\right] \\ + \frac{1}{(j-i)} \left[y_k \sin\left(\frac{(j-i)\pi y_k}{\ell}\right) - y_{k-1} \sin\left(\frac{(j-i)\pi y_{k-1}}{\ell}\right)\right] \\ - \frac{1}{(j+i)} \left[y_k \left(\frac{(j+i)\pi y_k}{\ell}\right) - y_{k-1} \sin\left(\frac{(j+i)\pi y_{k-1}}{\ell}\right)\right] \end{array} \right] \tag{2.47}$$

The results for a few polyenes are given in Table 2.1. The notation (i,j) signifies that the monopoles are for the transition in which the excited state contains the j-th FEM MO in place of the i-th FEM MO in the ground state.

In each case the sum of the monopoles must be zero because of the orthogonality of the wave functions. The signs of the monopoles for a given transition may be changed simultaneously without affecting the result, since the quantity of significance is the square of the matrix element.

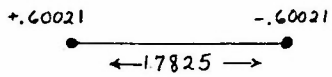
For a polyene with N double bonds, the transition (N, N + 1) represents the largest contribution and is the only one that is listed for hexatriene. We shall speak of such transitions as principal transitions.

Table 2.1 Monopoles for Linear Polyenes.

The numbers given above the lines are the strengths of the monopoles $q_{ij}(k)$ given in units of e. The numbers given below the lines are the distances in Å between the monopoles. The transitions (i, j) are given on the left hand side of this chart.

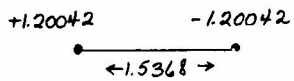
ETHYLENE

(1, 2)



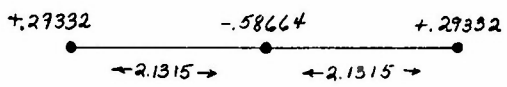
ACETYLENE

(1, 2)

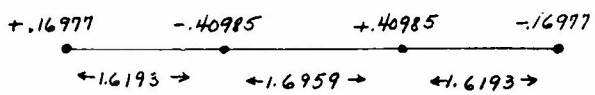


BUTADIENE

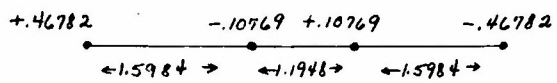
(1, 3)



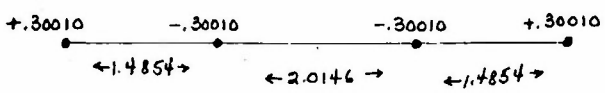
(1, 4)



(2, 3)

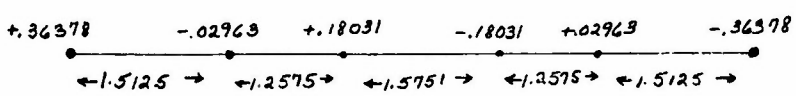


(2, 4)



HEXATRIENE

(3, 4)



III. Results.

A. Ethylene

Ethylene is the simplest example of a molecule containing pi-electrons. We shall now discuss the calculation of the dispersion energy for ethylene. We first consider the energy arising from the interaction of pi-electrons in one molecule with the pi-electrons in the other and shall compare the results with those obtained by Coulson and Davies who used the LCAO orbitals. Then we calculate the complete dispersion energy by taking account of the sigma-electrons as well as the pi-electrons, and we compare with the experimental data.

The qualitative behavior of the $E_{\pi\pi}$ interactions in ethylene are easy to understand in terms of Eqs. (2.6) and (2.13). According to Table 2.1 there is only one important transition in ethylene, (1, 2) and there are only two monopoles associated with this transition. These monopoles being equal in magnitude and opposite in sign correspond to a transition dipole having a dipole moment

$$\mu_{12} = q_{12}(1)\left[X_{12}(2) - X_{12}(1)\right] = 5.14 \quad \text{debye} \tag{3.1}$$

According to Eq. (2.30)

$$\epsilon_2 - \epsilon_1 = \frac{h^2}{8ml^2}(4-1) = 1.0244 \times 10^{-11} \text{ ergs} = 6.39 \text{ e.v.} \tag{3.2}$$

For separations R between the centers of the molecules large compared to the separation between the monopoles, Eq. (2.6) reduces to

$$E_{\pi\pi} = -\frac{G}{R^6}\left[-2\cos\theta_A\cos\theta_B + \sin\theta_A\sin\theta_B\cos(\phi_A - \phi_B)\right]^2 \tag{3.3}$$

where

$$G = \frac{\mu_{12}^4}{2(\epsilon_2 - \epsilon_1)} = 3.403 \times 10^{-11} \text{ (ergs } - \text{Å}^{-6}) \tag{3.4}$$
$$= 21.25 \text{ (e.v.} - \text{Å}^{-6})$$

and the angles θ_A and θ_B are the angles which the two molecules make with a radial vector joining their centers and ϕ_A and ϕ_B are the azimuthal angles which these molecules make with a plane passing through the radius vector.

At smaller separations Eq. (3.3) is not quite correct because the monopoles form a real dipole with a separation of 1.7825 Å between the charge elements as contrasted to an ideal dipole with no separation between the charge elements. The lack of ideality of the dipole-dipole interaction can be taken into account by introducing a function $\gamma(R, \theta_A, \theta_B, \phi_A, \phi_B)$ into the equation for $E_{\pi\pi}$,

$$E_{\pi\pi} = -\gamma \frac{G}{R^6}\left[-2\cos\theta_A \cos\theta_B + \sin\theta_A \sin\theta_B \cos(\phi_B - \phi_A)\right]^2 \quad (3.5)$$

The values of $\gamma(R, \theta_A, \theta_B, \phi_A, \phi_B)$ are calculated using Eq. (2.13) to compute values of $E_{\pi\pi}$ for different configurations. In the case of ethylene where there is only one principal transition, (1, 2) and only a single pair of monopoles Eq. (2.13) can be written in the simple form:

$$E_{\pi\pi} = -\frac{G}{R^4_{M_1M_2}}\left[\frac{1}{R_{M_1M_3}} + \frac{1}{R_{M_2M_4}} - \frac{1}{R_{M_1M_4}} - \frac{1}{R_{M_2M_3}}\right]^2 \quad (3.6)$$

where the $R_{M_iM_j}$ are the distances between the i-th and j-th monopoles as shown in Fig. (3.2); M_1 and M_2 being the monopoles on one molecule and M_3 and M_4 the monopoles of the other molecule. Thus the following results were obtained:

(a) <u>Parallel and Opposed.</u> $\begin{matrix} C = C \\ C = C \end{matrix} \quad \begin{matrix}\uparrow \\ d \\ \downarrow\end{matrix}$ (Å)

The results for this case can be summarized by the equation:

$$E_{\pi\pi} = -(21.25/d(\text{Å})^6)\ \gamma \text{ e.v.} \quad (3.7)$$

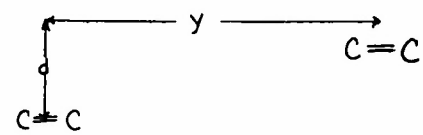
Here γ is a slowly varying function of the separation d (Å) which should approach a constant value at large separations. In Table 3.1 the present results (HH) are compared with those of Coulson and Davies (CD) who used LCAO orbitals. The values of $E_{\pi\pi}$ or of γ which Coulson and Davies calculate are uniformly 4/3 of our values (except for

the calculations at 50 Å separation).

Table 3.1, Ethylene Parallel and Opposed
Calculated Values of the Coefficient γ Defined by Equation (3.7)

d(Å)	γ_{HH}	γ_{CD}	γ_{HH}/γ_{CD}
4	0.760	1.009	1.328
8	0.929	1.245	1.340
10	0.955	1.280	1.340
15	0.981	1.318	1.344
20	0.988	1.315	1.331
50	1.000	1.079	1.079

(b) <u>Parallel and Displaced:</u>



For this case, $R^2 = y^2 + d^2$; $\cos\theta_A = \cos\theta_B = \frac{y}{R}$; and $\phi_A = \phi_B = 0$. Thus Eq. (3.5) can be written

$$E_{\pi\pi} = -\frac{21.25}{R^6(\text{Å})}\left(2 - 3\frac{d^2}{R^2}\right)^2 \gamma \text{ e.v.} \tag{3.8}$$

Comparing the values of $E_{\pi\pi}$ calculated from Eq. (2.13) and the expression for $E_{\pi\pi}$ of Eq. (3.8) we obtain the values of γ given in Table 3.2.

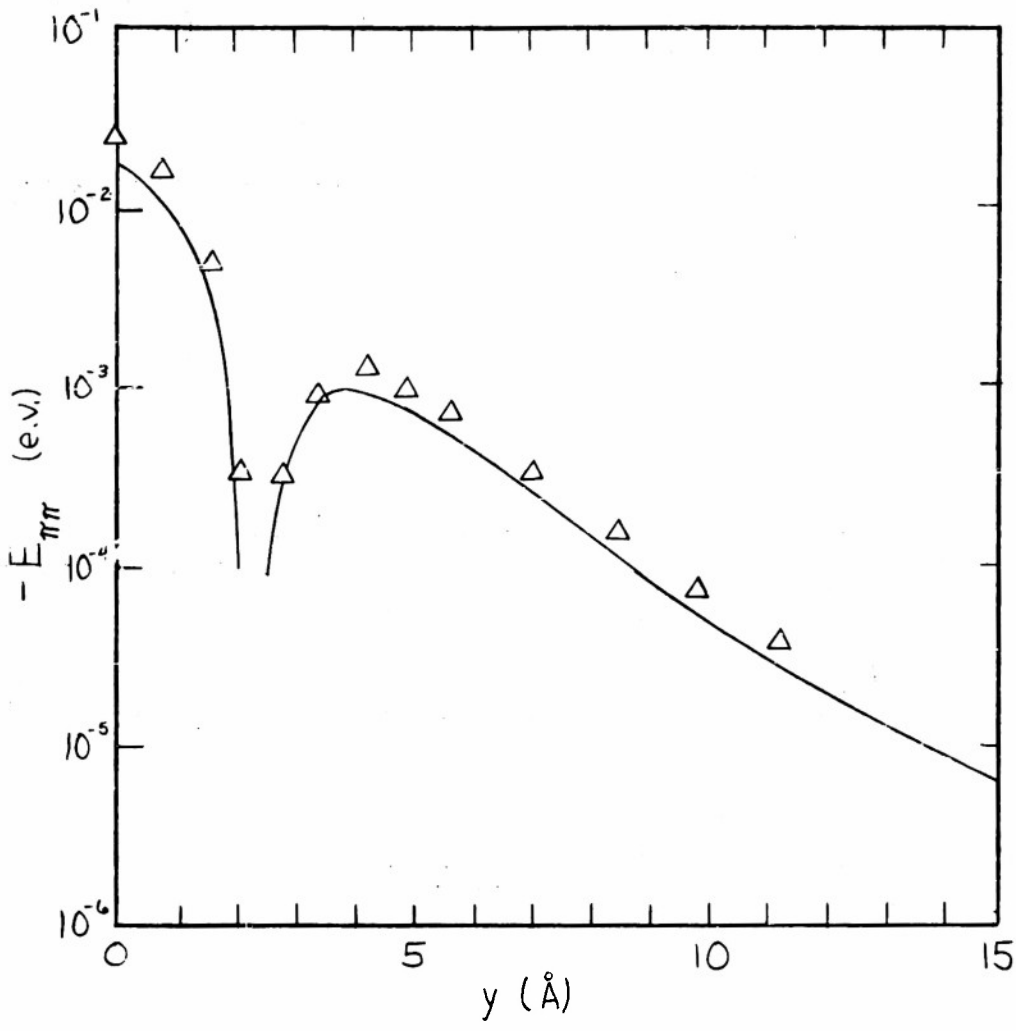


Figure 3.1 $E_{\pi\pi}$ for Ethylene in Displaced Parallel Configuration for d = 3 Å Triangles are Results of Coulson and Davies.

Table 3.2

γ For Ethylene Parallel Displaced (Eq. 3.8)

y (Å)	d=3Å	d=8Å
0	0.6312	0.9289
1	0.4722	0.9376
2	8.3913	1.1527
3	0.4918	1.0052
4	0.8514	1.0677
5	0.9819	1.3140
6	1.0305	.4625
7	1.0451	.8475
8	1.0471	.9197
9	1.0458	.9547
10	1.0420	.9718
11	1.0363	
12	1.0340	.9932
13	1.0255	
14	1.0267	1.0031
15	1.0237	
16		1.0071
18		1.0060
20		1.0071

Figure 3.1 gives the values of $E_{\pi\pi}$ for $d = 3$Å and shows the excellent agreement which is obtained with the more exact calculations of Coulson and Davies.

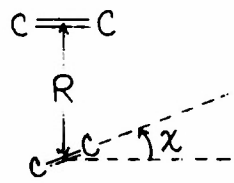
The most characteristic feature of the curve for $E_{\pi\pi}$ is the node which occurs between $y = 2$Å and $y = 3$Å for the case of $d = 3$Å. If the monopoles behaved like an ideal dipole, then according to Eq. (3.7), the node should occur when $y = d/\sqrt{2}$ or for $d = 3$ Å, the nodal y should be 2.12 Å. Actually, since the monopoles lie a distance of 1.78 Å apart, the corrections for lack of ideality are very large for this small separation. This is seen from the large value of γ in Table 3.2 for $y = 2$Å and d = 3Å. Actually we find that the node should occur for $y = 2.43$ Å. This is in almost perfect agreement with Coulson and Davies who find the node occurring for $y = 2.45$ Å. For $d = 8$ Å we obtain equally good agreement with Coulson and Davies for $E_{\pi\pi}$ as a

function of y. In this case we find the node occurring at 5.58 Å while Coulson and Davies calculations lead to 5.60 Å. For d = 8 Å the node would occur at y = 5.66 Å if the monopoles were ideal. The larger the value of d, the more closely does the node occur at the ideal-dipole value, y = .707 d.

(c) One Molecule Rotated in Plane of Other Molecule and the Radius Vector

Here $\epsilon_A = \frac{\pi}{2}$; $\theta_B = \frac{\pi}{2} - \chi$

and $\phi_A = \phi_B = 0$



According to Eq. (3.3) for this case,

$$E_{\pi\pi} = -\frac{21.25\,\gamma}{R(\text{Å})^6}\cos^2\chi \qquad (3.9)$$

For R = 7 Å, the values of γ which we calculate are given in Table 3.3. For this case the ideal-dipole approximation is very good. Coulson and Davies obtained the same qualitative behaviour as our results except that here

Table 3.3 γ For Ethylene Rotated in Plane of other Molecule and the Radius Vector. (Eq. (3.9)) Here R = 7 Å.

χ Degrees	γ
0	1.101
15	1.080
30	1.042
45	0.980
60	1.006
75	0.882
90	1.000

again their values are 4/3 of ours.

Complete Dispersion Energy for Ethylene

The formulae for $E_{\sigma\sigma}$ and for $E_{\sigma\pi}$ are given by Eqs. (2.32) and (2.44) respectively. Let us perform the calculation for 12 separate orientations of the two molecules when their centers are separated by 10 Å. In the calculations of $E_{\sigma\pi}$ and of $E_{\sigma\sigma}$ we use the bond polarizabilities of $(C-C)_{aliph}$ in place of $C = C$ since we do not wish for the bond polarizabilities to include the contribution of the pi-electrons. For the C-H bonds we neglect the assymetry of the polarizability tensor and use the average polarizability in place of $\alpha_{\parallel}$ and $\alpha_{\perp}$. This greatly simplifies the numerical calculations. It is convenient to number the monopoles (M) and centers of bonds (H) and (C) as shown in Fig. (3.2)

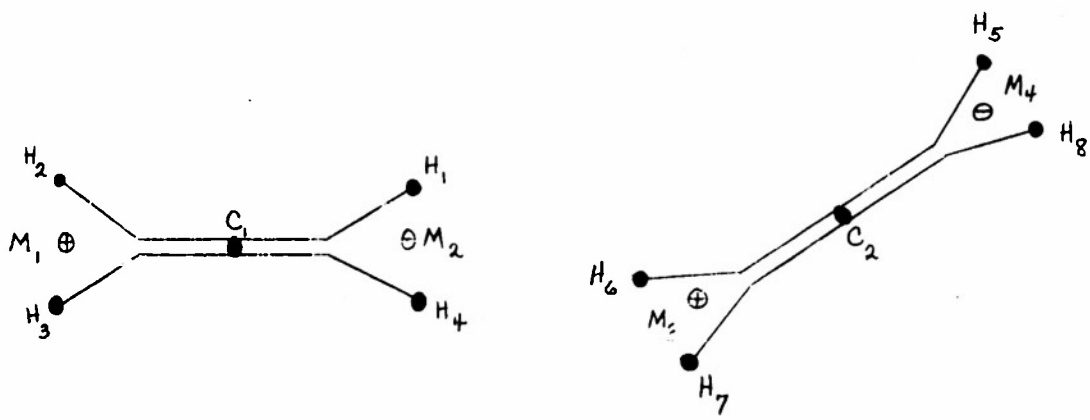


Fig. (3.2)

For these calculations the C-H bond length is taken to be 1.07 Å and the C=C distance is 1.34 Å. The angle between adjacent C-H bonds is 100°. Let the distances between the centers of two C-H bonds be called $R_{H_iH_j}$; between the center of the first C=C bond and the center of C-H bond, $R_{C_1H_j}$; between the first monopole and the center of a C-H bond, $R_{M_1H_j}$; etc. The twelve cases considered are shown schematically in Figure 3.3. For these cases the expressions for $E_{\sigma\sigma}$ is (in e.v. when distances are in Å),

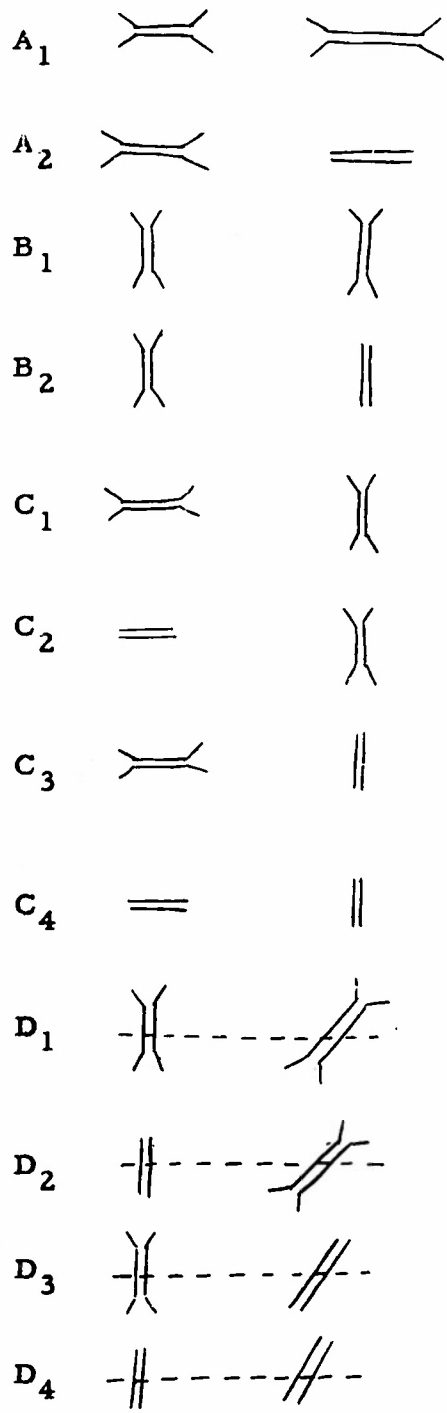
$$E_{\sigma\sigma} = -3.93 \sum_{i=1}^{4} \sum_{j=5}^{8} \frac{1}{R^6_{H_iH_j}} - 0.645 \sum_{j=5}^{8} \frac{1}{R^6_{C_1H_j}} \left[6 + 2.9\left(3\cos^2\theta_{C_1} - 1\right)\right]$$

$$-0.645 \sum_{i=1}^{4} \frac{1}{R^6_{C_2H_i}} \left[6 + 2.9\left(3\cos^2\theta_{C_1} - 1\right)\right]$$

$$-\frac{0.635}{R^6_{C_1C_2}} \left[\begin{array}{l} 0.2 + 0.29\left(\cos^2\theta_{C_1} + \cos^2\theta_{C_2}\right) \\ +8.41\left(2\cos\theta_{C_1}\cos\theta_{C_2} - \sin\theta_{C_1}\sin\theta_{C_2}\cos(\phi_{C_1} - \phi_{C_2})\right)^2 \end{array}\right] \quad (3.10)$$

Here $(\theta_{C_1}, \phi_{C_1})$ and $(\theta_{C_2}, \phi_{C_2})$ are the angles that the C = C bonds make with the radius vector and a plane including the radius vector joining the center of the two bonds. Also, for the cases considered, the expression for $E_{\sigma\pi}$ is (in e.v. when distances are in Å),

Fig. 3.3. Twelve configurations of two ethylene molecules. The A_1, B_1, C_1, and D_1 represent four orientations of the carbon-carbon bonds. The other orientations differ from these by rotations of 90° about the C-C axes as indicated.



A_1 — Molecules in same plane.

A_2 — Second molecule rotated perpendicular to plane of first molecule.

B_1 — Molecules in same plane.

B_2 — Second molecule rotated in plane perpendicular to first molecule.

C_1 — Molecules in same plane.

C_2 — First molecule rotated into plane perpendicular to second.

C_3 — Second molecule rotated into plane perpendicular to first.

C_4 — Both molecules rotated by 90° into new plane.

D_1 — First molecule in xz plane second in yz plane.

D_2 — First molecule rotated by 90°.

D_3 — Second molecule rotated by 90°.

D_4 — Both molecules rotated by 90°.

$$E_{\sigma\pi} = -1.113 \sum_{i=1}^{4} \left[\frac{1}{R^4_{H_i M_3}} + \frac{1}{R^4_{H_i M_4}} - \frac{\left(R^2_{H_i M_3} + R^2_{H_i M_4} - R^2_{M_3 M_4}\right)}{R^3_{H_i M_3} \; R^3_{H_i M_4}} \right]$$

$$- 1.113 \sum_{j=5}^{8} \left[\frac{1}{R^4_{H_j M_1}} + \frac{1}{R^4_{H_j M_2}} - \frac{\left(R^2_{H_j M_1} + R^2_{H_j M_2} - R^2_{M_1 M_2}\right)}{R^3_{H_j M_1} \; R^3_{H_j M_2}} \right]$$

$$-(\text{only in cases } A_1 \text{ and } A_2)\; 3.218 \left[\left(\frac{1}{(Z_{M_3} - Z_{C_1})^2} - \frac{1}{(Z_{M_4} - Z_{C_1})^2} \right)^2 + \left(\frac{1}{(Z_{M_1} - Z_{C_2})^2} - \frac{1}{(Z_{M_2} - Z_{C_2})} \right)^2 \right] \tag{3.11}$$

Here the Z_C and Z_M are the coordinates in the direction of the radius vector from C_1 to C_2; and $R_{M_1M_2} = R_{M_3M_4} = 1.783$. For general orientations of the two molecules, the last term in Eq. (3.11) becomes somewhat more complicated but can easily be worked out from Eq. (2.44).

The results for the 12 different configurations of the ethylene molecules is given in Table 3.4. In order to obtain mean values of the dispersion energy corresponding to spatially averaging the molecules over all orientations, first of all we must average with respect to rotations about the C-C bonds. This is accomplished by averaging the results for A_1 and A_2 to give an average A; average B_1 and B_2 to get an average B; average C_1, C_2, C_3, and C_4 to get an average C; average D_1, D_2, D_3, and D_4 to get an average D. In the above averaging each of the orientations is given equal weight. The resulting four orientations of the C-C axes correspond to the four configurations of the H-H axes in the interaction of two hydrogen

molecules problem which Evett and Margenau[10] studied. They found that in this case, the most reliable mean values of the interaction energies is attained by assuming the weights 0.085, 0.25, 0.415, and 0.25 for the configurations A, B, C, and D. Using these weights we obtained the results indicated in Table 3.4. First of all, it is surprising how little difference the orientation of the

Table 3.4 Energy of Interaction Between Two Ethylene Molecules Separated by a Distance of 10 Å. (All energies are given in units of 10^{-4} e.v.)

Orientation	$-E_{\pi\pi}$	$-E_{\sigma\sigma}$	$-E_{\sigma\pi}$	$-E_{total}$
A_1	0.91	1.93	2.28	5.12
A_2	0.91	1.93	2.28	5.12
B_1	0.20	0.85	0.29	1.34
B_2	0.20	0.82	0.28	1.30
C_1	0.00	1.18	0.75	1.93
C_2	0.00	1.18	0.75	1.93
C_3	0.00	1.13	0.73	1.86
C_4	0.00	1.13	0.73	1.86
D_1	0.00	0.79	0.28	1.07
D_2	0.00	0.77	0.27	1.04
D_3	0.00	0.77	0.27	1.04
D_4	0.00	0.74	0.27	1.01
Mean Values	0.13	1.04	0.64	1.81
Experimental Dispersion Energy from Lennard-Jones Potential (6, 12)				4.06

C-H bonds make in the $E_{\sigma\sigma}$ and $E_{\sigma\pi}$.

When one uses the Lennard-Jones (6, 12) potential to fit the experimental

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10. A. Evett and H. Margenau, Phys. Rev. 90, 1021 (1953).

data of viscosity of Ethylene as a function of temperature, the force constants ϵ and σ are found to be 0.0177 e.v. and 4.232 Å respectively. If this Lennard-Jones potential were correct, the energy of dispersion would be equal to $4 \epsilon \sigma^6/R^6$. This empirical potential energy curve therefore provides an experimental comparison of our average value of E_{total}. The fact that our theoretical value is smaller by a factor of $1.81/4.06 = 0.45$ is not surprising since most theoretical values of dispersion energies are smaller than the Lennard-Jones values by about this ratio[11].

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11. See "Molecular Theory of Gases and Liquids", p. 966, Table 13.3-1.

Acetylene

The forces between two acetylene molecules are much the same as between two ethylenes. In acetylene the triple bond contains two pi-bonds but these pi-electrons can be treated in exactly the same manner as the pi-electrons in ethylene. The carbon-carbon bond length in acetlene is 1.207 Å and the carbon-hydrogen bond length is 1.060 Å. Using the monopole strengths and separation given in Table 2.1 we obtain the skeletal structure of the acetylene molecule shown in Fig. 3.4. As in the case of ethylene, there is only one principal transition which needs to be considered, (1, 2), so

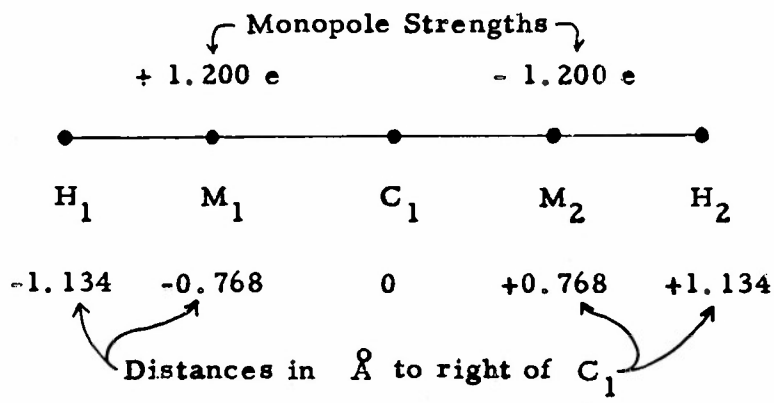

Fig. 3.4, Skeletal structure of acetylene. Here C_1 is the center of the C-C bond and H_1 and H_2 are the centers of the C-H bonds. The M_1 and M_2 are the two monopoles for the principal transition.

that the formulae for the three different types of electron interaction are simple. For acetylene, the transition dipole moment is $\mu_{12} = 8.86$ debye and the transition energy is $\epsilon_2 - \epsilon_1 = 8.60$ e.v. At large separations $E_{\pi\pi}$ is given by Eq. (3.3) where now $G = 140$ e.v. - $Å^{-6}$. At smaller separations $E_{\pi\pi}$ is given by Eq. (3.6) where $R_{M_1M_2} = 1.537$ Å. The

formula for $E_{\sigma\sigma}$ is given by Eq. (3.10) where now the summation over "i" includes only 1 and 2 and the summation over "j" includes only 3 and 4. For the purposes of computation for the present paper, we consider only four basic orientations of the two acetylene molecules, namely the same orientations of the C-C bonds as were considered in the case of ethylene; A, B, C, D of Fig. 3.3. For acetylene, which is a linear molecule, it is not necessary to consider the sub-cases indicated by subscripts on the A, B, C, and D. For these cases, the sigma-pi interactions for acetylene are given by

$$
\begin{aligned}
E_{\sigma\pi} = & - 3.978 \sum_{i=1}^{2} \left[\frac{1}{R^4_{H_i M_3}} + \frac{1}{R^4_{H_i M_4}} - \frac{\left(R^2_{H_i M_3} + R^2_{H_i M_4} - R^2_{M_1 M_2} \right)}{R^3_{H_i M_3} \; R^3_{H_i M_4}} \right] \\
& - 3.978 \sum_{j=3}^{4} \left[\frac{1}{R^4_{H_j M_1}} + \frac{1}{R^4_{H_j M_2}} - \frac{\left(R^2_{H_j M_1} + R^2_{H_j M_2} - R^2_{M_1 M_2} \right)}{R^3_{H_j M_1} \; R^3_{H_j M_2}} \right] \\
& - \text{(only in case A)} \; 11.51 \left[\left(\frac{1}{(Z_{M_1} - Z_{C_2})^2} - \frac{1}{(Z_{M_2} - Z_{C_2})^2} \right)^2 + \left(\frac{1}{(Z_{M_3} - Z_{C_1})^2} - \frac{1}{(Z_{M_4} - Z_{C_1})^2} \right)^2 \right]
\end{aligned}
\tag{3.12}
$$

Here again the Z's are coordinates in the direction of the radius vector going from C_1 to C_2, and again the formula for a general orientation would have a last term which is somewhat more complicated.

The results of these calculations are given in Table 3.5. The mean values are obtained, as in the case of ethylene, by assigning the weights: 0.085, 0.25, 0.415, and 0.25 to the configurations A, B, C, and D. Using the Lennard-Jones parameters $\epsilon = 0.016$ e.v. and $\sigma = 4.221$ Å

Table 3.5. Energy of Interaction Between Two Acetylene Molecules Separated by a Distance of 10 Å. (Energies are given in units of 10^{-4} e.v.)

Orientation	$-E_{\pi\pi}$	$-E_{\sigma\sigma}$	$-E_{\sigma\pi}$	$-E_{total}$
A	1.97	0.89	2.22	5.08
B	0.45	0.97	0.37	1.79
C	0.00	1.81	0.97	2.78
D	0.00	0.22	0.36	0.58
Mean Values	0.28	1.12	0.77	2.17
Experimental Dispersion Energy from Lennard-Jones (6, 12) Potential				3.62

determined from fitting experimental viscosity of gas data, we obtain an empirical check on our theoretical calculations. In this case our theoretical dispersion energy is smaller than the empirical value by the factor 2.17/3.62 = 0.60 which is exactly the same as for the case of ethylene.

Butadiene

Now let us consider the pi-pi dispersion energy for Butadiene. This example is much more complicated than either the ethylene or the acetylene cases. There are four transitions which must be considered. They are, in the order of their importance: (2, 3), (2, 4), (1, 3), and (1, 4). At large separations, the (2, 3) and the (1, 4) charge distributions could be approximated by a dipole but the (2, 4) and (1, 3) are essentially quadrupole charge distributions. Naturally, the positions of the nodes and maxima in the energy of interaction is difficult to describe in terms of simple equations. Nevertheless, the " long-polyene approximation" which considered presently gives a surprisingly good representation at large separations. In this approximation only the principal transition, (2, 3), is considered. However, at small separations there is no satisfactory way of avoiding the detailed calculations. Let us use the symbol (i i', j j') to indicate the transition (i, j) in molecule A and the transition (i', j') in the molecule B. The numbers preceding each term indicates its degeneracy. Let us consider two configurations.

(a) Parallel and Opposed.

The results for this case are given in Table 3.6. From symmetry considerations it is easy to see that the transitions (11, 34), (21, 33), (21, 44) and (22, 34) do not contribute to the energy of dispersion. It is seen that the principal transition (22, 33) is always the largest contributor, followed by (21, 34) and (22, 44). However, at large separations only the (22, 33) is important.

(b) Displaced Parallel Configuration.

Here the symbols y and d have the same significance as in the case of ethylene. The contributions of the various transitions and the values of $E_{\pi\pi}$ are given in Table 3.7 for various values of y when d = 8 Å. The variation of $E_{\pi\pi}$ with y is shown in Fig. 3.4. Because the dispersion energy is the sum of a number of terms each having different nodal points, $E_{\pi\pi}$ has a minimum value different from zero.

Table 3.6

Contributions to $-E_{\pi\pi}$ (e.v.) for Butadienes in Parallel Opp and Conformation

Term	a = 4 (Å)	8	15	20	30	50
1 (11,44)	5.98×10^{-6}	-	-	-	-	-
2 (21,34)	8.08×10^{-6}	1.20×10^{-6}	1.08×10^{-7}	2.40×10^{-8}	2.46×10^{-9}	1.25×10^{-10}
1 (22,33)	2.51×10^{-2}	9.29×10^{-4}	2.86×10^{-5}	5.39×10^{-6}	4.93×10^{-7}	2.35×10^{-8}
1 (11,33)	7.42×10^{-4}	2.35×10^{-6}	6.35×10^{-9}	3.70×10^{-10}	-	-
2 (21,43)	1.07×10^{-3}	4.45×10^{-6}	1.33×10^{-8}	8.18×10^{-10}	-	-
1 (22,44)	2.76×10^{-4}	2.22×10^{-6}	7.25×10^{-9}	4.56×10^{-10}	-	-
Total Value $-E_{\pi\pi}$ (e.v.)						
Present Calculations	2.72×10^{-2}	9.39×10^{-4}	2.87×10^{-5}	5.41×10^{-6}	4.94×10^{-7}	2.36×10^{-8}
Coulson and Davies	4.06×10^{-2}	1.48×10^{-3}	4.59×10^{-5}	8.62×10^{-6}	7.99×10^{-7}	3.47×10^{-8}

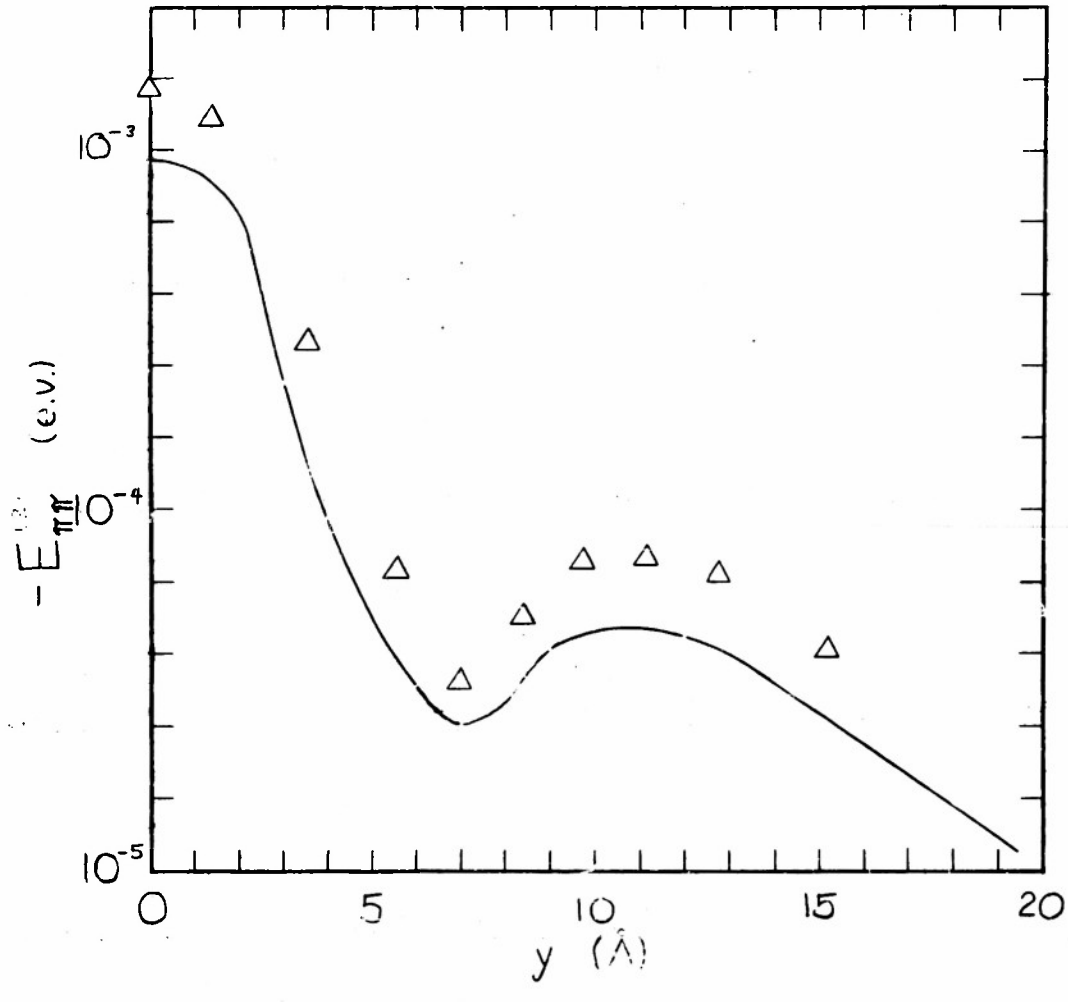

Figure 3.4 $-E_{\pi\pi}$ for Butadiene in Displaced Parallel Configuration for d = 8 Å. The triangles are the results of Coulson and Davies calculations.

Table 3.7

Contributions to $-E_{\pi\pi}$ (e.v.) for Butadienes in Displaced Parallel Configuration for $d = 8$ Å.

y(Å)	-(22,33)	-(22,44)	-(11,33)	-2(21,43)	-2(22,34)	-2(2,33)	-Total $E_{\pi\pi}$
0	9.29×10^{-4}	2.22×10^{-6}	2.35×10^{-6}	4.46×10^{-6}	0	0	9.38×10^{-4}
1	8.41×10^{-4}	1.68×10^{-6}	1.72×10^{-6}	3.32×10^{-6}	7.44×10^{-6}	8.12×10^{-6}	8.63×10^{-4}
2	6.20×10^{-4}	6.44×10^{-7}	5.65×10^{-7}	1.10×10^{-6}	2.32×10^{-5}	2.48×10^{-5}	6.81×10^{-4}
3	3.63×10^{-4}	4.31×10^{-8}	1.53×10^{-8}	5.26×10^{-8}	3.46×10^{-5}	3.62×10^{-5}	4.35×10^{-4}
4	1.58×10^{-4}	8.24×10^{-8}	1.36×10^{-7}	2.10×10^{-7}	2.10×10^{-7}	3.46×10^{-5}	2.28×10^{-4}
5	4.15×10^{-5}	3.27×10^{-7}	3.68×10^{-7}	6.32×10^{-7}	2.60×10^{-5}	2.56×10^{-5}	9.45×10^{-5}
6	1.84×10^{-6}	4.10×10^{-7}	4.01×10^{-7}	8.08×10^{-7}	1.51×10^{-5}	1.44×10^{-5}	3.30×10^{-5}
7	5.75×10^{-6}	3.38×10^{-7}	2.89×10^{-7}	6.18×10^{-7}	7.02×10^{-6}	6.42×10^{-6}	2.04×10^{-5}
8	2.36×10^{-5}	2.05×10^{-7}	1.61×10^{-7}	3.58×10^{-7}	2.50×10^{-6}	2.18×10^{-6}	2.90×10^{-5}
9	3.91×10^{-5}	1.01×10^{-7}	7.37×10^{-8}	1.70×10^{-7}	5.96×10^{-7}	4.84×10^{-7}	4.05×10^{-5}
10	4.71×10^{-5}	4.17×10^{-8}	2.86×10^{-8}	6.80×10^{-8}	4.80×10^{-8}	2.86×10^{-8}	4.73×10^{-5}
12	4.50×10^{-5}	3.95×10^{-9}	2.31×10^{-9}	5.94×10^{-9}	1.06×10^{-7}	1.15×10^{-7}	4.52×10^{-5}
14	3.37×10^{-5}	1.60×10^{-11}	5.44×10^{-16}	6.78×10^{-12}	2.10×10^{-7}	2.08×10^{-7}	3.41×10^{-5}
16	2.29×10^{-5}	2.25×10^{-10}	2.17×10^{-10}	4.34×10^{-10}	1.89×10^{-7}	1.81×10^{-7}	2.33×10^{-5}
18	1.50×10^{-5}	3.35×10^{-10}	2.81×10^{-10}	6.02×10^{-10}	1.33×10^{-7}	1.26×10^{-7}	1.53×10^{-5}
20	9.77×10^{-6}	2.70×10^{-10}	2.18×10^{-10}	4.76×10^{-10}	8.52×10^{-8}	8.10×10^{-8}	9.94×10^{-6}

It is interesting to compare the results of the present calculations using the FEM orbitals with the calculations of Coulson and Davies using the LCAO orbitals. The first difference to note is that the degeneracy of the terms is not always the same for the LCAO and the FEM treatments. For example in the parallel opposed configuration, in the LCAO treatment the (22, 44) is 4-fold degenerate whereas in the FEM treatment the (22, 44) is singly degenerate. However, in the FEM treatment the singly degenerate (11, 33) and the doubly degenerate (21, 43) have very nearly the same values for the matrix elements. There is therefore very little physical effect of this difference in the degeneracies. Rather uniformly, the Coulson and Davies results give values of $-E_{\pi\pi}$ larger than ours by a factor of 5/3. Such a difference could arise through the particular empirical value of the resonance integral which Coulson and Davies used or it could result from errors in the FEM approximation or in honest differences between the LCAO and the FEM approximations.

Hexatriene

For hexatriene, we consider only the principal transition, (33, 44) whereas Coulson and Davies consider a large number of transitions. Table 3.8 compares our results with those of Coulson and Davies for the parallel opposed configuration. Uniformly, the Coulson and Davies values are 5/3 of ours.

Table 3.8 $-E_{\pi\pi}$ (e.v.) for Hexatriene in the Parallel Opposed Configuration.

d (Å)	Our Results	Coulson and Davies
4	6.04×10^{-2}	11.35×10^{-2}
8	3.57×10^{-3}	6.07×10^{-3}
15	1.43×10^{-4}	2.42×10^{-4}
20	2.86×10^{-5}	4.85×10^{-5}
30	2.75×10^{-6}	4.70×10^{-6}
50	1.35×10^{-7}	4.01×10^{-7}

Approximate Treatment of Long Polyenes

Let us develop an approximate method for treating the dispersion energy between linear polyenes for the case that the number of double bonds, N, is large and the separation between the two molecules is large compared to the length of the molecule. Consider the energy arising from the interaction of pi-electrons with pi-electrons, $E_{\pi\pi}$, the energy arising from the interaction of sigma-electrons with sigma-electrons, $E_{\sigma\sigma}$, and the energy arising from the interaction of sigma-electrons with pi-electrons, $E_{\sigma\pi}$.

We include only the principal transition for the pi-electrons so that the transition charge density is given by:

$$\rho = \frac{2^{3/2} e}{\ell} \sin \frac{N\pi x}{\ell} \sin \frac{(N+1)\pi x}{\ell} \tag{3.13}$$

Using a familiar trigonometric identity this may be rewritten:

$$\rho = \frac{\sqrt{2}\, e}{\ell} \left[\cos \frac{\pi x}{\ell} - \cos \frac{(2N+1)\pi x}{\ell} \right] \tag{3.14}$$

For large N the second term in the brackets is a rapidly oscillating function so we make the approximation that it may be neglected. Our approximate charge density is then given by:

$$\rho = \frac{\sqrt{2}\, e}{\ell} \cos \frac{\pi x}{\ell} \tag{3.15}$$

In using the London approximation we then obtain a "dipole" and it may easily be seen to consist of a positive and negative charge of magnitude $q^{B}_{N,N+1}(+) = -q^{B}_{N,N+1}(-) = (\sqrt{2}/\pi)\, e$ separated by a distance of $2\ell/\pi$. The dipole moment is then $(2\sqrt{2}\, e\ell)/\pi^2$ In Table 3.9 we compare the dipole moment with the dipole moments for the principal transitions for ethylene, butadiene, and hexatriene.

Table 3.9

Comparison of Principal Transition Dipole Moments with Asymptotic Value

Molecule	$\mu_{N,N+1}$ Transition Dipole Moment
Ethylene	0.25473 $e\ell$
Butadiene	0.27512 $e\ell$
Hexatriene	0.28073 $e\ell$
Asymptotic Value	0.28658 $e\ell$

It is seen, even that for ethylene the deviation is not great and that the asymptotic value is rapidly approached which suggests that the approximation is a good one. We now make a further approximation that the interaction of two such dipoles may be given by the interaction of two ideal dipoles as in Eq. (3.3). Finally, making use of the fact that the length of the molecule is $(2N + 1) \times 1.4$ Å we obtain the following result for the dispersion energy arising from pi-pi interaction:

$$E_{\pi\pi} = -0.14003(2N+1)^5 \frac{\left[-2\cos\theta_a\cos\theta_b + \sin\theta_a\sin\theta_b\cos(\phi_b-\phi_a)\right]^2}{R^6} \tag{3.16}$$

where R, the separation, is measured in Å. Averaging over angles introduces a factor of 2/3 and gives the result:

$$\overline{E_{\pi\pi}} = -0.09335\ \frac{(2N+1)^5}{R^6} \tag{3.17}$$

It is seen that $E_{\pi\pi}$ is proportional to the fifth power of the length of the polyene, a result also reported by Coulson and Davies. However, their coefficient is somewhat larger. Thus for $\theta_a = \theta_b = \pi/2, \phi_a = \phi_b$ their coefficient is 0.246 compared to the above value of 0.14003.

In treating $\overline{E_{\sigma\sigma}}$ we use Eq. (2.32); treat all bonds as if they were at the center of the molecule; and average over all orientations of the molecules. The averaging over all orientations has the effect of making all of the terms with δ's vanish so that

$$\overline{E}_{\sigma\sigma} = -\frac{3}{4} I \left(\sum_{k_A} \alpha_{k_A}\right)\left(\sum_{\ell_B} \alpha_{\ell_B}\right)/R^6 \tag{3.18}$$

Here the sums are to be taken over all of the chemical bonds in the two molecules. Since a polyene with N double bonds has (2N-1) C-C bonds and (2N+2) C-H bonds, it follows that

$$\overline{E}_{\sigma\sigma} = -\frac{3.91\,(4N+1)^2}{R^6} \quad (\text{e.v.} - \text{Å}^{-6}) \tag{3.19}$$

We have, of course, regarded all double bonds as single bonds in this calculation inasmuch as we do not wish to include the pi-electrons in this expression. It is seen that $E_{\sigma\sigma}$ varies approximately as the square of the length of the molecule so that for sufficiently long molecules it is negligible compared with $E_{\pi\pi}$.

In order to obtain a simple form for the average value of $E_{\sigma\pi}$ for long polyenes at large separations, let us assume: (1) that each of the chemical bonds has a mean polarizability $\alpha = 0.645 \times 10^{-24}\,\text{cm}^3$ and we ignore the difference between the perpendicular and parallel polarizabilities as well as the difference between the polarizabilities of the C-C and of the C-H bonds. (2) We assume that the centers of each of the chemical bonds coincides with the center of the molecule. Let h = distance between the monopoles and R_+ and R_- be the distances from the center of the molecule to the plus and minus monopoles respectively. The geometry is then as shown in Fig. 3.5. Then:

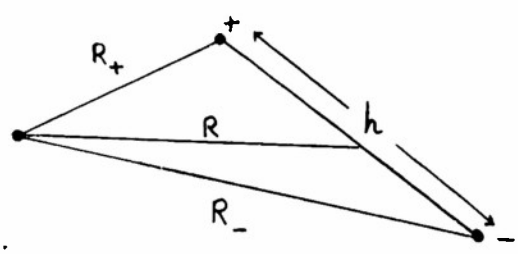

Fig. 3.5

$$E_{\sigma\pi} = -\frac{2[4N+1]\alpha q^2}{2\left[1+\frac{\epsilon_{N+1}-\epsilon_N}{I}\right]}\left[\frac{1}{R_+^4}-\frac{1}{R_-^4}-\frac{R_+^2+R_-^2-h^2}{R_+^3\,R_-^3}\right] \tag{3.20}$$

Here the factor 2 in the numerator is due to the fact that the sigma-pi energy is the sum of contributions from the sigma electrons of A interacting with the pi's of B and the sigmas of B interacting with the pi's of A; and 4N + 1 is the number of chemical bonds in one molecule. From the geometry of Fig. 3.5 it follows that

$$\begin{aligned} R_+^2 &= R^2 + \frac{h^2}{4} - Rh\cos\chi \\ R_-^2 &= R^2 + \frac{h^2}{4} + Rh\cos\chi \end{aligned} \tag{3.21}$$

Substituting these expressions into Eq. (3.20) and expanding the resulting equation in powers of h/R, it follows that the term in $1/R^6$ is the leading term and it is given by

$$E_{\sigma\pi} = -\frac{\alpha q^2[4N+1]}{\left[1+\frac{\epsilon_{N+1}-\epsilon_N}{I}\right]}\frac{h^2}{R^6}\left(1+3\cos^2\chi\right) \tag{3.22}$$

Now remembering that $(\epsilon_{N+1}-\epsilon_N) = 19.17/(2N+1)$ e.v.; $I = 12.4$ e.v.; $h = 2.8\,(2N+1)\times10^{-8}/\pi$; and $q = \sqrt{2}\,e/\pi$, it follows that

$$E_{\sigma\pi} = -\frac{0.747\,(4N+1)(2N+1)^3}{(N+1.27)\,R^6}\left(1+3\cos^2\chi\right) \tag{3.23}$$

Averaging $E_{\sigma\pi}$ over all orientations of the two molecules corresponds to averaging $\cos^2\chi$. Since the spatially averaged value of $\cos^2\chi = 1/3$, it follows that

$$\overline{E}_{\sigma\pi} = -\frac{1.49\,(4N+1)(2N+1)^3}{(N+1.27)\,R^6} \tag{3.24}$$

We see that $E_{\sigma\pi}$ varies approximately as the cube of the length of the molecule so that its significance for large molecules is greater than $E_{\sigma\sigma}$ but less than $E_{\pi\pi}$.

In Table 3.10 we present the coefficients of $1/R^6$ for the three dispersion energy terms for various values of N. It is interesting to compare the results for N equals one with our previous results for ethylene

Table 3.10

Coefficients of $1/R^6$ for Different Polyenes Using "Long Polyene Approximation" The Coefficients are given in Units of e. v. $-\mathring{A}^{-6}$.

N	$-E_{\sigma\sigma} R^6$	$-E_{\sigma\pi} R^6$	$-E_{\pi\pi} R^6$	$-E_{total} R^6$
1	98	89	23	210
2	317	512	292	1120
3	661	1560	1570	3790
4	1139	3520	5510	10160
6	2440	8800	34700	45900
8	4260	26200	133000	163500
10	6570	50400	381000	438000

which are given in Table 3.11. It may be concluded that the long polyene approximation is fairly satisfactory even in the case of ethylene, the smallest polyene.

Table 3.11

Comparison of "Long Polyene Approximation" with Accurate FEM Calculations for Ethylene. The Coefficients are given in units of e. v. $-\mathring{A}^{-6}$, and have the Values Approached when the Molecules are Separated by Large Distances.

	$-E_{\sigma\sigma} R^6$	$-E_{\sigma\pi} R^6$	$-E_{\pi\pi} R^6$	$-E_{total} R^6$
Accurate FEM	104	64	13	181
"Long Polyene Approx"	98	89	23	210

Benzene

The FEM MO's for benzene[12] which we shall regard as having a circular free electron path, are given by:

$$\phi_0 = \frac{1}{\sqrt{2\pi}}$$

$$\left.\begin{aligned} \phi_{nc} &= \frac{1}{\sqrt{\pi}} \cos n\theta \\ \phi_{ns} &= \frac{1}{\sqrt{\pi}} \sin n\theta \end{aligned}\right\} n = 1, 2, 3 \qquad (3.25)$$

Their energy is given by

$$\epsilon_n = \frac{n^2 h^2}{2mC^2}, \quad n = 0, 1, 2, 3 \qquad (3.26)$$

Here θ is the angular coordinate of the electron and C is the circumference of the ring. We assume that all the carbon-carbon separations are 1.4 Å so that, roughly speaking, $C \sim 6 \times 1.4$ Å. Note that for n greater than zero the molecular orbitals are doubly degenerate.

In the ground state of benzene, the six π electrons are located in the three orbitals ϕ_0, ϕ_{1c}, and ϕ_{1s}.

In treating benzene we shall consider only the principal transitions which result from transitions of π electrons from either the 1 c or the 1 s orbitals to either the 2 c or the 2 s orbitals.

Substituting the FEM MO's as given by (3.25) we have the following expressions for the transition charge densities:

$$\begin{aligned} \rho_a = \rho_{1s;2c} &= \frac{\sqrt{2}\, e}{\pi} \sin\theta \cos 2\theta \\ \rho_b = \rho_{1s;2s} &= \frac{\sqrt{2}\, e}{\pi} \sin\theta \sin 2\theta \\ \rho_c = \rho_{1c;2c} &= \frac{\sqrt{2}\, e}{\pi} \cos\theta \cos 2\theta \\ \rho_d = \rho_{1c;2s} &= \frac{\sqrt{2}\, e}{\pi} \cos\theta \sin 2\theta \end{aligned} \qquad (3.27)$$

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12. H. Kuhn, Helv. Chim. Acta 31, 1441 (1948), 31, 1780 (1948), J. Chem. Phys. 16, 840 (1948), 17, 1198 (1949); Bayliss, J. Chem. Phys. 16, 287 (1948); Simpson, J. Chem. Phys. 16, 1124 (1948); Ruedenberg and Scherr, J. Chem. Phys. 21, 1565, (1953); Scherr, J. Chem. Phys. 21, 1582 (1953); Platt, J. Chem. Phys. 17, 484 (1949), 21, 1597 (1953).

The energy associated with these transitions may be deduced from Eq. (3.26) and has the value:

$$\epsilon_2 - \epsilon_1 = \frac{3h^2}{2mc^2} \tag{3.28}$$

In calculating the monopoles it is helpful to note that

$$\begin{aligned} \rho_c &= (\text{Rotation by } 90^\circ) \times \rho_a \\ \rho_d &= (\text{Rotation by } 90^\circ) \times \rho_b \end{aligned} \tag{3.29}$$

so that we need carry out calculations only for ρ_a and ρ_b. In each charge density region we locate the effective charge by calculating the first moment, i.e., we obtain the mean values of x and y and find that in general the monopoles are not located on the ring but are inside it. Thus we obtain the monopoles which are illustrated in Figure 3.6. The position of the atoms relative to the monopoles is of no importance in the FEM model.

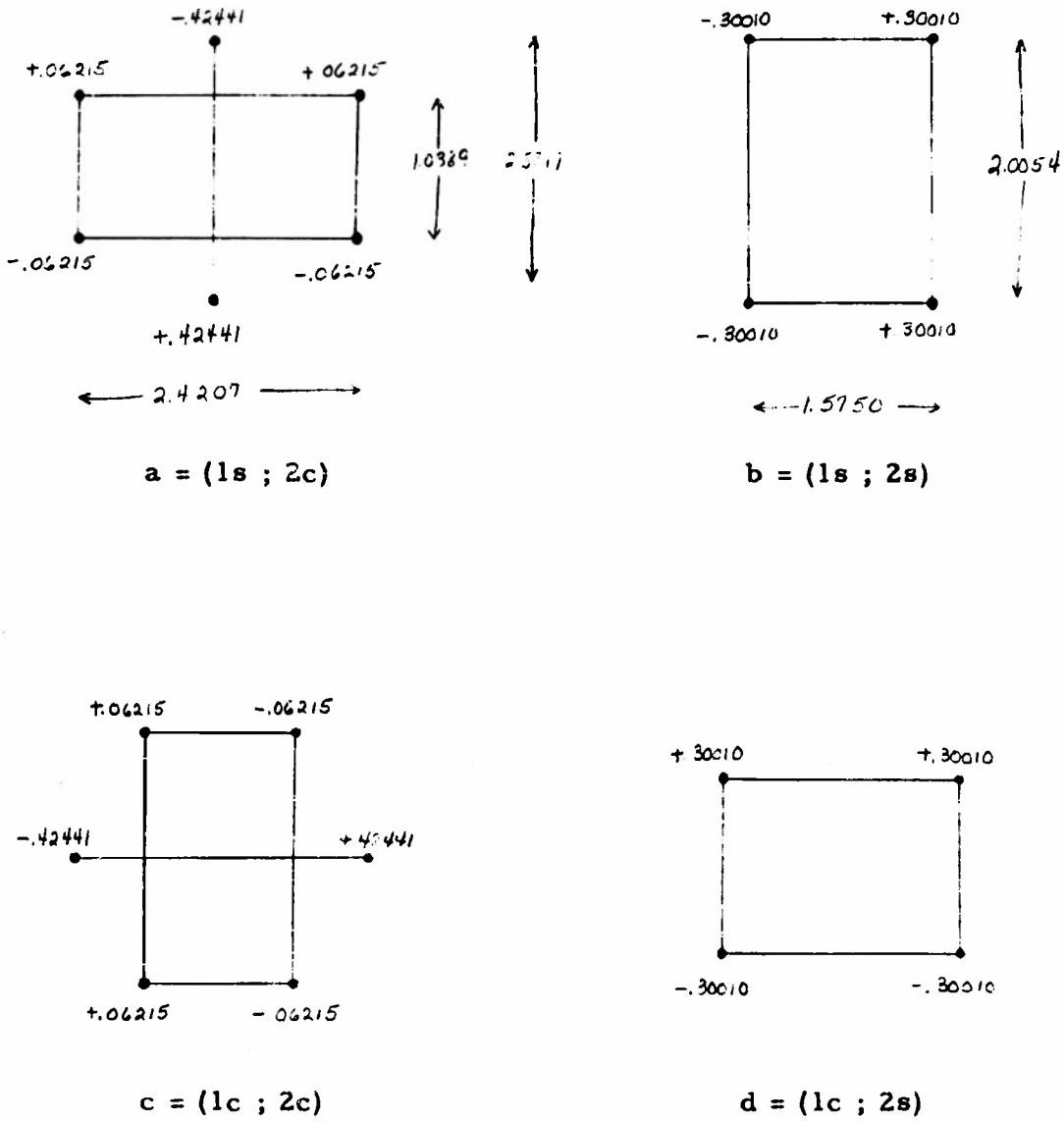

Figure 3.6. Monopoles for Principal Transitions for Benzene (Units are Angstroms and electronic charge, e).

Let us calculate the dispersion energy between two benzene molecules arising from pi-pi interaction for the orientation in which the two benzene rings are parallel and facing each other and are separated by a distance, d (see Figure 3. 7).

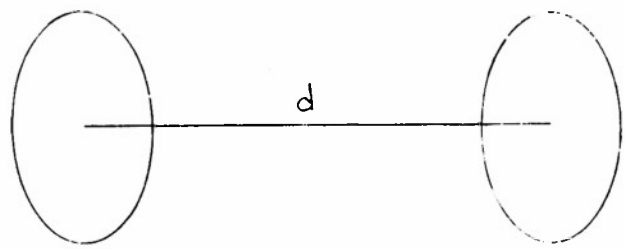

Figure 3.7
Parallel Opposed Configuration
for Benzene.

Let us denote the energy arising from the interaction of monopole distribution (1s; 2c) = a with monopole distribution (1s ; 2s) = b by the symbol (a, b,) and so forth. From symmetry considerations we see that the terms (a, b), (a, c), (b, d) and (c, d) are zero. The terms which contribute are (a, a) = (c, c), (b, b) = (d, d) and (a, d) = (b, c), the last two being each two-fold degenerate. It is then a straight forward matter to calculate the different energy terms and the results are presented in Table 3.12. In Table 3.12 the term values are multiplied by their degeneracy to give their contribution to the total dispersion energy.

Table 3.12

$-E_{\pi\pi}$ Dispersion Energy for Benzene for Parallel Opposed Configuration (in e.v.)

d (Å)	-2(a, a)	-2(b, b)	-4(a, d)	$-E_{\pi\pi}$	γ
5	3.07×10^{-3}	1.17×10^{-3}	2.31×10^{-3}	6.55×10^{-3}	0.705
10	6.19×10^{-5}	2.36×10^{-5}	4.71×10^{-5}	1.33×10^{-4}	0.916
15	5.72×10^{-6}	2.18×10^{-6}	4.36×10^{-6}	1.23×10^{-5}	0.965
25	2.74×10^{-7}	1.04×10^{-7}	2.09×10^{-7}	5.87×10^{-7}	0.987
50	4.34×10^{-9}	1.65×10^{-9}	3.30×10^{-9}	9.29×10^{-9}	1.000

To a good approximation, $E_{\pi\pi}$ varies inversely as the sixth power of the separation so that it is convenient to write it in the form:

$$E_{\pi\pi} = -\frac{145\,\gamma}{d^6} \qquad (\text{e.v.} - \text{Å}^{-6}) \tag{3.30}$$

where γ is a slowly varying function with values given in Table 3.12.

Davies[13] has made a rather extensive study of the π-π interactions of two benzene molecules using the LCAO method. His results agree well with the values given in Table 3.12 except that they are larger in the ratio 228/145 = 1.57. Davies also considered the variation of the π-π dispersion forces with angles and with various types of displacements. He concludes that the σ-π and σ-σ forces must be much larger than the π-π forces in order to account for the properties of crystalline benzene. As a matter of fact de Boer[14] succeeded in explaining the heat of sublimation of benzene without ever considering π electrons.

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13. P. L. Davies, PH.D. Dissertation, King's College, University of London (1949).

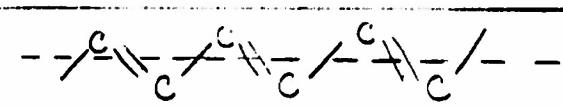
14. J. de Boer, Trans. Faraday Soc. 32, 10 (1936).

APPENDIX.

Polarizability of the Polyenes.

The longitudinal polarizability of the polyenes arising from the π electrons may be calculated using equations (2.44) and (2.40). For this calculation we shall not assume the polyene to be linear. Rather let us consider all C-C bonds to be 120° and that the polyene is in the configuration (see Fig. A1). Because of the angle of 120°, equation (2.40) must be written

Fig. A.1



Trans-Polyene for N=3. The extra bonds correspond to the free electron path and the dashed line represents the axis at the polyene.

$$\mu_{ij} = \sqrt{2}\, e \int \phi_i(x)\, \frac{\sqrt{3}}{2}\, x\, \phi_j(x)\, dx \tag{A.1}$$

Inserting the free-electron functions (2.29) for the transition $N \rightarrow N+1$ for an N-polyene gives the result:

$$(\mu)_{N,N+1} = \frac{\sqrt{6}\, e l}{\pi^2} \left[\frac{1}{(2N+1)^2} - 1 \right] \tag{A.2}$$

It then follows from (2.44) that the polarizability is:

$$\alpha_N = 1.81 \times 10^{-25}\, \frac{[(2N+1)^2 - 1]^2}{2N+1}\ \mathrm{cm}^3 \tag{A.3}$$

Results using this equation are compared in Table A.1 with values obtained by Davies* who used LCAO molecular orbitals.

For large polyenes (A.3) becomes:

$$\alpha_N = 1.81 \times 10^{-25} (2N+1)^3\ \mathrm{cm}^3 \tag{A.4}$$

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* P. L. Davies, Trans. Faraday Soc. 48, 789 (1952)

so that the polarizability is proportional to the cube of the length of the molecule. Davies obtains nearly the same result:

$$(\alpha_N)_{Davies} = 1.22 \times 10^{-25} (2N - 2)^3 \ cm^3 \tag{A.5}$$

Table A.1 Polarizabilities of the N-Polyenes

N	H-H	Davies
1	$38 \times 10^{-25} cm^3$	$35 \times 10^{-25} cm^3$
2	209	204
3	596	596
4	1290	
5	2370	2400

In the case of ethylene it is more significant to calculate the polarizability along the axis of the double bond. From Fig. 2 we see that the dipole moment integral (2.40) must be written:

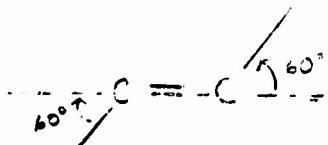

Fig. 2 Ethylene

$$\mu_{12} = \sqrt{2}\, e \left[\int_0^{2l/3} \phi_1\left(\frac{\sqrt{3}}{2} - x\right) \phi_2 \, dx + \int_{2l/3}^{4l/3} \phi_1 x \, \phi_2 \, dx + \int_{4l/3}^{l} \phi_1\left(\frac{\sqrt{3}}{2} - x\right) \phi_2 \, dx \right] \tag{A.6}$$

It is then found that $\alpha_{\parallel} = 9.1 \times 10^{-25} \ cm^3$. This compares well with the bond polarizabilities of Denbigh (Trans. Far. Soc. 36, 936 (1940)), who found that $\alpha_{\parallel}$ for a double bond is $28.6 \times 10^{-25} cm^3$ and for a single bond is $18.8 \times 10^{-25} cm^3$. The difference which is presumably the contribution of the pi-electrons, is $9.8 \times 10^{-25} cm^3$, which agrees well with our value of $9.1 \times 10^{-25} cm^3$.

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