Table VIII. Experimental Value and Prediction of $a(^{19}F)$ Based on Equation 3 with Various Values of Q^{F}_{F}, Q^{F}_{C}, and Q^{F}_{CF}[a]

Radical	Eq 23	Eq 24	SZC[b]	HM[b]	Expt[b]
2-Fluorobenzyl	+12.8	+12.4	+11.1	+5.9	8.17
3-Fluorobenzyl	−5.6	−6.0	−5.1	−2.7	(−)4.87
4-Fluorobenzyl	+13.1	+13.9	+12.4	+6.7	14.53

[a] The spin density obtained after spin annihilation by the INDO unrestricted SCF calculation was used as d or D in the equations. [b] Taken from ref 33.

VII for their Q values). All of them agree with experiments almost to the same extent. As Icli and Kreilick pointed out,[13] the near proportionality between ρ^{π}_{F} and ρ^{π}_{C} (and also ρ^{π}_{CF}) in actual free radicals makes it almost impossible to determine reliable individual Q values by fitting experimental $a(^{19}F)$ against spin densities. On the other hand, our results are based on physical models that would retain the significance of individual Q values. Therefore it is not surprising that existing values which are already well scattered did not agree with our values.

A few words of caution may be added to our results. First, even though our DZS set is anticipated to give a reliable overall picture, the individual Q values could be more sensitive to the choice of basis set. Also, our model of analysis using an artificially modified half-occupied π^* orbital is certainly a good way of obtaining Q values, but it is not necessarily the only way of doing so. Different models may result in somewhat different results. Also there is the lack of the quantitative agreement of experiment $a(^{19}F)$ with the theory for the CH_2F molecule. As the result an an arbitrary scaling factor of 2 had to be introduced. A better wave function may alter the interpretation somewhat, but the qualitative conclusion would not be affected.

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Calculation of Ground and Excited State Potential Surfaces of Conjugated Molecules.[1] I. Formulation and Parametrization

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Abstract: A formulation is developed for the consistent calculation of ground and excited state potential surfaces of conjugated molecules. The method is based on the formal separation of σ and π electrons, the former being represented by an empirical potential function and the latter by a semiempirical model of the Pariser–Parr–Pople type corrected for nearest-neighbor orbital overlap. A single parameter set is used to represent all of the molecular properties considered; these include atomization energies, electronic excitation energies, ionization potentials, and the equilibrium geometries and vibrational frequencies of the ground and excited electronic states, and take account of all bond length and bond angle variations. To permit rapid determination of the potential surfaces, the σ potential function and SCF–MO–CI energy of the π electrons are expressed as analytic functions of the molecular coordinates from which the first and second derivatives can be obtained. Illustrative applications to 1,3-butadiene, 1,3,5-hexatriene, α,ω-diphenyloctatetraene, and 1,3-cyclohexadiene are given.

A detailed interpretation of electronic transitions and concomitant photochemical processes in conjugated molecules requires a knowledge of the ground and excited state potential surfaces. The determination of such surfaces has long been a goal of theoretical chemistry. Difficulties in a reliable *a priori* approach to the problem for a system as simple as ethylene[2] are such that calculations for more complicated molecules are prohibitive at present. Consequently, a variety of methods that utilize experimental data have been introduced. Completely empirical treatments, in which the energy surface is expressed as a function of potential parameters fitted to the available information (equilibrium geometry, vibrational frequencies, etc.), have had considerable success in applications to molecules for which a localized electron description is applicable.[3] The great advantage of this type of approach, which leaves open questions of reliability when extended from one class of molecules to another, is the ease and speed of the calculations; this had made possible applications to systems as large as certain nucleic acids and globular proteins.[4] For conjugated molecules, however, the importance of delocalization introduces difficulties into such an empirical treatment.[5]

(1) Supported in part by Grant EY00062 from the National Institute of Health.

(2) U. Kaldor and I. Shavitt, *J. Chem. Phys.*, **48**, 191 (1968); R. J. Buenker, S. D. Peyerimhoff, and W. E. Kammer, *ibid.*, **55**, 814 (1971).

(3) (a) See, for example, J. E. Williams, P. J. Stand, and P. v. R. Schleyer, *Annu. Rev. Phys. Chem.*, **19**, 531 (1969); (b) S. Lifson and A. Warshel, *J. Chem. Phys.*, **49**, 5116 (1968); A. Warshel and S. Lifson, *ibid.*, **53**, 8582 (1970).

(4) M. Levitt and S. Lifson, *J. Mol. Biol.*, **46**, 269 (1969); M. Levitt, *Nature (London)*, **224**, 759 (1969).

(5) C. Tric, *J. Chem. Phys.*, **51**, 4778 (1969).

Moreover, a completely empirical approach to the problems under consideration would appear to require a systematic method for introducing different parameter sets for each molecular electronic state. This suggests that it would be better to proceed by means of one of the semiempirical procedures, of which there are many for π-electron systems. One possibility is to use a method which includes all valence electrons (*e.g.*, extended Hückel, INDO, PCILO, MINDO).[6] Although very promising, these treatments have not been developed to the state of refinement necessary to provide accurate results for ground and excited state potential surfaces.[7] The other possibility is to assume a separation between σ and π electrons and treat the σ electrons *via* empirical potential functions and the π electrons by a semiempirical approach. Many calculations of this type have been performed and considerable success has been achieved with appropriately chosen parameters in the evaluation of ground-state properties (*e.g.*, conformations, dissociation energies).[8] Most of this work, which has used bond-order, bond-length relationships[9] to simplify the treatment of the σ-electron framework, has been limited to an examination of the carbon skeleton with fixed bond angles and has ignored nonbonded interactions.[10] Corresponding calculations have been made for excitation energies, but these have usually required large changes in the basic parameters to obtain agreement with experiment, *e.g.*, different values of the resonance integral β in a Hückel calculation or the core parameter β in a Pariser–Parr–Pople treatment.[9]

In the present paper, we introduce a unified approach to the ground and excited state potential surfaces of conjugated molecules. The method is based on a formal separation of the σ and π electrons, with the former represented by an empirical potential and the latter by a semiempirical model of the Pariser–Parr–Pople type corrected for orbital overlap. A single parameter set is used to represent all of the properties considered: these include atomization energies, excitation energies, ionization potentials, and the equilibrium geometries and vibrations of the ground and excited states, taking account of all bond-length and bond-angle variations. The use of the method for the accurate evaluation of Franck–Condon factors for electronic transitions is described in another paper.[11] Applications to photochemical cis–trans isomerization will be given subsequently.

The essential elements in implementing the present model are the choice of the functional forms for the different energy contributions and the determination of the required parameters by comparison with experimental data. To be able to include a sufficient range of parameter variation and a large enough body of data to provide reliable results, the energy function must be expressed in such a form that it and its derivatives with respect to coordinates and parameter changes can be evaluated efficiently. For the σ electrons, this goal is achieved by writing the potential as an analytical function that consists of a sum of energy terms for the appropriately selected internal coordinates (bond lengths, bond angles, torsional angles, nonbonded distances, etc.). The σ-electron potential is thus an empirical function similar to those used previously for saturated molecules.[3] However, somewhat greater generality in the potential is required here because of the large changes in geometry that have to be encompassed in a treatment that is applicable to several electronic states, which can have significantly different equilibrium geometries (*e.g.*, the N and V states of ethylene). For the π electrons, the semiempirical configuration–interaction SCF–MO energy is developed as an analytic function of the coordinates by means of a perturbation treatment. Nearest-neighbor overlap, which is essential for obtaining a satisfactory description of the excited states,[12] is included by utilizing an orthogonalized (Löwdin) basis.[13] The resulting expressions are reduced to a convenient form by expanding them to second order as functions of the molecular coordinates. This permits a search for the minimum energy conformation and the determination of vibrational frequencies to be made without prohibitive amounts of computation time.

The present treatment can be regarded as an extension of the so-called "consistent-force field" (CFF)[3b] to conjugated molecules. In this approach the empirical potential is determined by choosing parameters and functional forms such that the calculated values of molecular properties depending on the zeroth, first, and second derivatives of the Taylor's expansion agree in a least-squares sense with the corresponding experimental results. For finding the equilibrium geometry, a combination of steepest descent and Newton–Raphson procedures is used; the complete minimization with respect to all of the molecular coordinates usually requires on the order of 40 iterations of the former and four to six of the latter. The method has been used previously for alkanes[3b] and, in a somewhat more approximate form, for other molecules[4,14] that can be described in terms of localized bonds.

In section I, the total energy of the molecule is expressed as a sum of σ- and π-electron contributions and the second-order π-electron SCF–MO–CI energy (including nearest-neighbor overlap) is formulated as an analytical function of the corrdinates. Section II describes the determination of the σ and π parameters by a simultaneous fit to a wide range of experimental data for ethylene, butadiene, benzene, and propylene. The requirement for consistency with ground and excited state results are shown to introduce significant constraints on the parameters. In section III are given applications of the method to the ground-state properties of *s-trans*- and *s-cis*-butadiene, to the ground and first excited states of 1,3-cyclohexadiene and of 1,3,5-hexatriene, and the ground state of α,ω-diphenyloctatetraene.

(6) For recent reviews, see R. Daudel and C. Sandorfy, "Semiempirical Wave Mechanical Calculations on Polyatomic Molecules," Yale University Press, New Haven, Conn., 1971; G. Klopman and B. O'Leary, *Top. Curr. Chem.*, **15**, 415 (1970).

(7) For recent examples of such calculations, see K. Machida, M. Nakatsuji, H. Kato, and T. Yonezawa, *J. Chem. Phys.*, **53**, 1305 (1970); J. M. McIver, Jr., and A. Komorwicki, *Chem. Phys. Lett.*, **10**, 303 (1971).

(8) For a review, see M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969.

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

(10) For some exceptions, see M. J. S. Dewar, and A. J. Harget, *Proc. Roy. Soc., Ser. A*, **315**, 443 (1970), and B. Honig and M. Karplus, *Nature (London)*, **229**, 558 (1971).

(11) A. Warshel and M. Karplus, to be published.

(12) N. C. Baird, *Mol. Phys.*, **18**, 39 (1970).

(13) I. Fisher-Hjalmars, *J. Chem. Phys.*, **42**, 1962 (1965).

(14) A. Warshel, M. Levitt, and S. Lifson, *J. Mol. Spectrosc.*, **33**, 84 (1970); S. Karplus and S. Lifson, *Biopolymers*, **10**, 1973 (1971).

I. Functional Form of Potential Surfaces

The potential surface of the Nth π-electronic state $V^N(\mathrm{r})$ is assumed to have the form, as a function of the configurational coordinate r

$$V^N(\mathrm{r}) = V_\sigma(\mathrm{r}) + V_\pi^0(\mathrm{r}) + \Delta V_\pi^N(\mathrm{r}) \tag{1}$$

where the σ-bond energy, $V_\sigma(\mathrm{r})$, is given by an empirical function, $V_\pi^0(\mathrm{r})$ is the SCF–MO π-electron energy for the closed-shell ground state, and $\Delta V_\pi^N(\mathrm{r})$ is the configuration interaction excitation energy for the Nth state. In some cases (*e.g.*, highly twisted double bonds as in 90° ethylene), the ground-state energy function $V_\pi^0(\mathrm{r})$ is corrected by a CI calculation that includes the essential double excitations.

(a) **π-Electron Energy Expression.** The π-electron energy is calculated in the Pariser–Parr–Pople (PPP) approximation corrected for nearest-neighbor overlap. The overlap correction is included because it is necessary for the proper torsional energy dependence of double bonds, as is evident already from the classic calculations of Parr and Crawford[15] and has been recently stressed by Baird;[12] *e.g.*, in the V and T states of ethylene, a π-electron energy independent of angle is obtained in the zero-overlap PPP approximation. Since it is inefficient to include the overlap integrals explicitly in the SCF–MO equations, we follow the procedure of Fisher-Hjalmars[13] and use an atomic basis consisting of Löwdin orthogonalized orbitals (λ). Assuming that the λ basis satisfies the zero-differential-overlap conditon, we find the molecular orbitals $\Phi_n(r)$

$$\Phi_n(\mathrm{r}) = \sum_\mu v_{n\mu}(\mathrm{r})\lambda_\mu \tag{2}$$

with expansion coefficients $v_{n\mu}(r)$ and the atoms designated by μ, from the SCF–MO equations

$$^\lambda\mathrm{F}(\mathrm{r})\mathrm{v}_n(\mathrm{r}) = \epsilon_n(\mathrm{r})\mathrm{v}_n(\mathrm{r}) \tag{3}$$

The matrix $^\lambda\mathrm{F}(r)$ has the PPP form in the λ basis; that is

$$^\lambda\mathrm{F}_{\mu\mu}(\mathrm{r}) = {}^\lambda W_\mu(\mathrm{r}) + {}^1\!/_2{}^\lambda\gamma_{\mu\mu}(\mathrm{r})P_{\mu\mu}(\mathrm{r}) - \sum_{\nu\neq\mu}{}^\lambda\gamma_{\mu\nu}(\mathrm{r})Q_\nu(\mathrm{r}) \tag{4}$$

$$^\lambda\mathrm{F}_{\mu\nu}(\mathrm{r}) = {}^\lambda\beta_{\mu\nu}(\mathrm{r}) - {}^1\!/_2P_{\mu\nu}(\mathrm{r}){}^\lambda\gamma_{\mu\nu} \quad (\mu \neq \nu)$$

where $P_{\mu\nu}(\mathrm{r})$ is the bond order

$$P_{\mu\nu}(\mathrm{r}) = 2\sum_n^{\mathrm{occ}} v_{n\mu}(\mathrm{r})v_{n\nu}(\mathrm{r}) \tag{5a}$$

and $Q_\nu(\mathrm{r})$ is the atomic change

$$Q_\nu(\mathrm{r}) = (Z_\nu - P_{\nu\nu}(\mathrm{r})) \tag{5b}$$

The standard notation of Pople[16] is being followed in eq 2–5 except that the superscript λ is used to designate quantities defined in terms of Löwdin orbitals and the variable r indicates the dependence on the molecular coordinates. To obtain explicit expressions in terms of nonorthogonalized Slater orbitals, we make use of the relation

$$\lambda = S^{-1/2}\chi, \qquad \mathbf{S}^{-1/2} = \mathbf{I} + {}^1\!/_2(\mathbf{I} - \mathbf{S}) + {}^3\!/_8(\mathbf{I} - \mathbf{S})^2 + \ldots \tag{6}$$

where λ and χ are vectors composed of the Löwdin and Slater orbitals, respectively, and $\mathbf{S}$ is the Slater-orbital overlap matrix. Substitution of eq 6 into eq 4, keeping nearest-neighbor terms through $S^2_{\mu,\mu\pm1}$, neglecting non-nearest-neighbor overlap $S_{\mu,\mu\pm2}$, and making use of the Mulliken approximation,[17] yields the desired expressions. For the Coulomb integrals $^\lambda\gamma_{\mu\nu}$, the procedure is straightforward and one obtains (suppressing the configurational coordinate r)

$$\begin{aligned} {}^\lambda\gamma_{\mu,\mu} &= \gamma_{\mu,\mu} + {}^1\!/_2S^2_{\mu,\mu+1}(\gamma_{\mu,\mu} - \gamma_{\mu,\mu+1}) + {}^1\!/_2S^2_{\mu,\mu-1}(\gamma_{\mu,\mu} - \gamma_{\mu,\mu-1}) \\ {}^\lambda\gamma_{\mu,\mu\pm1} &= \gamma_{\mu,\mu\pm1} - {}^1\!/_2S^2_{\mu,\mu\pm1}(\gamma_{\mu,\mu} - \gamma_{\mu,\mu\pm1}) \\ {}^\lambda\gamma_{\mu,\mu\pm m} &= \gamma_{\mu,\mu\pm m} \quad (m > 1) \end{aligned} \tag{7}$$

where the $\gamma_{\mu\nu}$ without the superscript λ correspond to integrals over Slater orbitals. To develop expressions for the core integrals $^\lambda\beta_{\mu\nu}$ and $^\lambda W_\mu$, given by

$$\begin{aligned} {}^\lambda\beta_{\mu\nu} &= {}^\lambda\langle\mu|H_{\mathrm{core}}|\nu\rangle \quad \nu = \mu \pm 1 \\ {}^\lambda\beta_{\mu\nu} &= 0 \quad \nu = \mu \pm 2, \mu \pm 3, \ldots \\ {}^\lambda W_\mu &= {}^\lambda\langle\mu|H_{\mathrm{core}}|\mu\rangle \end{aligned} \tag{8}$$

with H_{core} the standard core Hamiltonian,[16] is somewhat more complicated. We use relations given by Löwdin[18] in his classic papers on nonorthogonal orbitals and follow a procedure similar to, though not identical with, that of Fisher-Hjalmars.[13]

For $^\lambda\beta_{\mu,\mu\pm1}$, we neglect terms in S^2 and non-nearest-neighbor contributions to obtain[13]

$$\begin{aligned} {}^\lambda\beta_{\mu,\mu\pm1} &\cong {}^\lambda\langle\mu|T + U_\mu + U_{\mu\pm1}|\mu \pm 1\rangle \\ &\cong \langle\mu|T + U_\mu + U_{\mu\pm1}|\mu \pm 1\rangle - \\ &\quad {}^1\!/_2S_\pm(\langle\mu|T + U_\mu|\mu\rangle + \langle\mu \pm 1|T + U_{\mu\pm1}|\mu \pm 1\rangle) \end{aligned} \tag{9}$$

where U_μ is the core potential for a neutral atom and $S_\pm = \langle\mu|\mu \pm 1\rangle$. Introducing the potential U_μ^+ for the positively charged carbon core

$$\langle\mu|U_\mu^+|\mu \pm 1\rangle = \langle\mu|U_\mu|\mu \pm 1\rangle - \langle\mu\mu|\mu\mu \pm 1\rangle \cong \langle\mu|U_\mu|\mu \pm 1\rangle - {}^1\!/_2S_\pm(\gamma_{\mu\mu} + \gamma_{\mu,\mu\pm1}) \tag{10}$$

where the approximate equality follows from the Mulliken approximation, we can write (eq 76 of ref 13)

$$^\lambda\beta_{\mu,\mu\pm1} = \beta^+_{\mu,\mu\pm1} - S_\pm[{}^1\!/_2(W_\mu^+ + W^+_{\mu\pm1}) - \gamma_{\mu,\mu\pm1}] \tag{11}$$

with the standard definitions of the Slater-orbital core parameters

$$\beta^+_{\mu,\mu\pm1} = \langle\mu|T + U^+_\mu + U^+_{\mu\pm1}|\mu \pm 1\rangle \tag{12a}$$

$$W^+_\mu = \langle\mu|T + U^+_\mu|\mu\rangle \tag{12b}$$

To find an expression for $^\lambda W_\mu$, we proceed similarly and write (neglecting terms in S^3)

$$\begin{aligned} {}^\lambda W_\mu &\cong {}^\lambda\langle\mu|T + U_\mu + U_{\mu+1} + U_{\mu-1} + U_x|\mu\rangle - {}^\lambda\gamma_{\mu,\mu} \cong \langle\mu|T + U_\mu + U_{\mu+1} + U_{\mu-1} + U_x|\mu\rangle + \\ &\quad {}^3\!/_4(S^2_+ + S^2_-)\langle\mu|T + U_\mu|\mu\rangle + \\ &\quad {}^1\!/_4\{S^2_+\langle\mu + 1|T + U_{\mu+1}|\mu + 1\rangle + S^2_-\langle\mu - 1|T + U_{\mu-1}|\mu - 1\rangle\} - \\ &\quad S_+\langle\mu|T + U_\mu + U_{\mu+1}|\mu + 1\rangle - \\ &\quad S_-\langle\mu|T + U_\mu + U_{\mu-1}|\mu - 1\rangle - {}^\lambda\gamma_{\mu\mu} \end{aligned} \tag{13}$$

(15) R. G. Parr and B. L. Crawford, *J. Chem. Phys.*, **16**, 526 (1948).
(16) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953); see also ref 8 and 9.
(17) R. S. Mulliken, *J. Chim. Phys.*, 46, 497 (1949).
(18) P. O. Lowdin, *J. Chem. Phys.*, **18**, 365 (1950); **21**, 496 (1953).

where ${}^{\lambda}\gamma_{\mu\mu}$ is given in eq 7 and U_x represents the potential of the third ligand (*e.g.*, another carbon or a hydrogen). Making use of eq 7, 10, and 12, we obtain

$$\begin{aligned}{}^{\lambda}W_{\mu} = W^0_{\mu} - S_+\beta^+_{\mu,\mu+1} - S_-\beta^+_{\mu,\mu-1} + \\ S^2_+[{}^3/_4W^+_{\mu} + {}^1/_4W^+_{\mu+1} - {}^1/_4(\gamma_{\mu\mu} - \gamma_{\mu+1,\mu+1}) - \\ {}^1/_2(\gamma_{\mu\mu} + \gamma_{\mu,\mu+1})] + S^2_-[{}^3/_4W^+_{\mu} + {}^1/_4W^+_{\mu-1} - \\ {}^1/_4(\gamma_{\mu\mu} - \gamma_{\mu-1,\mu-1}) - {}^1/_2(\gamma_{\mu\mu} + \gamma_{\mu,\mu-1})] \quad (14)\end{aligned}$$

where W^0_{μ} is the ionization energy for an electron from atom μ, including the nearest-neighbor penetration terms

$$W^0_{\mu} = W^+_{\mu} + \langle\mu|U_{\mu+1} + U_{\mu-1} + U_x|\mu\rangle \quad (15)$$

For a conjugated π system made up of identical atoms with the same nearest neighbors, eq 14 simplifies to

$$\begin{aligned}{}^{\lambda}W_{\mu} = W^0_{2p} + S^2_+[-\beta^+_{\mu,\mu+1}/S_+ + W^+_{2p} - \\ {}^1/_2(\gamma_{\mu\mu} + \gamma_{\mu,\mu+1})] + S^2_-[-\beta^+_{\mu,\mu-1}/S_- + \\ W^+_{2p} - {}^1/_2(\gamma_{\mu\mu} + \gamma_{\mu,\mu-1})] \quad (16)\end{aligned}$$

Ground-State Energy. Equations 7, 11, and 16 contain the expressions used for the basic parameters of the SCF π-electron theory (eq 4) in this paper. Once the bond orders $P_{\mu\nu}(\mathrm{r})$ are determined by solving the SCF equations for a given geometry r, the ground-state π-electron energy $V_{\pi}{}^0(\mathrm{r})$ of eq 1 is given by

$$\begin{aligned}V_{\pi}{}^0(\mathrm{r}) = \sum_{\mu}P_{\mu\mu}(\mathrm{r})[{}^{\lambda}W_{\mu}(\mathrm{r}) + {}^1/_4P_{\mu\mu}(\mathrm{r}){}^{\lambda}\gamma_{\mu\mu}(\mathrm{r})] + \\ 2\sum_{\nu>\mu}P_{\mu\nu}(\mathrm{r}){}^{\lambda}\beta_{\mu\nu}(\mathrm{r}) - \sum_{\nu>\mu}[{}^1/_2P^2_{\mu\nu}(\mathrm{r}) - \\ Q_{\mu}(\mathrm{r})Q_{\nu}(\mathrm{r})]{}^{\lambda}\gamma_{\mu\nu}(\mathrm{r}) \quad (17)\end{aligned}$$

To employ eq 17 for determining $V_{\pi}{}^0(\mathrm{r})$ in the neighborhood of a given geometry $\mathrm{r} = \mathrm{r}_s$, we consider two approximations. The first consists of calculating the bond orders $P_{\mu\nu}(\mathrm{r}_s)$ at r_s and using their values for a neighboring configuration r; *i.e.*

$$\begin{aligned}V_{\pi}{}^0(\mathrm{r})^1 = \sum_{\mu}P_{\mu\mu}(\mathrm{r}_s)[{}^{\lambda}W_{\mu}(\mathrm{r}) + {}^1/_4P_{\mu\mu}(\mathrm{r}_s){}^{\lambda}\gamma_{\mu\mu}(\mathrm{r})] + \\ 2\sum_{\nu>\mu}P_{\mu\nu}(\mathrm{r}_s){}^{\lambda}\beta_{\mu\nu}(\mathrm{r}) - \\ \sum_{\nu>\mu}[{}^1/_2P^2_{\mu\nu}(\mathrm{r}_s) - Q_{\mu}(\mathrm{r}_s)Q_{\nu}(\mathrm{r}_s)]{}^{\lambda}\gamma_{\mu\nu}(\mathrm{r}) \quad (18)\end{aligned}$$

Equation 18 yields the exact first derivative with respect to bond lengths or other parameters, as can be demonstrated by use of the Hellmann-Feynman theorem or related methods.[19] This result is of particular importance for the direct use of semiempirical or *a priori* SCF-LCAO-MO potential surfaces for classical trajectory calculations of reaction dynamics. To obtain accurate results for the second derivative, which requires that the variation of the bond orders with ${}^{\lambda}\beta_{\nu\beta}$ and ${}^{\lambda}\gamma_{\mu\nu}$ be included, we use the second-order expression

$$\begin{aligned}V_{\pi}{}^0(\mathrm{r})^2 = V_{\pi}{}^0(\mathrm{r})^1 + \sum_{\mu>\nu}\sum_{\sigma>\tau}(\partial P_{\mu\nu}/\partial^{\lambda}\beta_{\sigma\tau})_{\mathrm{r}_s}({}^{\lambda}\beta_{\mu\nu}(\mathrm{r}) - \\ {}^{\lambda}\beta_{\mu\nu}(\mathrm{r}_s))({}^{\lambda}\beta_{\sigma\tau}(\mathrm{r}) - {}^{\lambda}\beta_{\mu\nu}(\mathrm{r}_s)) + \\ \sum_{\mu>\nu}\sum_{\sigma>\tau}(\partial P_{\mu\nu}/\partial^{\lambda}\gamma_{\sigma\tau})_{\mathrm{r}_s}({}^{\lambda}\gamma_{\mu\nu}(\mathrm{r}) - {}^{\lambda}\gamma_{\mu\nu}(\mathrm{r}_s)) \times \\ ({}^{\lambda}\gamma_{\sigma\tau}(\mathrm{r}) - {}^{\lambda}\gamma_{\sigma\tau}(\mathrm{r}_s)) = V_{\pi}{}^0(\mathrm{r})^1 + \\ \sum_{\mu>\nu}\sum_{\sigma>\tau}\pi^{\beta}{}_{\mu\nu,\sigma\tau}\Delta^{\lambda}\beta_{\mu\nu}\Delta^{\lambda}\beta_{\sigma\tau} + \sum_{\mu>\nu}\sum_{\sigma>\tau}\pi^{\gamma}{}_{\mu\nu,\sigma\tau}\Delta^{\lambda}\gamma_{\mu\nu}\Delta^{\lambda}\gamma_{\sigma\tau} \quad (19)\end{aligned}$$

(19) See, for example, R. Moccia, *Theor. Chim. Acta*, 8, 8 (1967).

where $\pi^{\beta}{}_{\mu\nu,\sigma\tau}$ and $\pi^{\gamma}{}_{\mu\nu,\sigma\tau}$ are the appropriate mutual polarabilities.[9] Equations 18 and 19 yield $V_{\pi}{}^0(\mathrm{r})$ as a continuous function of r with continuous derivatives, if the parameters themselves are represented by suitable functional forms (see below). The first two derivatives of the ground-state π-electron energy required for finding the minimum energy conformation and the vibrational frequencies will be obtained from these expressions.

Excitation Energy. To evaluate the potential surface of the Nth excited state, the excitation energy $\Delta V_{\pi}{}^N(\mathrm{r})$ (eq 1) must be determined This is done by expressing the configuration interaction energy of the excited state as an explicit function of the coordinates r. We describe here the formulation for a one-electron excitation to a singlet state; for a triplet state or for excitations involving more than one electron, the appropriate modifications must be introduced. Writing the excited state Ψ_N in the form

$$\Psi_N(\mathrm{r}) = \sum_n C_{Nn}(\mathrm{r})^1\psi_n \quad (20)$$

where

$${}^1\psi_n = {}^1\psi_{n_1\rightarrow n_2}$$

represents the singlet wave function corresponding to the excitation from the SCF orbital n_1 to n_2 and $\mathbf{C}_N(\mathrm{r})$ is the vector of coefficients obtained from the secular equations

$${}^1\mathbf{A}(\mathrm{r})\mathbf{C}_N(\mathrm{r}) = \Delta V_{\pi}{}^N(\mathrm{r})\mathbf{C}_N(\mathrm{r}) \quad (21)$$

with

$$\begin{aligned}({}^1A)_{nn} = \langle{}^1\psi_{n_1\rightarrow n_2}|H|{}^1\psi_{n_1\rightarrow n_2}\rangle - \langle{}^1\psi_0|H|\psi_0\rangle = \\ \epsilon_{n_2} - \epsilon_{n_1} - \langle n_1n_2|n_1n_2\rangle + 2\langle n_1n_2|n_2n_1\rangle \quad (22a)\end{aligned}$$

$$\begin{aligned}({}^1A)_{nm} = \langle{}^1\psi_{n_1\rightarrow n_2}|H|{}^1\psi_{m_1\rightarrow m_2}\rangle = \\ 2\langle m_1n_2|m_2n_1\rangle - \langle m_1n_2|n_1m_2\rangle \quad (22b)\end{aligned}$$

where

$$\begin{aligned}\langle nm|kl\rangle = \int\int\Phi_n(1)\Phi_m(2)(1/r_{12})\Phi_k(1)\Phi_l(2)\mathrm{d}\tau_1\mathrm{d}\tau_2 = \\ \sum_{\mu\nu}v_{n\mu}v_{k\mu}v_{m\nu}v_{l\nu}{}^{\lambda}\gamma_{\mu\nu} \quad (23)\end{aligned}$$

(All coefficients are assumed real for simplicity.)

To obtain $\Delta V_{\pi}{}^N(\mathrm{r})$ as a function of r, we proceed as for the ground state π-electron energy, $V_{\pi}{}^0(\mathrm{r})$, and approximate $\Delta V_{\pi}{}^N(\mathrm{r})$ in the neighborhood of the reference geometry r_s by use of the eigenvectors $C^s{}_N = C_N(\mathrm{r}_s)$. We have

$$\begin{aligned}\Delta V_{\pi}{}^N(\mathrm{r}) \cong \mathbf{C}^s{}_N{}^1\mathbf{A}(\mathrm{r})\mathbf{C}_N{}^s = \sum_m(C^s{}_{Nm})^2({}^1\mathbf{A}(\mathrm{r}))_{mm} + \\ 2\sum_{k>m}C^s{}_{Nm}C^s{}_{Nk}({}^1\mathbf{A}(\mathrm{r}))_{mk} = \sum_m(C^s{}_{Nm})^2\Big\{\epsilon_{m_2}(\mathrm{r}) - \epsilon_{m_1}(\mathrm{r}) - \\ \sum_{\mu\nu}[(v^s{}_{m_1\mu}v^s{}_{m_2\nu})^2 - 2v^s{}_{m_1\mu}v^s{}_{m_1\nu}v^s{}_{m_2\mu}v^s{}_{m_2\nu}]\Big\}{}^{\lambda}\gamma_{\mu\nu}(\mathrm{r}) + \\ 2\sum_{k>m}C^s{}_{Nm}C^s{}_{Nk}\Big\{\sum_{\mu,\nu}[2v^s{}_{m_1\mu}v^s{}_{m_2\mu}v^s{}_{k_1\nu}v^s{}_{k_2\nu} - \\ v^s{}_{m_1\mu}v^s{}_{k_1\nu}v^s{}_{m_2\mu}v^s{}_{k_2\nu}]{}^{\lambda}\gamma_{\mu\nu}(\mathrm{r})\Big\} \quad (24)\end{aligned}$$

where $v^s{}_{m\nu} = v_{m\nu}(\mathrm{r}_s)$ (see eq 2). Making use of the fact that, to the same approximation

$$\epsilon_m(\mathrm{r}) = \mathbf{v}^s{}_m\mathbf{F}(\mathrm{r})\mathbf{v}^s{}_m \quad (25)$$

with $\mathbf{F}(\mathrm{r})$ defined in eq 4 and evaluated as are the corresponding terms in eq 18, we can rewrite eq 24 in the form

$$\Delta V_\pi{}^N(\mathrm{r}) = \sum_\nu R^W{}_\nu{}^\lambda W_\nu(\mathrm{r}) + \sum_\nu R^\gamma{}_{\nu\nu}{}^\lambda\gamma_{\nu\nu}(\mathrm{r}) + \sum_{\nu>\mu} R^\beta{}_{\mu\nu}{}^\lambda\beta_{\mu\nu}(\mathrm{r}) + \sum_{\nu>\mu} R^\gamma{}_{\mu\nu}{}^\lambda\gamma_{\mu\nu}(\mathrm{r}) \quad (26)$$

where the expressions for the coefficients $R^W{}_\nu$, $R^\gamma{}_{\nu\nu}$, $R^\beta{}_{\nu\mu}$, and $R^\gamma{}_{\nu\mu}$ of the various integrals are given in the Appendix. The values of the coefficients, which depend on the state N, refer to the reference geometry $\mathrm{r_s}$, while the molecular integrals are determined for the geometry r.

(b) π-Electron Integral Parameters. In section Ia, expressions were derived for the π-electron contribution to the ground and excited states by modifying the Pariser–Parr–Pople method to include nearest-neighbor overlap. The resulting formulas depend on the values of the three integral parameters ${}^\lambda W(\mathrm{r})$, ${}^\lambda\beta_{\mu,\mu\pm1}(\mathrm{r})$, and ${}^\lambda\gamma_{\mu,\nu}(\mathrm{r})$ defined with respect to orthogonalized orbitals; the final equations for these parameters are eq 16, 11, and 7, respectively. To reduce these expressions to convenient computational form, a number of additional simplifying assumptions were made. Penetration integrals were neglected (except as their effect is subsumed in the empirical σ-electron potential) and the distance dependences of several of the terms in the equations were taken to be the same, as described below.

For the core resonance integral ${}^\lambda\beta_{\mu,\mu\pm1}$, we assume that $\beta^+{}_{\mu,\mu\pm1}$ and $S_{\mu,\mu\pm1}$ have the same distance and dihedral angle dependence and write the empirical formula as

$$ {}^\lambda\beta_{\mu,\mu\pm1} = \beta_0 \exp\{-\mu_\beta(b_{\mu,\mu\pm1} - b_0{}^1)\} \times [1 + k_\beta(b_{\mu,\mu\pm1} - b_0{}^1)] \times [\cos\tau_{\mu,\mu\pm1}(1 - \epsilon_\tau P_{\mu,\mu\pm1}\cos\tau_{\mu,\mu\pm1})]/[1 - \epsilon_\tau P_{\mu,\mu,\pm1}] \quad (27)$$

where $\tau = {}^1/_4(\phi_1 + \phi_2 + \phi_3 + \phi_4)$ with ϕ_i the torsional dihedral angles of the conjugated bond C_μ–$\mathrm{C}_{\mu\pm1}$. The first three factors in eq 27 represent the distance dependence of ${}^\lambda\beta_{\mu,\mu\pm1}$ for a planar system and the last factor corrects for nonplanarity in terms of the effective torsional angle τ. Thus, ${}^\lambda\beta_{\mu,\mu\pm1}$ depends on the parameters β_0, μ_β, $b_0{}^1$, k_β, and ϵ_τ; $b_0{}^1$ was fixed at the benzene value of 1.397 Å.

Although the distance dependence of ${}^\lambda\beta_{\mu,\mu\pm1}$ as expressed in eq 27 is dominated by the usual exponential term, it was found necessary to introduce the more complicated function involving a two-term polynomial in the distance (or some similarly behaved function) to be able to simultaneously represent the ground and excited state potential surfaces. Correspondingly, although the ordinary (cos τ) torsional angle dependence for ${}^\lambda\beta_{\mu,\mu\pm1}$ is a reasonable first approximation, it appeared that calculation of the torsional frequencies required a correction term. This was introduced by taking account of the possibility of incomplete π-orbital following relative to the values of the various X–C–C′–Y torsional angles.[20] The form used incorporates a weak dependence on the bond order $P_{\mu,\mu\pm1}$; *i.e.*, the larger the bond order, the greater the tendency of the π orbitals to remain parallel, independent of the orientation of the adjacent bonds.

(20) For a discussion of orbital following, see D. M. Schrader and M. Karplus, *J. Chem. Phys.*, **40**, 1593 (1964); D. M. Schrader, *ibid.*, **46** 3895 (1967); D. M. Schrader and K. Morokuma, *Mol. Phys.*, **21**, 1033 (1971).

For ${}^\lambda W_\mu$ as given in eq 16, the variation with distance and torsional angle arises primarily from $S^2{}_+$ and $S^2{}_-$. For these, we use the approximation

$$\begin{aligned} S^2{}_+ &= S^2{}_{\mu,\mu+1} = S^2{}_0 \times \exp\{-2\mu_\beta(b_{\mu,\mu+1} - b_0{}^1)\}\cos^2\tau_{\mu,\mu+1} \\ S^2{}_- &= S^2{}_{\mu,\mu-1} = S^2{}_0 \times \exp\{-2\mu_\beta(b_{\mu,\mu-1} - b_0{}^1)\}\cos^2\tau_{\mu,\mu-1} \end{aligned} \quad (28)$$

which corresponds to the lowest order contribution included in eq 27; here $S^2{}_0$ is the value of the square of the overlap integral at a distance equal to $b_0{}^1$. Neglecting other sources of distance dependence in ${}^\lambda W_\mu$, we can write the simplified empirical formula

$$ {}^\lambda W_\mu = W^0{}_{2\mathrm{p}} + \beta'[\exp\{-2\mu_\beta(b_{\mu,\mu+1} - b_0{}^1)\} \times \cos^2\tau_{\mu,\mu+1} + \exp\{-2\mu_\beta(b_{\mu,\mu-1} - b_0{}^1)\}\cos^2\tau_{\mu,\mu-1}] \quad (29)$$

The additional parameters required for ${}^\lambda W_\mu$ are, thus, $W^0{}_{2\mathrm{p}}$ and β', where the quantity β' is introduced to take account of the factors in brackets in eq 16, as well as $S^2{}_0$.

The formulas in eq 7 for the integrals ${}^\lambda\gamma_{\mu,\nu}$ are approximated correspondingly. The factors involving $S_{\mu,\mu\pm1}$ appearing in ${}^\lambda\gamma_{\mu,\mu}$ and $\gamma_{\mu,\mu\pm1}$ are assumed to have the distance and torsional angle dependence given in eq 28. As to the expression for the Coulomb integral $\gamma_{\mu\nu}$ itself, the form

$$\gamma_{\mu\nu} = G'\exp\{-\mu_\gamma b_{\mu\nu}\} + e^2/(D + b_{\mu\nu}), \qquad G' = (I - A) - G_0, \qquad D = e^2/G_0 \quad (30)$$

was chosen; here μ_γ and G_0 are parameters and A and I are the valence-state electron affinity and ionization potential, respectively.[8] Equation 30 is a combination of a Nishimoto–Mataga type expression,[21] which gives satisfactory bond lengths in the ground and excited states, with an exponential, to provide the added flexibility required for other molecular properties. A variety of other functional forms, including that of Ohno,[22] was tried and found to yield unsatisfactory results. Introducing eq 28 and 30 into eq 7, we obtain

$$\begin{aligned} {}^\lambda\gamma_{\mu,\mu} &= (I - A) + G_s[\exp\{-2\mu_\beta(b_{\mu,\mu+1} - b_0{}^1)\} \times \cos^2\tau_{\mu,\mu+1} + \exp\{-2\mu_\beta(b_{\mu,\mu-1} - b_0{}^1)\}\cos^2\tau_{\mu,\mu-1}] \\ {}^\lambda\gamma_{\mu,\mu\pm1} &= G'\exp\{-\mu_\gamma b_{\mu,\mu\pm1}\} + e^2/(D + b_{\mu,\mu\pm1}) - G_s\exp\{-2\mu_\beta(b_{\mu,\mu\pm1} - b_0{}^1)\}\cos^2\tau_{\mu,\mu\pm1} \\ {}^\lambda\gamma_{\mu,\nu} &= G'\exp[-\mu_\gamma r_{\mu,\nu}] + e^2/(D + r_{\mu,\nu}) \qquad (\nu \neq \mu, \mu \pm 1) \end{aligned} \quad (31)$$

The new parameters are G' (defined in terms of A, I, and G_0), G_0, μ_γ, and G_s, which includes $S^2{}_0$ and the factors in parentheses in eq 7; $r_{\mu,\nu}$ is the distance between atom μ and ν.

Substitution of eq 27, 29, and 31 into eq 18 (or eq 17 and 19) and eq 26 yields the complete expression for the π-electron energies. It remains only to discuss the determination of the parameters appearing in these equations. This is done in the following section; the values obtained for the parameters are given in Table I.

(21) K. Nishimoto and N. Mataga, *Z. Phys. Chem.* (*Frankfurt am Main*), **12**, 335 (1957).
(22) K. Ohno, *Theor. Chim. Acta*, **2**, 219 (1964).

(c) **σ-Electron Potential Function.** The σ-electron potential function $V_\sigma^0(\mathrm{r})$ is written

$$V_\sigma^0(\mathrm{r}) = V_\sigma^0(\mathrm{r})_{\mathrm{sat}} + V_\sigma^0(\mathrm{r})_{\mathrm{conj}} + V_\sigma^0(\mathrm{r})_{\mathrm{sat-conj}} \quad (32)$$

where the subscripts sat, conj, and sat–conj refer to the saturated, the conjugated, and the connection of the saturated and conjugated parts of the molecule, respectively; *i.e.*, $V_\sigma^0(\mathrm{r})_{\mathrm{sat}}$ corresponds to carbon atoms with nominally sp^3 hybridization, $V_\sigma^0(\mathrm{r})_{\mathrm{conj}}$ to carbon atoms with nominally sp^2 hybridization, and $V_\sigma^0(\mathrm{r})_{\mathrm{sat-conj}}$ to the connection between the two. For $V_\sigma^0(\mathrm{r})_{\mathrm{sat}}$ we use a slightly modified form of the alkane potential function developed previously by Lifson and Warshel.[3b] It is

$$V_\sigma^0(\mathrm{r})_{\mathrm{sat}} = {}^1/_2\sum_i[K_b(b_i - b_0)^2 + 2D_b] + {}^1/_2\sum_i K_\theta(\theta_i - \theta_0)^2 + {}^1/_2\sum_i F(q_i - q_0)^2 + \sum_{ij} f(r_{ij}) + {}^1/_2\sum_i K_\phi^{(3)}(1 + \cos 3\phi_i) + \sum_i K_{\theta\theta'}(\theta_i - \theta_0)(\theta_i' - \theta_0)\cos\phi_i \quad (33)$$

where the subscripts i indicate the summations over all appropriate terms. The b_i, θ_i, and ϕ_i represent the bond lengths (CC and CH), bond angles (CCC and CCH), and torsional angles (XCC′Y), respectively; the q_i are the 1–3 nonbonded distances, while the r_{ij} are all higher order nonbonded distances; and the pair θ_i and θ_i' are two bond angles XCC′ and CC′Y of a CC′ bond. For each CC′ bond, $K_\theta^{(3)}$ is chosen to conform to the fact that only one torsional angle XCC′Y (with X and Y carbons) is included; for the terminal methyl group, all XCCH angles are counted. The $K_{\theta\theta'}$ for XCC′Y constants require inclusion of all pairs of atoms X and Y. The nonbonded function f was chosen to be $f(r_{ij}) = Ae^{-\mu r_{ij}} - Br_{ij}^{-6}$ instead of the function $2\epsilon[(r^*/r_{oj})^9 - {}^3/_2(r^*/r_{ij})^6] + e_ie_j/r_{ij}$ used in the alkane potential. This modification allows us to employ the same nonbonded function for the saturated and unsaturated parts (see below). It was observed that the residual charge term e_ie_j/r_{ij} can be omitted from the nonbonded potential without introducing significant errors for conjugated hydrocarbons.

For $V_\sigma^0(\mathrm{r})_{\mathrm{conj}}$, we use the similar function

$$V_\sigma^0(\mathrm{r})_{\mathrm{conj}} = \sum_i M(b_i) + {}^1/_2\sum_i[k_a(a_i - a_0)^2 + 2D_a] + {}^1/_2\sum_i K_\theta(\theta_i - \theta_0)^2 + {}^1/_2\sum_i F(q_i - q_0)^2 + \sum_{ij} f(r_{ij}) + {}^1/_2\sum_i K_\phi^{(1)}\cos\phi_i + {}^1/_2\sum_i K_\phi^{(2)}\cos 2\phi_i + {}^1/_2\sum_i K_\chi(\chi_i - \chi_0)^2 + \sum_i K_{\theta\theta'}(\theta_i - \theta_0)(\theta_i' - \theta_0)\cos\phi_i \quad (34)$$

where the b_i and the a_i represent the CC and CH bond lengths, respectively, and the χ are "out-of-plane" angles defined for the atoms A, B, and C attached D as[14]

$$\cos\chi = \left(\frac{\mathbf{e}_{\mathrm{AC}} \times \mathbf{e}_{\mathrm{BD}}}{\sin\theta_{\mathrm{ADB}}}\right)\left(\frac{\mathbf{e}_{\mathrm{BD}} \times \mathbf{e}_{\mathrm{DC}}}{\sin\theta_{\mathrm{BDC}}}\right)$$

otherwise the notation is the same as in eq 33. The CC bond potential is given by a Morse function of the form

$$M(b) = D_b[\exp(-2\alpha\{b - b_0\}) - 2\exp(-\alpha\{b - b_0\})] \quad (35)$$

Table I. Parameters for the π-Electron Integrals

Integral	Parameter	Value
$^\lambda\beta$	β_0	−2.438 eV
	μ_β	2.035 Å^{-1}
	k_β	0.405 Å^{-1}
	ϵ_T	0.03
	$b_0{}^1$	1.397 Å
$^\lambda W$	$W^0{}_{2\mathrm{p}}$	−9.97 eV
	β'	0.235 eV
$^\lambda\gamma$	$I - A$	9.81 eV
	G_0	5.14 eV
	G_3	0.69 eV
	μ_γ	0.232 Å^{-1}

instead of the quadratic expression in eq 33, because the distances for different degrees of conjugation and the changes resulting on excitation are such that the harmonic approximation is not valid; by contrast, the harmonic form can still be used for the CH bonds and for bond-angle bending. The angles ϕ_i include the four torsional angles for each CC bond in the conjugated system; that is, for X$_1$X$_2$CC′X$_1$′X$_2$′, they are the dihedral angles X$_1$CC′X$_1$′, X$_1$CC′X$_2$′, X$_2$CC′X$_1$′, and X$_2$CC′X$_2$′ with $\phi_i = 0$ for the cis-planar geometry. The potential includes a onefold term ($K_\phi^{(1)}$) and a twofold term ($K_\phi^{(2)}$) in these angles, in contrast to the threefold term that is dominant in the saturated part of the molecule (see eq 33). All the other contributions to the potential in eq 34 have the same form as in eq 33, though the constants are adjusted to take account of the differences between saturated ("sp^3") and conjugated ("sp^2") carbon valences.

For the term $V^0(\mathrm{r})_{\mathrm{sat-conj}}$, the appropriate, somewhat simplified, combination of the functional forms given in eq 33 and 34 was used. The resulting expression is

$$V^0(\mathrm{r})_{\mathrm{sat-conj}} = {}^1/_2\sum_i[K_b(b_i - b_0)^2 + 2D_b] + {}^1/_2\sum_i K_\theta(\theta_i - \theta_0)^2 + {}^1/_2\sum F(q_i - q_0)^2 + \sum_{ij} f(r_{ij}) + {}^1/_2\sum_i K_\phi^{(3)}(1 - \cos 3\phi_i) \quad (36)$$

Here the torsional angle ϕ_i is an C=C—C—X angle; the form of the function is such that the minimum occurs with the double bond C=C eclipsing the CX bond, in agreement with experiment.[23] If X is a carbon atom (*i.e.*, except at a propylene end) only a single ϕ_i angle is included to simplify the calculations; for the propylene end, all the C=C—C—H torsional angles are included with appropriate adjustment of the constants.

The complete σ-electron potential for each hydrocarbon molecule, relative to that of the dissociated atoms, is obtained by introducing terms of the type given in eq 33, 34, and 36 for the bonds and their interactions. The method and data used to obtain the parameters appearing in the potential functions are described below with some discussion of the special importance of certain terms. A list of the complete σ-parameter set is given in Table II.

II. Determination of Potential Parameters

The development of section I has led to a formulation for the total energy surface $V^N(\mathrm{r})$ (relative to the sep-

(23) S. Kondo, E. Hirota, and Y. Morino, *J. Mol. Spectrosc.*, **28**, 471, (1968).

Table II. Parameters for the σ Potential Functions[a]

Bond	D	α	$^1/_2K_b$	b_0
C–C	86.0		110	1.490
C^p–C^p	87.94	1.756		1.466
C^p–C	88.0		250	1.450
C–H	104.0		286	1.100
C′–H	104.0		311	1.090
C^p–H	103.1		339	1.080
Bond angle[b]	$^1/_2K_0$		$^1/_2F$	q_0
C–C–C[c]	15.5		55.0	2.50
C^p–C^p–C^p	52.8		32.0	2.56
C–C–H	25.3		42.9	2.20
C–C′–H	18.3		51.7	2.20
C^p–C^p–H	24.0		29.5	2.18
H–C–H	39.5		1.7	1.8
H–C^p–H	29.4		3.0	1.9
Out of plane			$^1/_2K_\chi$	
C^p			10.2	
Torsion[d]	$^1/_2K_\phi{}^{(1)}$	$^1/_2K_\phi{}^{(2)}$	$^1/_2K_\phi{}^{(3)}$	$K_{\theta\theta}{}^1$
C–C–C–C			1.161	−2.3
X–C^p–C^p–X	2.3	0.66		−6
C^p–C–^{p}C–X			0.9	
H–C–C–H				−9.5
Nonbonded	A		μ	B
C···C	92431		3.60	747
C···H	11297		3.68	120
H···H	1642		3.76	19

[a] The units used are energies in kilocalories per mole, lengths in ångströms, angles in radians; the force constants are expressed correspondingly. Saturated carbon atoms are designated by C and unsaturated carbon atoms by C^p and, where differentiated from methylene carbon atoms, carbons in methyl groups as C′. [b] The parameters of C–C^p–C^p and C–C^p–H were set equal to those of C^p–C^p–C^p and C^p–C^p–H, respectively. The parameters of C^p–C–H were set equal to the C–C–H parameters (ref 3). [c] For CCC an additional linear term of the form $k_\theta'(\theta - \theta_0)$ is used with $K_\theta' = -6.2$. [d] X and X′ may be either carbon or hydrogen. The torsional potential of the C^p–C^p bond is equally distributed over all four torsional angles. The torsional potential of the C^p–C is attributed only to one torsional angle where X is the heavier atom among the three atoms which are connected to the C side of the bond. The torsional potential of the C–CH_3 group is distributed equally over all nine pairs X_i–C–C′H of the C–C′ bond.

arated atoms) of a conjugated molecule in electronic state N. Since the expression for $V^N(\mathrm{r})$ involves a mixture of semiempirical and empirical concepts implemented in terms of rather complicated functions that depend on many parameters, it is clear that the results can be regarded as meaningful only if they apply to a significant number of properties for a variety of conjugated hydrocarbon molecules. Also, the fitting procedure itself requires considerable input information and so can be carried out only if the necessary data are available.

The method utilized for the molecular property calculation and parameter determination is an extension of the "consistent-force field"[3b] to conjugated molecules. In this method, a least-squares procedure is employed to determine a set of parameters which yield satisfactory agreement between the calculated and experimental values of molecular properties depending on the zeroth, first, and second derivative terms in a Taylor's expansion of the potential energy function. Since the details of the consistent-force-field procedure have been given previously,[3b] we mention here only a few points that are of importance in its application to conjugated systems. An essential element in the effectiveness of the procedure is the availability of analytic expressions for the potential energy and the required derivatives. These can be obtained from the formulas developed in section I, as described below.

The σ-electron energy $V_\sigma{}^0(\mathrm{r})$, as given by eq 32, and its derivatives can be evaluated directly at each point in coordinate space without excessive use of computer time. However, the π-electron energy, $V_\pi{}^0(\mathrm{r}) + \Delta V_\pi{}^N(\mathrm{r})$, was estimated by a simplified procedure. For the steepest descent method employed in the initial stages of finding the minimum energy configuration, the first derivatives of the potential energy are required. The bond orders are calculated at the beginning of each step and then eq 18 and 26 are used to determine the change in energy as a function of the coordinates. Moreover, it is found that the new bond orders for each step can be calculated to sufficient accuracy by only a single iteration of eq 3. For the modified Newton–Raphson method, the second derivatives of the potential energy with respect to the system coordinates must be obtained; that is, the change in coordinates, $\Delta\mathrm{r}$, to go from the steepest descent result toward the equilibrium value, is obtained from the equation

$$\Delta\mathrm{r} = -\mathbf{F}_N{}^{-1}\nabla V^N(\mathrm{r}) \tag{37}$$

where $\nabla V^N(\mathrm{r})$ is the gradient and $\mathbf{F}_N$, the second derivative matrix of the potential energy function for the Nth state of the molecule. Since $\mathbf{F}_N$ is singular in Cartesian coordinates, the generalized inverse[3b,24] is used. The π-electron contribution to the matrix $\mathbf{F}_N$ is obtained by use of eq 17 for the ground state and includes the contribution from eq 26 for the excited states. Once the equilibrium conformation is determined, the vibrations are evaluated by finding the mass-weighted normal coordinates $(\mathcal{L}_N)_I$ as linear combinations of the Cartesian displacements from the secular equations

$$\mathfrak{F}_N(\mathcal{L}_N)_I = (2\pi\nu_I{}^N)^2(\mathcal{L}_N)_I \tag{38}$$

where $\mathfrak{F}_N = \mathbf{M}^{-1/2}\mathbf{F}_N\mathbf{M}^{-1/2}$ with $\mathbf{M}$ a diagonal matrix composed of the atomic masses.

Use of the Newton–Raphson procedure is essential for obtaining an accurate equilibrium conformation since the steepest descent method converges rather slowly. In practice, on the order of 40 steepest descent followed by four to six Newton–Raphson iterations are sufficient to obtain convergence.

(a) **Empirical Data Used in Fitting Procedure.** A large number of experimental data were employed in the fitting procedure. They include the equilibrium conformations and vibrational frequencies of the ground states of ethylene, butadiene, benzene, and propylene. Also used were the energies of formation of ground-state ethylene, benzene, and butadiene, as well as certain excitation and ionization energies of ethylene and benzene. In addition, the ground-state rotation barrier around the C=C bond in ethylene and estimates of certain excited state properties of ethylene and benzene were fitted. All these data are listed in Table III, where the results obtained with the final parameter set are given as well. It is seen that satisfactory agreement has been achieved for all of the properties.

To determine the nonbonded interaction parameters in the exponential-six potential, an independent procedure was used because the data included above are

(24) R. Fletcher, *Comput. J.*, 10, 392 (1968).

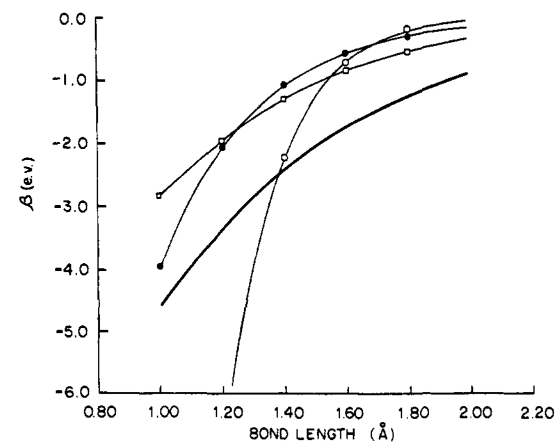


Figure 1. Resonance integral as a function of bond length: (—) present calculation; (●—●) ref 27; (□—□) ref 28; (O—O) ref 26.

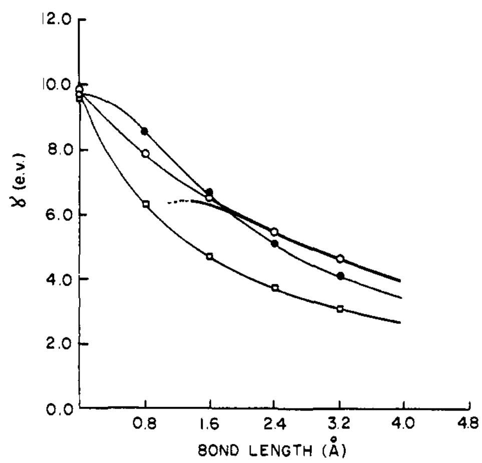


Figure 2. Coulomb integral as a function of bond length: (—) $^{\lambda}\gamma$, present calculation; (●—●) ref 22; (□—□) ref 21; (O—O) γ, present calculation.

not sufficiently sensitive to these interactions. The properties of n-hexane, n-octane, and some data for aromatic molecules were considered. For all n-hexane and n-octane crystals, the procedure described previously was used.[3b] For aromatic molecules, the results of Williams[25] were employed; that is, his potentials for the interaction of two aromatic CH bonds were fitted by the present potentials over a series of distances and orientations. Reasonable fits were obtained, although Williams used origins for the interactions that were not centered on the atoms (in case of hydrogen) while the present ones are centered on the atoms.

The consistent fit achieved in Table III represents a strong requirement on the form of the potential function and on the values of its parameters. None of the previous semiempirical studies on π-electron systems have tried to incorporate as great a variety of independent properties. The agreement between the calculated and observed results gives some hope that the prediction of related properties in similar molecules will be of corresponding accuracy.

(b) Results for π-Electron Integral Parameters. It is of some interest to present the functions obtained for certain of the π-electron integral parameters by the fitting procedure and to compare them with those used by others. Since there is no "correct" functional form in such semiempirical theories, the variability found in the different models is not surprising.

In Figure 1, we plot the core resonance parameter $^{\lambda}\beta$ as a function of distance. For comparison we include the values of β obtained by other workers with schemes that neglect nearest-neighbor overlap and correlate a more restricted set of properties: they are the Pariser and Parr fit to excitation energies,[26] the Longuet-Higgins and Salem fit to bond lengths and stretching frequencies,[27] and the Dewar, *et al.*, fit to atomization energies.[28]

A corresponding plot of the Coulomb integrals $\gamma_{\mu,\nu}$ and $^{\lambda}\gamma_{\mu,\mu\pm1}$ is presented in Figure 2. Also in-

(25) D. J. Williams, *J. Chem. Phys.*, **45**, 3770 (1966); **47**, 4680 (1967).

(26) R. Pariser and R. G. Parr, *ibid.*, **21**, 767 (1953).

(27) H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc., Ser. A*, **251**, 172 (1959).

(28) M. J. S. Dewar and G. Klopman, *J. Amer. Chem. Soc.*, **89**, 3089 (1967).

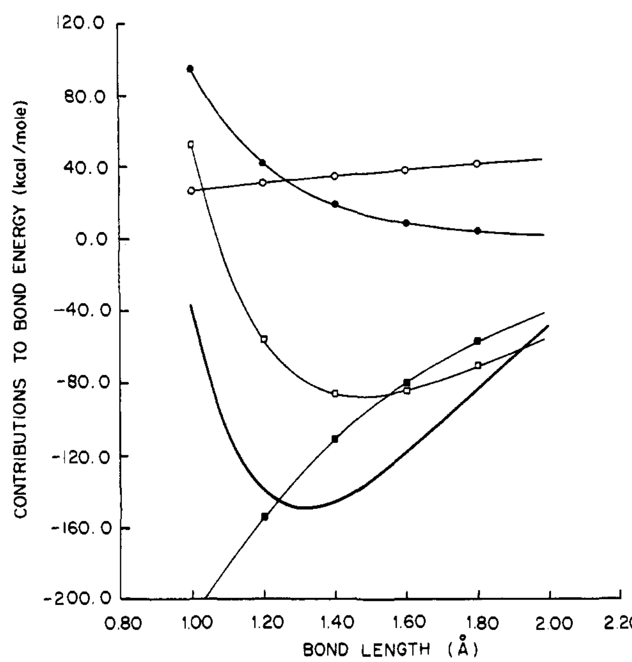


Figure 3. Bond energy contributions as a function of bond length (see eq 39 and 40): (—) total energy; (●—●) from $O(S^2)$ term; (□—□) from Morse potential for σ bond; (■—■) from $2^{\lambda}\beta$; (O—O) from $^1/_2(\gamma_{\mu,\mu} - \gamma_{\mu,\mu+1})$.

cluded in the plot are the more standard expressions of Mataga[21] and Ohno[22] for $\gamma_{\mu,\nu}$; a similar comparison is given in the recent paper of Beveridge and Hinze.[29] It should be noted that the functional form of $^{\lambda}\gamma_{\mu,\mu\pm1}$ is valid only to about 1.3 Å, because for a smaller bond length the simple exponential formula for the S^2 term (eq 28) overestimates the overlap contribution to $^{\lambda}\gamma_{\mu,\mu\pm1}$ (eq 7 and 31). Inasmuch as the shortest CC bond length of interest in the present calculation is greater than 1.2 Å, this restriction is not important; a modified expression, taking account of the true distance dependence of S^2, would be valid for smaller distances as well.

To summarize the various contributions to the dissociation energy of a conjugated bond, we plot in Figure 3 the results obtained for the case of unit bond

(29) D. L. Beveridge and J. Hinze, *ibid.*, **93**, 3107 (1971).

Table III. Experimental and Calculated Properties Used in the Optimization of Energy Parameters[a]

A. Vibrational Frequencies ($1/P = 50$)

	Obsd	Calcd		Obsd	Calcd
	Ethylene[b]			*s-trans*-Butadiene[d]	
A_g	3026	2982	A_g	3101	3080
	1623	1654		3014	3063
	1342	1321		3014	2987
				1643	1680
B_{1g}	3102	3055		1442	1456
	1222	1177		1279	1303
				1205	1228
B_{2u}	3105	3070		890	877
	826	792		513	545
B_{3u}	2989	2993	A_u	3095	3094
	1443	1452		3030	3062
				3000	2988
B_{1u}	949	913		1599	1616
				1385	1401
B_{2g}	943	965		1283	1303
				978	990
A_u	1023	1058		309	353
			B_g	967	999
				910	980
	Benzene[c]			680	679
A_{1g}	3062	3091			
	992	1046	B_u	1014	1067
A_{2g}	1340	1389		909	932
				520	541
B_{2g}	995	1025		170	176
	703	615			
				Propylene[e]	
E_{2g}	3047	3089	A′	3090	3087
	1596	1614		3010	3062
	1178	1149		2992	2988
	606	665		2954	2963
				2933	2898
E_{1g}	849	833		1652	1676
				1474	1461
A_{2u}	675	668		1419	1444
				1378	1434
B_{1u}	3071	3093		1298	1294
	1010	1068		1172	1171
				963	999
B_{2u}	1310	1460		920	934
	1150	1158		428	490
E_{2u}	973	997	A″	2954	2962
	403	398		1443	1466
				1045	1063
E_{1u}	3063	3087		991	1000
	1473	1502		912	951
	1036	1046		578	578
				173	183

order, including the correction due to nearest neighbors in the π system but neglecting Urey–Bradley and nonbonded interactions. The energy expression has the form (eq 17 and 34)

$$E_{\text{bond}} = V_\sigma{}^0 + V_\pi{}^0 \cong M(b) + \{2^\lambda\beta + 2^\lambda W_\mu + {}^1/_2({}^\lambda\gamma_{\mu\mu} - {}^\lambda\gamma_{\mu,\mu+1}) - 2W^0{}_{2p}\} = M(b) + 2^\lambda\beta + {}^1/_2(\gamma_{\mu\mu} - \gamma_{\mu,\mu+1}) + O(S^2) \quad (39)$$

where the terms contributing to $O(S^2)$, which arise from ${}^\lambda W_\mu$, ${}^\lambda\gamma_{\mu\mu}$, and ${}^\lambda\gamma_{\mu,\mu\pm1}$, are

$$O(S^2) = 2\beta' e^{-2\mu_\beta(b-b_0{}^1)} + {}^1/_2 G_s e^{-2\mu_\beta(b-b_0{}^1)} \quad (40)$$

It is evident from Figure 3 that the major portion of the distance dependence comes from $M(b)$ and ${}^\lambda\beta$, but that the $O(S^2)$ terms are significant as well.

(c) Special Relationships between Potential Function and Experimental Results. In the fitting procedure, it was found that certain of the experimental data (see section IIa, above) could be duplicated only by including specific elements in the potential function. In the $V^0{}_{\text{sat}}(\text{r})$ and $V^0{}_{\text{conj}}(\text{r})$ parts of $V_\sigma{}^0(\text{r})$ the cross terms of the form $K_{\theta\theta'}(\theta_i - \theta_0)(\theta_i' - \theta_0) \cos \phi_i$ were found to be necessary to obtain the correct frequencies for the symmetric B_{1g} and antisymmetric B_{2u} rocking modes of ethylene.[30,31] These rocking frequencies are experimentally at 826 and 1222 cm^{-1}, respectively, while the corresponding calculated values in the absence of the coupling term are 950 and 1100 cm^{-1}; with the coupling term, the values obtained are 792 and 1177 cm^{-1}. Shimanouchi[31] attributed the large difference between the two frequencies to "the flexibility of the C=C bond" and proposed a special dynamical model for this. His model, which is different from the present one, represents a correction to the Urey–Bradley force field

(30) K. Machida, *J. Chem. Phys.*, **44**, 4186 (1966); W. L. Smith and I. M. Mills, *ibid.*, **40**, 2095 (1964).
(31) T. Shimanouchi, *ibid.*, **26**, 594 (1957).

Table III (*Continued*)

B. Other Properties	Obsd	Calcd	$1/P$		Obsd	Calcd	$1/P$
	Conformations (a) Ethylene[f]				Energy of formation[l] (a) Ethylene		
C=C	1.335	1.331	0.005	E_0	562.0	560.4	2.0
C—H	1.086	1.084	0.09				
C—C—H	121.3	120.9	0.5		(b) Benzene		
				E_0	1364.4	1365.8	2.0
	(b) *s-trans*-Butadiene[g]						
C=C	1.337	1.340	0.005		(c) *s-trans*-Butadiene		
C—C	1.476	1.479	0.01	E_0	1009.3	1006.0	2.0
C—C=C	122.9	122.2	1.0				
	(c) Benzene[h]				Barrier for Torsion of Ethylene (Ground State)[m]		
C=C	1.397	1.403	0.002	V_0	65	63	5.0
	(d) Propylene[i]						
=C—C	1.488	1.488	0.01		Excited ${}^1B_{2u}$ State Frequencies[n] (a) Ethylene-d_4		
				Torsion (B_1)	550	517	50
	Excitation Energies (a) Ethylene[j]			C=C stretching (A_1)	1270	1303	100
${}^1B_{2u}$	7.60	7.67	0.1		(b) Ethylene		
First ionization potential	10.52	10.43	0.1	Torsion (B_1)	800	780	50
	(b) Benzene[k]						
${}^1B_{2u}$	4.80	4.90	0.2		Excited State Bond Lengths (a) Ethylene (${}^1B_{1u}$)[o]		
${}^1B_{1u}$	6.14	6.00	0.2				
${}^1E_{1u}$	6.75	6.47	0.2	C=C	1.430	1.417	0.03
First ionization potential	9.38	9.68	0.2		(b) Benzene (${}^1B_{2u}$)[p]		
				C=C	1.433	1.314	0.002

[a] The units are frequencies in reciprocal centimeters, bond lengths in ångströms, angles in degrees, excitation energies in electron volts, energy of formation in kilocalories per mole, and torsional barrier in kilocalories per mole. The quantity P^{-1} is the estimated error in the experimental data used in the least-squares fit (see ref 3). [b] The observed values are from K. Machida, *J. Chem. Phys.*, **44**, 4186 (1966); W. L. Smith and I. M. Mills, *ibid.*, **40**, 2059 (1964). [c] The observed values are from R. B. Main and D. F. Hornig, *ibid*, **17**, 1236 (1949). [d] E. M. Popov and G. A. Kogan, *Opt. Spektrosk.*, **17**, 362 (1964). [e] L. M. Sverdlov, *Dokl. Akad. Nauk USSR*, **106**, 80 (1956). [f] D. R. Lide, *Tetrahedron*, **17**, 125 (1962); H. C. Allen, Jr., and E. K. Plyler, *J. Amer. Chem. Soc.*, **80**, 2673 (1958). [g] D. J. Marais, N. Sheppard, and B. P. Stoicheff, *Tetrahedron*, **19**, 163 (1962). [h] B. P. Stoicheff, *Can. J. Phys.*, **32**, 339 (1954). [i] D. R. Lide, Jr., and D. G Mann, *J. Chem. Phys.*, **27**, 868 (1957). [j] The ${}^1B_{1u}$ excitation energy is from R. G. Parr, "The Quantum Theory of Molecular Electronic Structure," W. A. Benjamin, New York, N. Y., 1964, p 58; the ionization energy is taken from K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957). [k] The excitation energies are taken from D. R. Kearns, *ibid.*, **36**, 1608 (1962). The ionization energy is taken from M. E. Wacks and V. H. Diebler, *ibid.*, **31**, 1557 (1959). [l] The energy of formation is from the gaseous element at 0°K corrected for zero-point vibrational energies. The energies of formation are taken from "1953 Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Institute Research Project 44, Carnegie Press, Pittsburgh, Pa. The zero-point energy correction is made with the observed frequencies. [m] J. E. Douglas, B. S. Rabinovitch, and F. S. Looney, *J. Chem. Phys.*, **23**, 315 (1955). [n] The torsional frequencies are from R. McDiarmid and E. Charney, *ibid.*, **47**, 1516 (1967). The assignment of the stretching frequency is based on our interpretation of their experimental results (see ref 11). [o] The bond length of ethylene in the ${}^1B_{1u}$ state is based on our interpretation of the observed vibronic structure (see ref 11). [p] E. F. McCoy and I. G. Ross, *Aust. J. Chem.*, **15**, 573 (1962).

used for a large number of hydrocarbon molecules.[32] It would be helpful to have quantum-mechanical calculations to analyze the importance of the two types of effects.

The term $K_\phi^{(1)} \cos \phi$ in eq 34 was required to reduce the calculated splitting between the two out-of-plane ethylene frequencies B_{1u} and B_{2g}. Experimentally these two frequencies almost coincide at 949 and 943 cm^{-1},[30] respectively, while the calculation without $K_\phi^{(1)} \cos \phi$ gives a splitting of $\sim$140 cm^{-1} with B_{1u} at $\sim$880 cm^{-1} and B_{2g} at $\sim$1020 cm^{-1}. Variation of the out-of-plane parameter, K_χ, or of the torsional parameter, $K_\phi^{(2)}$, changes both frequencies but does not reduce the splitting between the two. The term $K_\phi^{(1)} \cos \phi$, which has no influence on the torsional motion since the contributions from the four ϕ_i around each C=C cancel each other, reduces the splitting to a more reasonable value (see Table III). Theoretically, such a term can be justified by use of a simple localized orbital description.[33]

It is of interest to point out that the inclusion of the variation of bond order with distance (eq 19) is of importance, not only for the final minimization of the potential with respect to the conformation, but also for certain vibrational effect. If this dependence is neglected (*i.e.*, eq 18 is used), parameters that yield reasonable values for the symmetric modes of benzene (*e.g.*, A_{1g} and E_{2g}) give incorrect results for the antisymmetric modes; *e.g.*, the B_{2u} mode is calculated to have a value of over 1600 cm^{-1}, while the experimental result is 1310 cm^{-1}.[34] To obtain the correct value for B_{2u}, it is necessary to introduce cross terms between the stretching of different bonds. Those resulting from the Urey–Bradley 1,3 interaction are much too small. However, the introduction of the polarizability contributions (eq 19), as originally suggested by Coulson and Longuet-Higgins,[35] produces part of the desired effect;

(32) T. Shimanouchi, *J. Chem. Phys.*, 17, 245, 734, 848 (1949).
(33) A. Warshel and S. Lifson, *Chem. Phys. Lett.*, 4, 255 (1969).
(34) R. B. Mair and D. R. Hornig, *J. Chem. Phys.*, 17, 1236 (1949).

e.g., a value for B_{2u} of 1460 cm^{-1} is obtained, while the E_{2g} frequency remains in good agreement with experiment (1596 cm^{-1} *vs.* the calculated value of 1614 cm^{-1}).

A difficulty in the present form of the method is that the calculated benzene ring puckering B_{2g} frequency tends to be too low; it is near 600 cm^{-1} while the experimental value[34] is 703 cm^{-1}. By contrast, other torsional frequencies which have larger components of hydrogen motion (*e.g.*, the other B_{2g} vibrations) are calculated to be at somewhat *higher* frequencies than the observed values. This may result from the assumption that the angle between the p_π orbitals on carbons C and C′ is related to a single τ angle which is equally dependent on =C—C=C—C= and H—C=C′—H torsional angles (see section Ib). The real situation is probably that the π energy is affected more by the puckering motion involving the =C—C=C—C= angles than the H—C=C—H angles. Thus, the disagreement may be due to the fitting of all the torsional frequencies with the same parameter, disregarding possible differences between the orbital following. However, it does not seem worthwhile to introduce such a refinement without more detailed consideration of σ,π interaction.

III. Applications

As tests of the present method, applications are given in this section to the ground states of *s-trans-* and *s-cis-*butadiene, the ground and first excited states of 1,3-cyclohexadiene and hexatriene, and the ground state of α,ω-diphenyloctatetraene. The 1,3-cyclohexadiene molecule is of interest because the presence of the ring leads to nonplanarity of the conjugated system. Thus, the molecule provides information important for the understanding of other sterically hindered conjugated molecules, such as the visual pigment 11-*cis* retinal. Correspondingly, hexatriene serves as a simple model of a large class of polyenes, of which α,ω-diphenyloctatetraene is another important example.

Butadiene. Although a variety of data for butadiene was used in determining the parameters, the difference in energy between s-cis and s-trans was not included. We have calculated the minimum energy conformations for the two geometries (see Table IV). We see that the bond lengths and angles are similar, but that there is a significant increase in the $C_1C_2C_3$ angle of s-cis relative to s-trans that relieves the steric repulsion in the former. In contrast to Dewar and Harget,[10] we find that the s-cis geometry does correspond to a shallow energy minimum; that is, the second derivative matrix **F** is positive definite for this geometry. As to the energy differences, the s-trans conformation potential energy is 0.6 kcal lower than that of s-cis. When the zero-point vibrational energy is included, the energy difference becomes 1.0 kcal, to be compared with the experimental estimate of 2.3 kcal.[36] Since the latter figure involves a variety of assumptions, it would be useful to have an improved determination. The potential energy barrier to go from s-trans to s-cis is calculated to be 10 kcal relative to s-trans, as compared with the estimate of 5 kcal.[36] Table IV also includes the vibrational frequencies for

Table IV. *s-cis-* and *s-trans-*1,3-Butadiene

	s-trans		s-cis		s-trans		s-cis
			Calculated Geometry[a]				
C_1–C_2	1.3415		1.3429	C_2–C_4–H_1	120.3		119.7
C_2–C_3	1.4790		1.4748	C_2–C_1–H_1	121.7		122.8
C_4–H_4	1.0856		1.0860	C_1–C_2–C_3	122.2		125.3
C_1–H_1	1.0851		1.0836	C_1–C_2–H_3	119.9		119.3
C_2–H_2	1.0848		1.0865	C_2–C_3–H_3	117.9		115.4
			Calculated Vibrational Frequencies[b]				
A_g	3080	A_1	3085	B_g	999	A_1	1035
	3063		3063		980		992
	2987		2988		680		523
	1680		1676	B_u	1067	B_2	1093
	1456		1456		932		1039
	1303		1305		541		690
	1228		1083		176		207
	877		884				
	545		354				
A_u	3094	B_1	3083				
	3062		2063				
	2988		2989				
	1616		1640				
	1401		1442				
	1303		1278				
	990		1057				
	353		633				

[a] Distances are given in ångströms; bond angles in degrees. [b] Vibrational frequencies are given in reciprocal centimeters.

the two geometries. Most of the corresponding frequencies are very similar, as expected. However, important differences do occur for some frequencies that have large contributions from the torsion about the single bond or from the bending of angles involving the single bond; *e.g.*, the lowest frequency of each symmetry type and the 1210-cm^{-1} A_g vibration in s-trans, which corresponds to 1081 cm^{-1} (A_1) in s-cis. The s-trans experimental results are given in Table III since they were used in the parameter fit; no s-cis data are available for comparison.

One point to note in the experimental comparison is that somewhat more exact agreement for vibrational frequencies with specifically fitted force fields can be obtained,[37] so that the present approach is not the one to use if one is concerned simply with the vibrational analysis of molecules of known structure. It is for the calculation of a wider class of properties, as well as for simultaneous determination of an unknown geometry and vibrational frequencies, that our more general treatment is most suitable.

1,3-Cyclohexadiene. The ground-state equilibrium was calculated for 1,3-cyclohexadiene and the results are given in Table V. Two calculated geometries are included because the difference in energy between them is found to be very small; that is, the calculated potential function has a flat minimum for a distorted half-chair conformation and changes in the $C_4C_5C_6C_1$ dihedral angle of ~10° yield a difference of only 0.1 kcal/mol. Figure 4 illustrates this result in a two-dimensional contour diagram, which gives the energy (kilocalories) as a function of the torsional angles $C_1C_2C_3C_4$ (ϕ_{2-3}) and $C_4C_5C_6C_1$ (ϕ_{5-6}). It can be seen that there is a large flat basis for ϕ_{2-3} in the region 8–16° and ϕ_{5-6} in the region 25–42°. The dominant

(35) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc., Ser. A*, **191**, 39 (1947); **193**, 456 (1948).

(36) J. G. Aston, G. Szasz, H. W. Wooley, and F. G. Brickwedde, *J. Chem. Phys.*, 14, 67 (1946).

(37) E. R. Lippincott, C. E. White, and J. P. Sibilia, *J. Amer. Chem. Soc.*, **80**, 2926 (1958); E. R. Lippincott and T. E. Kenney, *ibid.*, **84**, 3641 (1962); E. M. Popov and G. A. Kogan, *Opt. Spectrosc.*, 17, 362 (1964); R. M. Gavin, Jr., and S. A. Rice, *J Chem. Phys.*, **55**, 2675 (1971).

Table V. Ground-State Properties of 1,3-Cyclohexadiene[a]

	Geometry				
	Experimental			Calculated[b]	
	c	*d*	*e*	min (1)	min (2)
$C_1{=}C_2$	1.339	1.350	1.348	1.347	1.346
C_2—C_3	1.468	1.468	1.465	1.471	1.475
C_4—C_5	1.494	1.523	1.418	1.490	1.492
C_5—C_6	1.510	1.534	1.538	1.540	1.548
C_1—C_2—C_3	121.6	120.1	120.3	120.0	120.5
C_3—C_4—C_5	118.2	120.1	120.2	121.4	121.8
C_4—C_5—C_6	111.5	110.7	110.9	112.1	113.4
C_1—C_2—C_3—C_4	17.0	18.3	18.0	12	11
C_4—C_5—C_6—C_1			46	40	34

	Vibrational Frequencies				
	Calcd	Exptl[f,g]		Calcd	Exptl[f,g]
B	3090	3057	A	1208	1177*
A	3089	3043	B	1175	1165
B	3087	3057	A	1117	1150
A	3086	3043	B	1028	
B	2982	3009*	A	1005	1058
A	2964	2938	B	1000	1018
B	2947	2875	A	990	994
A	2937	2859	A	961	947
B	1680	1604	B	951	931
A	1635	1575	A	884	850
A	1460	1460*	B	784	748
B	1442	1428	A	718	755
A	1438	1439	B	652	663
B	1430	1408	A	611	561
B	1408	1372	B	529	478
A	1318	1326	A	491	508
B	1274	1316*	B	312	298
A	1259	1239	A	160	201

[a] The units are bond lengths in ångströms, bond angles in degrees, and vibrational frequencies in reciprocal centimeters. [b] See discussion in text. [c] Reference 38. [d] Reference 39. [e] Reference 40. [f] Reference 44. [g] The frequencies with an asterisk differ in assignment from that in footnote *f*; see text.

interactions leading to this form for the potential function are the competition between the tendency of the π system to be planar and the stabilization of a nonplanar geometry by the CCC ring angles and nonbonded hydrogen repulsions. The comparison with electron-diffraction experiments[38–40] shows satisfactory agreement for all bond lengths and bond angles. There are a number of apparent differences but it is difficult to determine their significance because of the large disagreements among the different experimental results. As to the torsional angle $C_1C_2C_3C_4$, the electron-diffraction results are interpreted to give a value of 17–18° and a partial microwave structure determination[41] yields 17°, all of which contrast with the calculated value of 11–12°. There is also a value of 14° from an X-ray structure for the 1,3-cyclohexadiene ring in the antibiotic gliotoxin.[42] As has been pointed out in the analyses of Traetteberg[40] and of Butcher,[41] the value of the torsional angle obtained by interpreting the electron diffraction or microwave data depends on the assumption of planarity for the two ethylenic groups, nonplanarity leading to a lower torsional angle. Our calculations suggest that deviations from planarity of

(38) G. Dallinga and L. H. Toneman, *J. Mol. Struct.*, 1, 11 (1967–1968).
(39) H. Oberhammer and S. H. Bauer, *J. Amer. Chem. Soc.*, 91, 10 (1969).
(40) M. Traetteberg, *Acta Chem. Scand.*, 22, 2305 (1968).
(41) S. S. Butcher, *J. Chem. Phys.*, 42, 1830 (1965).
(42) A. F. Beecham, J. Fridrichsons, and A. McL. Mathieson, *Tetrahedron Lett.*, 27, 3131 (1966).

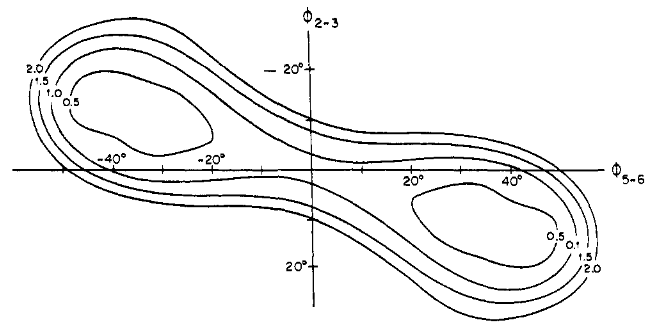


Figure 4. Calculated contour map for 1,3-cyclohexadiene showing the energy (kilocalories) as a function of the torsional angles $C_1C_2C_3C_4$ (ϕ_{2-3}) and $C_4C_5C_6C_1$ (ϕ_{5-6}); all other degrees of freedom have their minimized value for each choice of ϕ_{2-3} and ϕ_{5-6}.

~5° can occur. Also because of the rather flat form of potential discussed above, the calculated root-mean-square dihedral angle (at room temperature) is 14°. Thus, it is clear that both the analysis of the experiments and the comparison with the calculations are complicated by the possibility of large amplitude motion involving several degrees of freedom.[43]

The calculated vibrational frequencies for 1,3-cyclohexadiene are also given in Table V and compared with the measurements of DiLauro, Neto, and Califano.[44] The agreement between the calculated and the observed vibrational frequencies is generally good, though not quite as precise as that obtained by DiLauro, *et al.*, who used a valence-force field to fit the results for 1,3-cyclohexadiene. There is also some question concerning assignments. Our assignment of the experimental vibrational frequencies is similar to that of DiLauro, *et al.*; the differences, which are indicated in Table V, correspond to cases in which combination bands of DiLauro, *et al.*, are interpreted as fundamentals and/or a different symmetry choice is made; the system is such that both A and B vibrationals can be infrared and Raman active and that combination levels can be quite strong. To make a definitive interpretation of the vibrations, isotopically substituted species are needed.

It should be noted that the lower frequency vibrations (490, 300, 180 cm^{-1}) in 1,3-cyclohexadiene may all be rather inaccurate in the harmonic approximation. Of these, the lowest (160 cm^{-1}) corresponds to the $C_4C_5C_6C_1$ torsion, the next (300 cm^{-1}) to ring folding of $C_1C_2C_3C_4$ relative to $C_4C_5C_6C_1$, and the highest (490 cm^{-1}) to $C_1C_2C_3C_4$ torsion. All of these have double minimum potentials for which the barrier at the "planar" geometry is rather low; *e.g.*, it is 1 kcal for the 160-cm^{-1} torsion (see Figure 4). A more correct treatment would thus introduce a quartic oscillator or similar approximation for these vibrations. There is the added complication that there is also a very strong anharmonic coupling between torsional and bending modes. A similar effect of strong anharmonicity appears in other sterically hindered conjugated molecules (*e.g.*, 11-*cis* retinal) and may play an important role in determining their vibronic structure.

Ground State of Hexatriene and α,ω-Diphenyloctatetraene. The calculated ground-state structures of

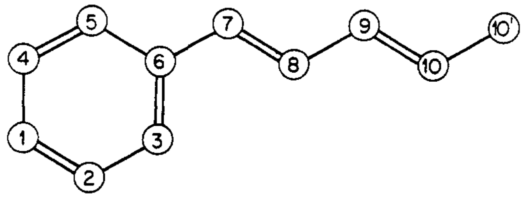
(43) For an example of the treatment of large amplitude motion in the interpretation of electron diffraction results, see A. Yokozeki, K. Kuchitsu, and Y. Morino, *Bull. Chem. Soc. Jap.*, 43, 2017 (1970).
(44) C. DiLauro, N. Neto, and S. Califano, *J. Mol. Struct.*, 3, 219 (1969).

1,3,5-*all-trans*-hexatriene and of α,ω-diphenyl-*all-trans*-octatraene are given in Table VI with the results of experimental measurements.[45,46] The CH bond lengths and the CCH bond angles are not included because unique experimental values are not available. From the table, it is clear that the general agreement is satisfactory. For hexatriene the ordering of the bond lengths is given correctly by the calculations, although the two "double" bonds are closer to each other in length than the experimental values and the "single" bond is somewhat too long. Also, the measured value of $C_2C_3C_4$ is significantly larger than the calculated result. For diphenyloctatetraene, both the ring and polyene chain bonds are well reproduced by the calculation. The calculated bond angles show generally reasonable agreement with experiment except in the middle of the chain (*i.e.*, $C_8C_9C_{10}$, $C_9C_{10}C_{10'}$), where the calculated values are somewhat smaller than the observed angles.

Table VI. Ground-State Structure of Hexatriene and Diphenyloctatetraene[a]

	1,3,5-Hexatriene Exptl[b]	Calcd
C_1–C_2	1.337	1.340
C_2–C_3	1.458	1.477
C_3–C_4	1.368	1.350
C_1–C_2–C_3	121.7	122.1
C_2–C_3–C_4	124.4	122.0

1,8-Diphenyl-1,3,5,7-octatetraene[c]



	Exptl[c]	Calcd		Exptl[c]	Calcd
C_1–C_2	1.391	1.402	C_3–C_6–C_5	118.2	118.6
C_2–C_3	1.387	1.403	C_2–C_3–C_5	120.9	120.3
C_3–C_6	1.404	1.415	C_4–C_5–C_6	121.1	120.6
C_2–C_4	1.398	1.403	C_1–C_4–C_5	119.7	119.8
C_4–C_5	1.392	1.400	C_3–C_6–C_7	122.7	122.6
C_5–C_6	1.405	1.415	C_5–C_6–C_7	119.2	118.6
C_6–C_7	1.468	1.482	C_6–C_7–C_8	126.8	125.1
C_7–C_8	1.350	1.353	C_7–C_8–C_9	123.9	121.0
C_8–C_9	1.438	1.468	C_8–C_9–C_{10}	124.8	122.4
C_9–C_{10}	1.359	1.355	C_9–C_{10}–$C_{10'}$	124.5	121.8
C_{10}–$C_{10'}$	1.441	1.467	C_5–C_6–C_7–C_8	4.9	2.5

[a] The units are bond lengths in ångströms and bond angles in degrees. [b] See ref 45. [c] See ref 46.

The most important point about including variation of bond angles in the calculation is the possibility of reducing steric repulsions by bond-angle distortion. Previous calculations of polyenes properties have assumed fixed bond angles so that steric effects manifested themselves only by changes in torsional angles. By minimization of the energy in the complete conformational space, the additional effect of bond-angle bending is introduced. An example of this is evident in the $C_6C_7C_8$ angle, which is very large (exptl 126.8°, calcd 125.1°) due to the C_3,C_8 hydrogen repulsion. The calculated ring torsion angle (2.5°) is somewhat smaller than the experimental value (5°); whether this is a real difference or a crystal effect is not clear since the potential function corresponds to a rather shallow minimum.

The calculated vibrational frequencies of 1,3,5-hexatrienes are compared with the experimental values[37] in Table VII. The agreement is similar to that for butadiene, which was used in the fitting procedure. This "conservation" of agreement implies that correspondingly accurate results are expected to be obtained for other polyenes.

Table VII. Vibrational Frequencies of Hexatriene[a]

	Exptl[b]	Calcd		Exptl[b]	Calcd
A_g	3085	3091	B_u	3091	3097
	3039	3078		3040	3081
	3039	3062		3012	3062
	2989	2987		3012	2987
	1623	1689		1623	1657
	1573	1606		1429	1448
	1394	1420		1294	1311
	1280	1353		1255	1290
	1238	1307		1130	1185
	1187	1216		941	947
	897	941		540[c]	587
	444	462			179
	347	393			
B_g	990	1035	A_u	1011	1089
	928	990		941	950
	897	861		899	922
	758[c]	603		658	642
	395[c]	231		475[c]	247
					109

[a] All frequencies in reciprocal centimeters. [b] See ref 37. [c] There is some question as to whether these frequencies are correctly assigned.

Excited States of Hexatriene and Cyclohexadiene. The details of the application of the present method to the excited states of conjugated molecules will be described in a subsequent paper together with analyses of the vibronic structure of electronic absorption bands. To provide an illustrative example of excited-state calculations, we present in Table VIII the calculated conformation and vibration frequencies of 1,3,5-hexatriene and 1,3-cyclohexadiene in their first-allowed excited electronic states. Compared with Table VI, we see that the most striking change in conformation on excitation of 1,3,5-hexatriene is the increase in length of the double bonds (C_1C_2 and C_3C_4) and the shortening of the single bond (C_2C_3); there is little change in the bond angles. There is also a significant reduction in the double-bond stretching frequencies (*e.g.*, the A_g ground-state frequencies 1689 and 1601 cm^{-1}). These results agree, as will be shown,[11] with the Franck–Condon factors and vibrational bands observed in the electronic spectrum.[47]

For 1,3-cyclohexatriene, similar changes in structure and vibrational frequencies are calculated. As expected, the C_2C_3 single bond is significantly shortened and the torsional angle is reduced. There are no quantitative experimental results for comparison because such a distorted, s-cis type of molecule has a diffuse vibronic structure in the excited state.[47]

(45) M. Tratteberg, *Acta Chem. Scand.*, 22, 628 (1968).
(46) W. Drenth and E. H. Weibenga, *Acta Crystallogr.*, 8, 755 (1955).
(47) H. Schuler, E. Lutz, and G. Arnold, *Spectrochim. Acta*, 17, 1043 (1961).

Table VIII. Calculated Geometry and Vibrational Frequencies of Hexatriene and Cyclohexadiene in First Excited Electronic State[a]

Conformation		Vibrational frequencies							
				1,3,5-Hexatriene					
C_1–C_2	1.389	A_g	3090	B_u	3093	B_g	953	A_u	1000
C_2–C_3	1.409		3078		3082		850		922
C_3–C_4	1.436		3062		3062		839		905
C_1–C_2–C_3	122.4		2984		2984		553		597
C_2–C_3–C_4	121.3		1596		1590		274		205
			1518		1466				111
			1396		1319				
			1345		1262				
			1292		1242				
			1203		933				
			944		566				
			453		173				
			386						
				1,3-Cyclohexadiene					
C_1–C_2	1.442	B	3090	A	1437	A	961		
C_2–C_3	1.388	A	3088	B	1427	B	947		
		B	3084	B	1399	A	878		
C_4–C_5	1.480	A	3083	A	1310	B	828		
C_5–C_6	1.540	B	2984	B	1278	B	758		
		A	2964	A	1250	A	690		
C_1–C_2–C_3	119.8	B	2948	A	1200	B	638		
C_3–C_4–C_5	122.3	A	2939	B	1170	A	592		
C_4–C_5–C_6	111.8	A	1600	A	1125	B	518		
		B	1543	A	1021	A	437		
C_1–C_2–C_3–C_4	5	A	1457	B	985	B	198		
C_4–C_5–C_6–C_1	30	B	1444	A	967	A	160		

[a] The units are bond lengths in ångströms, bond angles in degrees, and vibrational frequencies in reciprocal centimeters.

Appendix

$$\Delta V_\pi{}^N = \sum_\nu \Big\{ \Big[\sum_m (C^s{}_{Nm})^2 (v^s{}_{m_2}\nu^s{}_{m_2\nu} - v^s{}_{m_1\nu} v^s{}_{m_1\nu}) \Big] \times$$
$$({}^\lambda W(\mathrm{r}) + {}^1/{}_2 P^s{}_{\nu\nu}{}^\lambda\gamma_{\nu\nu}(\mathrm{r}) - \sum_{\mu\neq\nu} Q^s{}_\nu{}^\lambda\gamma_{\mu\nu}(\mathrm{r})) +$$
$$\Big[\sum_m (C^s{}_{Nm})^2 (v^s{}_{m_1\nu} v^s{}_{m_2\nu})^2 +$$
$$2\sum_{k>m} (C^s{}_{Nm} C^s{}_{Nk})(v^s{}_{m_1\nu} v^s{}_{m_2\nu} v^s{}_{k_1\nu} v^s{}_{k_2\nu}) \Big]^\lambda \gamma_{\nu\nu}(\mathrm{r}) \Big\} +$$
$$\sum_{\nu>\mu} 2 \sum_m (C^s{}_{Nm})^2 (v^s{}_{m_2\nu} v^s{}_{m_2\mu} - v^s{}_{m_1\nu} v^s{}_{m_1\mu})({}^\lambda\beta_{\nu\mu}(\mathrm{r}) -$$
$${}^1/{}_2 P^s{}_{\nu\mu}{}^\lambda\gamma_{\nu\mu}(\mathrm{r})) + \Big[\sum_m (C^s{}_{Nm})^2 (4 v^s{}_{m_1\nu} v^s{}_{m_1\mu} v^s{}_{m_2\nu} v^s{}_{m_2\mu} -$$
$$(v^s{}_{m_1\nu} v^s{}_{m_2\mu})^2 + (v^s{}_{m_1\mu} v^s{}_{m_2\nu})^2) \Big]^\lambda \gamma_{\nu\mu}(\mathrm{r}) +$$
$$\Big[\sum_{k>m} (C^s{}_{Nm} C^s{}_{Nk}) [4(v^s{}_{m_1\nu} v^s{}_{m_1\nu} v^s{}_{k_1\mu} v^s{}_{k_2\mu} +$$
$$v^s{}_{m_1\mu} v^s{}_{m_2\mu} v^s{}_{k_1\nu} v^s{}_{k_2\nu}) - 2(v^s{}_{m_1\nu} v^s{}_{m_2\mu} v^s{}_{k_1\nu} v^s{}_{k_2\mu} +$$
$$v^s{}_{m_1\mu} v^s{}_{m_2\nu} v^s{}_{k_1\mu} v^s{}_{k_2\nu}) \Big]^\lambda \gamma_{\nu\mu}(\mathrm{r})$$

$$\Delta V_\pi{}^N = \sum_\nu R^W{}_\nu{}^\lambda W(\mathrm{r}) + \sum_\nu R^\gamma{}_{\nu\nu}{}^\lambda\gamma^\gamma{}_{\nu\nu}(\mathrm{r}) +$$
$$\sum_{\nu>\mu} R^\beta{}_{\nu\mu}{}^\lambda\beta_{\nu\mu}(\mathrm{r}) + \sum_{\nu>\mu} R^\gamma{}_{\nu\mu}{}^\lambda\gamma_{\nu\mu}(\mathrm{r})$$

$$R^W{}_\nu = \sum_m (C^s{}_{Nm})^2 (v^s{}_{m_2\nu} v^s{}_{m_2\nu} - v^s{}_{m_1\nu} v^s{}_{m_1\nu})$$

$$R^\gamma{}_{\nu\nu} = \sum_m (C^s{}_{Nm})^2 [(v^s{}_{m_2\nu} v^s{}_{m_2\nu} - v^s{}_{m_1\nu} v^s{}_{m_1\nu}) \times$$
$$(P^s{}_{\nu\nu}/2) + (v^s{}_{m_1\nu} v^s{}_{m_2\nu})^2] +$$
$$\sum_{k>m} 2(C^s{}_{Nm} C^s{}_{Nk})(v^s{}_{m_1\nu} v^s{}_{m_2\nu} v^s{}_{k_1\nu} v^s{}_{k_2\nu})$$

$$R^\beta{}_{\nu\mu} = \sum_m (C^s{}_{Nm})^2 (v^s{}_{m_2\nu} v^s{}_{m_2\mu} - v^s{}_{m_1\nu} v^s{}_{m_1\mu})$$

$$R^\gamma{}_{\nu\mu} = \sum_m 2(C^s{}_{Nm})^2 \{ -(v^s{}_{m_2\nu} v^s{}_{m_2\mu} - v^s{}_{m_1\nu} v^s{}_{m_1\mu}) \times$$
$$(P^s{}_{\nu\mu}/2) + 2(v^s{}_{m_1\nu} v^s{}_{m_1\mu} v^s{}_{m_2\nu} v^s{}_{m_2\mu}) - ({}^1/{}_2)((v^s{}_{m_1\nu} v^s{}_{m_2\mu})^2 +$$
$$(v^s{}_{m_1\mu} v^s{}_{m_2\nu})) + (v^s{}_{m_2\nu} v^s{}_{m_2\nu} - v^s{}_{m_1\nu} v^s{}_{m_1\nu}) Q^s{}_\mu +$$
$$(v^s{}_{m_2\mu} v^s{}_{m_2\mu} - v^s{}_{m_1\mu} v^s{}_{m_1\mu}) Q^s{}_\nu \} +$$
$$\sum_{k>m} 2 C^s{}_{Nm} C^s{}_{Nk} \{ 2(v^s{}_{m_1\nu} v^s{}_{m_2\nu} v^s{}_{k_1\mu} v^s{}_{k_2\mu} +$$
$$v_{m_1\mu} v^s{}_{m_2\mu} v^s{}_{k_1\nu} v^s{}_{k_2\nu}) - (v^s{}_{m_1\nu} v^s{}_{m_2\mu} v^s{}_{k_1\nu} v^s{}_{k_2\mu} +$$
$$v^s{}_{m_1\mu} v^s{}_{m_2\nu} v^s{}_{k_1\mu} v^s{}_{k_2\nu}) \}$$