SCF MO Calculations on the *cis*-Butadiene-Ethylene

Charge-Transfer Complex

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The possible existence of a charge-transfer complex constituted by *cis*-butadiene and ethylene is discussed within the zero differential overlap approximation in the molecular orbital theory. By considering the resultant effect of stabilization due to conjugation, of core repulsion energy, and of van der Waals interactions, it is concluded that a complex made up of the two components situated in two parallel planes around 3 Å apart should be barely stable. The mutual orientation of the molecules in the two planes is given by the requirement that the carbon atoms of ethylene and the terminal carbon atoms of *cis*-butadiene are all in one plane perpendicular to the parallel ones.

Experimental studies of the kinetics of the Diels-Alder reaction have shown that the mutual orientation of the diene and the dienophile during their interaction leading to a transition state complex, is highly specific.[1] The nature of such complexes has been studied extensively,[2-5] and it has been assumed that the diene with its four π-electrons and the dienophile with its two π-electrons should be able to form a stable complex of charge-transfer type.

The actual geometry of the diene-dienophile complex, which is an intermediate in the formation of a cyclic adduct, has been the subject of considerable interest.[6] Due to steric hindrance a planar complex yielding a favourable model for the 4+2 cycloaddition has to be ruled out. Such a model is also not in agreement with the geometry of the final adduct. Kinetic studies of the retrodienic dissociation reaction have namely demonstrated that the geometry of the ground state of the adduct is similar to that of the transition state.[7] Furthermore it is natural to assume that a corresponding geometry should be exhibited by the charge-transfer complex. The existence of a non-planar complex leads to the conclusion that the formation of the new bonds is a result of a partial σ-type interaction between the π-electrons of the interacting components.

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Recently the mechanism of the Diels-Alder reaction has been discussed by one of us within the conventional Hückel approximation.[8-10] In these studies it was concluded that there is a linear relation between the energy of activation for the interaction of cyclopentadiene and various dienophiles and the energy of delocalization in the respective complexes. The obtained results concerning the problem of endo-exo isomerism were in agreement with Alder's "endo addition rule". A population analysis performed, demonstrated a transfer of electronic charge from the diene to the dienophile component.

The purpose of the present paper is to carry through calculations of the energy and the charge transfer in the ethylene *cis*-butadiene π-complex by using the Pariser-Parr-Pople approximation in the SCF MO theory. Core repulsions and van der Waals interactions are also included.

METHOD OF CALCULATION

The underlying model assumed for the complex is shown in Fig. 1. The two components are situated in parallel planes in such a way that the carbon
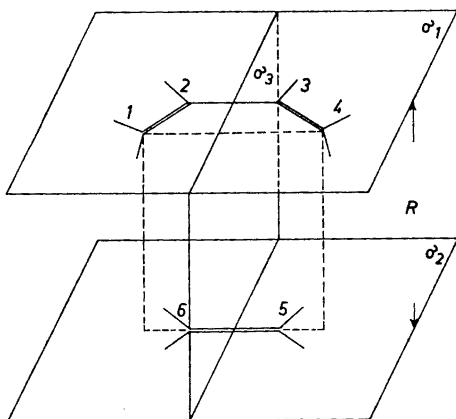

Fig. 1. Mutual position of the interacting molecules, and labelling of the atoms. The plane through the atoms 1, 4, 5, and 6 is orthogonal to the parallel planes σ_1 and σ_2. The plane σ_3 is a mirror plane for both molecules.

atoms of ethylene and the terminal carbon atoms of *cis*-butadiene are situated in one plane orthogonal to the parallel ones. This model is identical with the one discussed by Hoffmann and Woodward.[11]

The part of the energy of the complex depending on the distance between the parallel planes, R, has been decomposed as follows

$$E(R) = E_\pi(R) + E_{core}(R) + E_W(R) \tag{1}$$

where

$$E_\pi(R) = E_\pi^{compl.}(R) - [E_\pi^A + E_\pi^B] \tag{2}$$

$$E_{core}(R) = E_{core}^{compl.}(R) - [E_{core}^A + E_{core}^B] \tag{3}$$

and

$$E_W(R) = E_W^{compl.}(R) - [E_W^A + E_W^B] \tag{4}$$

In eqns. (1)—(4) the terms carrying superscripts A and B refer to the appropriate energies for the diene and dienophile component, respectively.

The semi-empirical parameters pertinent to the π-electron system, which varied as a function of the interplane distance R, were evaluated in a range of R-values from 2.0 Å to 4.0 Å with steps of 0.1 Å. For each parameter set thus obtained, the SCF equations were solved. The total wave function was approximated by a single determinant. The iterative solutions of the SCF equations were evaluated on a CDC 3300 computer by means of a programme written by Drs. B. Roos an T. Alm, and kindly put at our disposal. The van der Waals interactions were evaluated numerically on the same computer by means of a separate programme, written by Mr. R. Stølevik.

Choice of parameters. The semi-empirical parameters for the complex may be divided into two groups: 1) the intra-molecular parameters and 2) the inter-molecular parameters. The parameters belonging to the first group were determined for the isolated molecules, and they were kept fixed during the variation of the interplane distance R. This implies that deformations of the electronic distributions in the components due to the mutual interactions were neglected. Because of the assumption of zero differential overlap, the only two-electron integrals to be considered are of Coulomb type. For the one-center integral we have used the value 11.97 eV [12] which is based on atomic spectral data. For internuclear distances shorter than 2.8 Å a quadratic interpolation formula fitted to theoretical values at larger distances was applied. The remaining integrals of this kind were estimated by the uniformly charged sphere approximation, using orbital exponents based on Slater's rules.

In order to obtain a proper treatment of the inter-molecular two-electron integrals, the $2p\pi$-orbitals of the respective atoms have to be decomposed as illustrated in Fig. 2. This procedure leads to the following expression

$$(\mu\mu \,|\, \nu\nu)_\alpha = (\mu_\pi\mu_\pi \,|\, \nu_\pi\nu_\pi)\sin^4\alpha + (\mu_\sigma\mu_\sigma \,|\, \nu_\sigma\nu_\sigma)\cos^4\alpha$$
$$+ 2(\mu_\pi\mu_\pi \,|\, \nu_\sigma\nu_\sigma)\sin^2\alpha\,\cos^2\alpha + 4(\mu_\pi\mu_\sigma \,|\, \nu_\pi\nu_\sigma)\sin^2\alpha\,\cos^2\alpha \qquad (5)$$

where the angle α is defined in Fig. 2, and the remaining symbols have their usual meaning. The integrals $(\mu_\sigma\mu_\sigma \,|\, \nu_\sigma\nu_\sigma)$ and $(\mu_\pi\mu_\pi \,|\, \nu_\sigma\nu_\sigma)$ were estimated
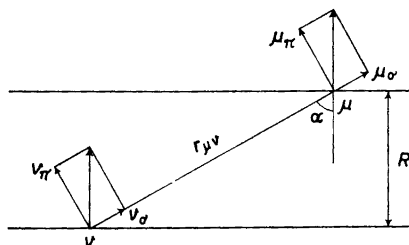

Fig. 2. Illustration of the way in which the basic atomic orbitals centered on atoms μ and ν are decomposed into π and σ-parts.

by a polynomial of second degree the coefficients of which were determined by a similar procedure as mentioned above. For the one-center integral $(\mu_\pi\mu_\pi \,|\, \mu_\sigma\mu_\sigma)$ the value 10.68 eV [12] was adopted. Theoretical values were employed for the integrals $(\mu_\pi\mu_\sigma \,/\, \nu_\pi\nu_\sigma)$ due to their small magnitudes.

As each atom contributes only one electron to the π-electron system, the diagonal elements of the core operator may, according to Goeppert-Mayer and Sklar,[13] be decomposed as

$$\alpha_\mu = W_\mu - \sum_{\nu \neq \mu} (\mu\mu \mid \nu\nu) \tag{6}$$

where W_μ may be defined by an approximate atomic valence state eigenvalue problem. However, we have estimated this parameter, and also the core resonance integral, β_0, by use of experimental values for the first ionization potential and the lowest singlet-singlet transition in ethylene. For this molecule the following relations are valid:

$$(\text{IP}) = W_\text{C} - \beta_0 - \tfrac{1}{2}[(11 \mid 11) - (11 \mid 22)] \tag{7}$$

and

$$\Delta^1 E(\pi \rightarrow \pi^*) = -2\beta_0 + \tfrac{1}{2}[(11 \mid 11) - (11 \mid 22)] \tag{8}$$

where the C-atoms in ethylene are labelled 1 and 2. The experimental values applied are 10.48 eV [14] and 7.62 eV [15] for the molecular ionization potential and the $\pi \rightarrow \pi^*$ transition, respectively. These assumptions lead to the value $W_\text{C} = -9.64$ eV which has been considered to be the same for all the carbon atoms in the complex. For β_0 the value -2.80 eV was obtained. The core resonance integrals for the remaining internuclear distances, all included, were evaluated by the simple relation

$$\beta_{\mu\nu} = \beta_0 S_{\mu\nu}/S_0 \tag{9}$$

where β_0 and S_0 refer to the ethylene molecule. The inter-molecular overlap integrals were decomposed in a way analogous to the treatment of the two-electron integrals:

$$S_{\mu\nu} = S_{\mu\nu}{}^{\pi\pi} \sin^2\alpha + S_{\mu\nu}{}^{\sigma\sigma} \cos^2\alpha \tag{10}$$

The repulsion between the positively charged core atoms has been estimated by using two different approximations. In one case the core energy was equated to the sum of the two-electron two-center integrals. This model yields the expression

$$E_\text{core}^{(\gamma)}(R) = 2\sum_{i=1}^{4} (\text{ii} \mid 55) \tag{11}$$

The other approximation was based on a pure point-charge model leading to

$$E_\text{core}^{(r)}(R) = 2\sum_{i=1}^{4} \frac{1}{r_{i5}} \tag{12}$$

in atomic units.

Van der Waals interactions. The contribution of van der Waals interactions to the energy of the complex has been estimated by a function of the type recently suggested by Scott and Sheraga [16]

$$E_W = \sum_{\mu < \nu} [a_{\mu\nu} \exp(-b_{\mu\nu} r_{\mu\nu}) - c_{\mu\nu} r_{\mu\nu}{}^{-6}] \tag{13}$$

Here the sum extends over all the pairs of atoms μ and ν, the distances between which are $r_{\mu\nu}$. The parameters $a_{\mu\nu}$, $b_{\mu\nu}$, and $c_{\mu\nu}$ depend on the nature of the atoms. In the evaluation of these parameters we have followed the scheme suggested by Scott and Sheraga, and the parameter values thus obtained are presented in Table 1. See also Ref. 17.

Table 1. Parameters in the potential function given by eqn. (13). Interaction energy in kcal/mole.

Interaction			
$H \cdots H$	9.17×10^3	4.54	45.2
$H \cdots C(sp^2)$	$78.1 \ \times 10^3$	4.56	211.0
$C(sp^2) \cdots C(sp^2)$	$16.0 \ \times 10^5$	4.59	756.97

RESULTS AND DISCUSSION

The energy function $E(R)$. As revealed by eqn. (1) the total energy of the complex may conveniently be decomposed into different terms. Evidently the variation of $E(R)$ will depend on the behaviour of each of the three components by changing values of R. We consider each of the terms in turn.

The term $E_\pi(R)$ given by eqn. (2) is clearly a function of the semi-empirical parameters entering the calculation of the π-electron system. Furthermore, in the particular case studied here, the variation of the parameters by a changing geometry of the complex will be decisive for the behaviour of the function $E_\pi(R)$.

The scheme chosen for the evaluation of the parameters is a very simple one. This particular choice is dictated by the fact that we are describing a complex which is built up in such a way that the electronic interactions are described in terms of orbitals of both σ- and π-character.

The parameter β has been included for all interactions across the region between the two molecules. Resonance interactions of this kind have to be included in order to avoid a model consisting of two isolated molecules. As most of the interatomic distances between the molecules are of the same order of magnitude for a given value of R, we found it desirable to include all the β's. This model is in accordance with Alder's "endo addition rule" which is firmly established.

To make the calculations strictly consistent with the zero differential overlap approximation, the "atomic" parameter W defined by eqn. (6) should be corrected for perturbations due to the neighbours.[18] However, in this case such corrections may safely be considered as having a negligible effect on the variation of E_π as a function of R. Due to the assumption of a fixed internal geometry of each of the components, the corrections imposed on W by neighbours within a component will be independent of the parameter R. The R-dependent corrections induced by the atoms of the neighbour component will also be of minor importance.

It is extremely difficult to give a quantitative estimate of the function $E_\pi(R)$ as it appears as a very small difference between numbers which are themselves uncertain. However, the approximations involved in the calculation of the matrix elements of the Fock operator for the components as well as for the complex are similar in nature. Consequently, one might expect most of the errors to be cancelled by forming the differences. This assumption should be particularly valid in this case where no hetero-atoms are present. A graph of the function $E_\pi(R)$ is presented in Fig. 3.

As mentioned above the core energy function has been estimated in two different ways, leading to two different sets of values. As expected the two-electron two-center integral approximation to $E_{core}(R)$ shown by eqn. (11) gives a less steep curve than the point charge model described by the inverse of the interatomic distances. The two curves are shown in Fig. 3. By using the first of these two approximations to the core-energy, the possible errors present in the two-electron integrals are at least partially cancelled. Consequently this model may be considered as the most realistic one.
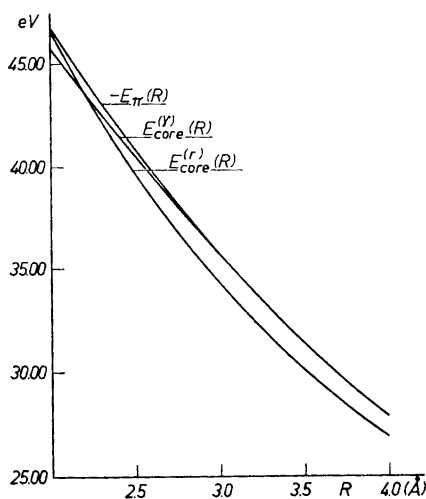

Fig. 3. Graphs of the functions $-E_\pi(R)$, $E_{core}^{(\gamma)}(R)$ and $E_{core}^{(r)}(R)$. For definition of the functions, see eqns. (2), (3), (11), and (12).
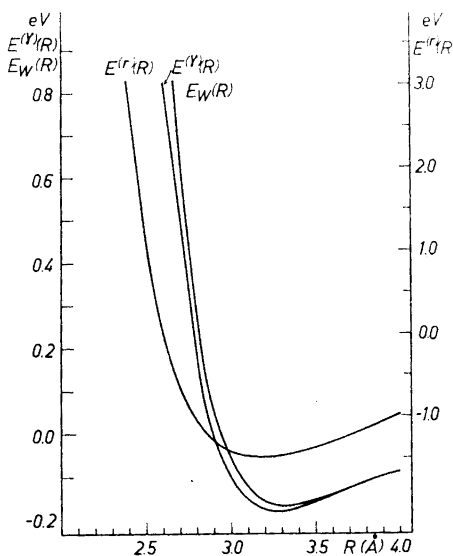
Fig. 4. Graphs of the functions $E^{(r)}(R)$, $E^{(\gamma)}(R)$, and $E_W(R)$. For definition of the functions see eqns. (1), (11), (12), and (13).

A quantitative estimate of the van der Waals interactions is rather difficult to perform. From the variety of interaction potentials suggested in the literature we have chosen the recent one introduced by Scott and Sheraga. Their functions, which ascribe a medium softness to the interacting atoms, may be said to represent typical averages of potential functions of this kind. Accordingly, these functions should be considered as realistic approximations to the

interactions studied here. The curve representing the function $E_W(R)$ is shown in Fig. 4.

The sum of the three terms discussed above yield the total energy function $E(R)$. In Fig. 4 the graph of two such functions, $E^{(\gamma)}(R)$ and $E^{(r)}(R)$, one for each of the chosen core-energy models, are shown. The two curves differ in some respects, but both show a rather well defined minimum at R-values around 3.20—3.30 Å. Furthermore, both functions lead to a negative minimum value of the total energy function. This implies that the system is predicted to have a net stabilization energy.

As to the magnitude of this energy, the two models differ appreciably. The two-electron integral approximation to $E_{core}(R)$, given by eqn. (11) leads to a value of around 4 kcal/mole, whereas the other model yields a value of 34 kcal/mole. From all the chemical and physical information available for such systems, it is safe to conclude that the latter value is far too high. This circumstance may be referred to an inadequacy of the point-charge model for the core energy.

It may be added, however, that for a system consisting of two rather weakly interacting, separate molecules, the effective van der Waals radii of the interacting atoms probably have to be considered as larger than those appropriate for an intramolecular situation. By using such a "hard" potential function, the calculated stabilization energies will be lowered. This fact, and other assumptions made, indicate clearly that the numbers obtained for the different energy terms should be interpreted with great reservations. A relaxation of the requirement of a fixed internal geometry would lead to an increased stabilization.

It is, however, rather satisfactory that previous considerations of systems of this kind have lead to conclusions in qualitative agreement with ours. Thus on the basis of dipole-dipole interactions Wasserman has found a value of around 2—3 kcal/mole for non-bonding diene-dienophile attraction.[19] Furthermore, in a general treatment of charge transfer complexes Mulliken has derived a value of 3.4 to 3.5 Å for the equilibrium distance.[20]

For the lowest R-values considered here, the function $E(R)$ shows a strongly increasing repulsive trend. It is hardly possible to discuss this part of the curve within the framework of the present calculations. By such short internuclear distances, a closer study of the electronic structures of the interacting species is required.

Analysis of charge transfer. In the formation of a complex of this kind it is fairly well established that the reaction centers are located at the atomic positions 1, 4, 5, 6 given in Fig. 1.

Previous calculations within the Hückel approximation [8-10] have shown that there is a transfer of electronic charge from the diene to the dienophile component of the complex. The magnitude of the charge transfer is dependent on the nature of the components and of the distance between them. These conclusions are in accordance with Woodwards hypothesis [4] for the mechanism underlying the Diels-Alder reaction.

The transfer of electronic charge from *cis*-butadiene to ethylene as a function of the interplane distance R is shown in Fig. 5. The net charge on an atom μ, ξ_μ, is defined by

$$\xi_\mu = 1 - 2 \sum_i c^2_{\mu i} \qquad (13)$$

where the sum extends over all the occupied molecular orbitals, and where $c_{\mu i}$ is the coefficient of the μ'th atomic orbital in the i'th molecular orbital. The total charge of the molecule is given by

$$Q = \sum_\mu \xi_\mu \qquad (14)$$

where the sum is taken over all the atoms in the molecule.

As revealed by Fig. 5, the charge on atoms 2 and 3 in the butadiene molecule is nearly invariable by a change in R. Thus it is clearly demonstrated that
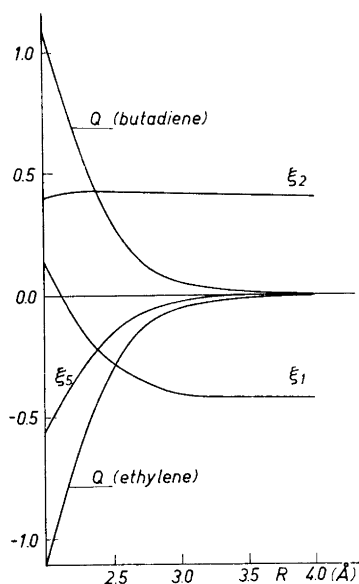

Fig. 5. Graphs of the variation of atomic and molecular π-electron charges as a function of the interplane distance R.
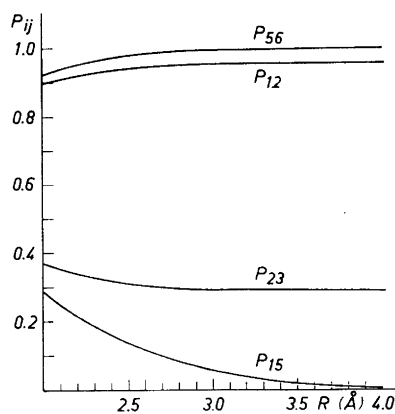
Fig. 6. Graphs of the variation of the different mobile bond orders as a function of the interplane distance R.

the charge transfer takes place between the four reaction centers 1, 4, 5, and 6. At a distance of $R=4$ Å there is no charge transfer in this system. This implies that the interaction between the molecules outside this region is small enough to be disregarded.

The variation of mobile bond orders for the different bonds as a function of the interplane distance R is given in Fig. 6.

The curves presented show a decrease in the π-electron population of the double bonds in both butadiene and ethylene as the molecules approach

another. This emptying of the double bonds is accompanied by increasing bond orders for the formal single bond 2—3, and the region 1—6 between the components. This trend in the flow of electrons is in conformity with the electronic distribution in the final adduct.

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