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A Study of Interaction of Two Ethylene Molecules by the Semiempirical Complete Configuration Interaction Method in π-Electron Approximation

By

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The semiempirical complete configuration interaction method in π-electron approximation has been used to calculate the energies of states of a system composed of two interacting ethylene molecules and having the D_{2h} symmetry. Oscillator strengths for the allowed transitions have been also calculated. If conjugation effects between the ethylene molecules are disregarded the hypochromism found by Nesbet is not obtained in this higher approximation. Consideration of conjugation effects results in hypochromism of the longest-wavelength allowed transition. The bathochromic shift of this band occurs at smaller distances between the two ethylene molecules than the hypochromic effect. Some general features of transannular interaction and the rôle of conjugation effects in the hypochromism of helical polynucleotides are discussed. The qualitative similarity of the cyclobutadiene energy spectra calculated by the semiempirical and by the theoretical methods of complete configuration interaction is pointed out.

Mittels der halbempirischen Methode der vollständigen Konfigurationswechselwirkung wurden die Eigenwerte der Energie eines Systems von π-Elektronen, bestehend aus zwei äthylenmolekülen mit der Symmetrie D_{2h}, sowie die Oszillatorstärke erlaubter Übergänge berechnet. Bei Vernachlässigung der Konjugationseffekte tritt der hypochrome Effekt Nesbets in dieser höheren Näherung nicht auf. Berücksichtigung von Konjugationseffekten ergibt eine Intensitätsschwächung der Bande des langwelligsten erlaubten Überganges. Bei dieser Bande überwiegt bei kleinem Abstand der Äthylenmoleküle der bathochrome Effekt. Einige allgemeine Aspekte transannularer Wechselwirkung und die Rolle von Konjugationseffekten im Hypochromismus spiraliger Polynukleotide werden erörtert. Die qualitative Ähnlichkeit von Cyclobutadienspektren, die einerseits nach der halbempirischen, andererseits nach der theoretischen Methode der vollständigen Konfigurationswechselwirkung berechnet wurden, wird aufgezeigt.

A l'aide de la méthode semiempirique de l'interaction de configuration complète, les valeurs propres de l'énergie d'un système d'électrons π, consistant en deux molécules d'éthylène et ayant la symétrie D_{2h}, et les forces oscillatrices des transitions permises ont été calculées. Si l'on néglige les effets de conjugaison, l'effet hypochrome de Nesbet n'apparaît pas dans cette approximation élevée. Si l'on tient compte des effets de conjugaison, il en résulte une diminution de l'intensité de la transition permise de plus grande longueur d'onde. Dans le cas de cette bande, l'effet bathochrome l'emporte, quand la distance entre les molécules d'éthylène est petite. Quelques aspects communs des interactions transannulaires et le rôle des effets de conjugaison dans l'hypochromisme des polynucléotides en hélice sont discutés. On montre la ressemblance qualitative entre les spectres du cyclobutadiène, calculés et par la méthode semiempirique et par la méthode théorique de l'interaction de configuration complète.

1. Introduction

This paper treats a system of two interacting ethylene molecules by the semiempirical complete configuration interaction (CCI) method in π-electron approximation in order to examine the effect of inclusion of higher excited configurations in the case of a system where transannular interaction occurs. By taking into account the conjugation effects the present paper complements the work of **Nesbet** [*19*] and generalizes it also by considering a higher number of configurations. Similarly as in **Nesbet**'s paper [*19*], the system studied may be regarded as a very simple model of interactions significant also for the explanation of hypochromism of helical polynucleotides [*5, 24, 27*]. Finally, cyclobutadiene is a limiting case of the system considered, which permits a comparison of **Craig**'s results [*1*] obtained by the theoretical CCI method with results of the analogous semiempriical method.

2. Model and Method of Calculation

Let us consider two ethylene molecules. Carbon atoms of these molecules lie in the vertices of a rectangular (Fig. 1). We take 1.33 Å for the length of the ethylene double bond and a variable parameter a for the distance between the two molecules. Molecular orbitals in the π-electron approximation (LCAO) are determined by symmetry:

$$\psi_k^n = \frac{1}{2} \sum_{\nu=0}^{1} \sum_{\mu=0}^{1} (-1)^{k\mu + n\nu} \chi_\mu^\nu = \frac{1}{\sqrt{2}} \sum_{\nu=0}^{1} (-1)^{n\nu} u_k^\nu ; \; (k, n = 0,1) \tag{1}$$

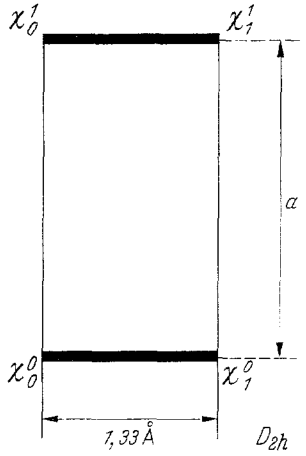

Fig. 1. The adopted model of two interacting ethylene molecules

where the subscript at the p_z atomic orbital χ_μ^ν distinguishes between various orbitals in the same molecule and the superscript denotes the respective ethylene molecule (cf. Fig. 1). u_k^ν is a molecular orbital of the ν-th ethylene molecule (a bonding molecular orbital if $k = 0$, an antibonding orbital if $k = 1$).

We shall be interested in singlet states only. We shall therefore find those linear combinations of **Slater** determinants formed from molecular orbitals ψ_k^n, which are eigenfunctions of the operator $\boldsymbol{S}^2$ belonging to a zero eigenvalue. The functions obtained may be further used to set up linear combinations, which can be easily interpreted in terms of the exciton nomenclature [*4, 17*]. Functions belonging to the irreducible representations of the D_{2h} group may be written symbolically as follows:

$$A_{1g}\colon \{0,0\} = O_{00} \cap O_{11}; \; \{0,2\}_0 = V_{00} \cap V_{11};$$

$$\{0,4\} = B_{00} \cap B_{11};$$

$$T = \frac{1}{\sqrt{3}} (T_{00}^{+} \cap T_{11}^{-} + T_{00}^{-} \cap T_{11}^{+} - T_{00}^{0} \cap T_{11}^{0});$$

$$\left.\begin{array}{l} A_{1g}\ (+) \\ \\ B_{2u}\ (-) \end{array}\right\} \colon \quad \begin{array}{l} \{0,2\}_1^{\pm} = \dfrac{1}{\sqrt{2}} (O_{00} \cap B_{11} \pm O_{11} \cap B_{00}) \\ \{1,2\}_p^{\pm} = \dfrac{1}{2} \, [O_{01} \cap (B_{00} \pm B_{11}) - (-1)^p B_{01} \cap (O_{00} \pm O_{11})], \quad p = 0,1; \end{array}$$

$$\{2,2\}^{\pm} = \frac{1}{\sqrt{2}} (O_{00} \cap B_{00} \pm O_{11} \cap B_{11}); \tag{2}$$

$$\left.\begin{array}{l} B_{3u}\,(+) \\ B_{1g}\,(-) \end{array}\right| : \begin{array}{l} \{0,1\}^{\pm} = \frac{1}{\sqrt{2}}(O_{00} \cap V_{11} \pm O_{11} \cap V_{00}); \\ \{0,3\}^{\pm} = \frac{1}{\sqrt{2}}(B_{00} \cap V_{11} \pm B_{11} \cap V_{00}); \\ \{1,1\}^{\pm} = \frac{1}{\sqrt{2}}(O_{00} \cap V_{10} \pm O_{11} \cap V_{01}); \\ \{1,3\}^{\pm} = \frac{1}{\sqrt{2}}(B_{00} \cap V_{01} \pm B_{11} \cap V_{10}). \end{array}$$

The symbol $\{i, j\}_p$ denotes a function corresponding to the state in which the ethylene molecules have $\pm\, i$ elementary charges and in which there are j electrons in the virtual states of both ethylenes. Accordingly, the function $\{i, j\}$ is a linear combination of SLATER determinants corresponding to j times excited configurations in the MO description. This notation is unambiguous as far as there is no crossing of levels arisen by splitting of energy levels of the frontier molecular orbitals of the isolated molecules, i.e. for $a > 1.33$ Å. The subscript p is added to differentiate functions characterized by the same values of both i and j. The functions O_{ij}, V_{ij}, B_{ij}, T_{ii} are defined as follows:

$$\begin{aligned} O_{ij} &= 2^{\frac{1}{2}|i-j|-1}\left(|u_0^i\,\bar{u}_0^j| + |u_0^j\,\bar{u}_0^i|\right); \\ \left.\begin{array}{l} V_{ij} \\ T_{ij}^0 \end{array}\right\} &= 2^{-\frac{1}{2}}\left(|u_0^i\,\bar{u}_1^j| \pm |u_1^j\,\bar{u}_0^i|\right); \qquad (3) \\ B_{ij} &= 2^{\frac{1}{2}|i-j|-1}\left(|u_1^i\,\bar{u}_1^j| + |u_1^j\,\bar{u}_1^i|\right); \\ T_{ii}^{+} &= |u_0^i\,u_1^i|;\ T_{ii}^{-} = |\bar{u}_0^i\,\bar{u}_1^i| \end{aligned}$$

where $|a, b|$ denotes normalized SLATER determinants constructed from one-electron spin-orbitals a, b. The symbol $A \cap B$ means

$$A \cap B = (3!)^{-\frac{1}{2}} \sum^{i_1 < i_2} (-1)^{1+i_1+i_2} A\,(i_1, i_2)\, B\,(i_3, i_4) \qquad (4)$$

where i_k ($k = 1, \cdots 4$) are coordinates of the electrons ($i_3, i_4 \neq i_1, i_2$).

The functions O_{ii}, V_{ii}, T_{ii}, B_{ii} may be simply interpreted as wave functions of the i-th ethylene molecule: O_{ii} corresponds to the ground state configuration, V_{ii} and T_{ii} to a singly excited configuration (singlet and triplet respectively), B_{ii} to the doubly excited configuration. The functions O_{01}, V_{01}, V_{10}, B_{01} appear only in functions of the $\{1, j\}$ type and in T, which are not locally singlet. The functions (2) may be constructed directly starting with all possible "products" $A \cap B$ [cf. Eq. (4)] of the functions O_{ii}, V_{ii}, B_{ii}, T_{ii} ($i = 0$ or 1), O_{01}, V_{01}, V_{10}, B_{01}, which result in singlet functions of the system. Obviously, the following relations hold:

$$\begin{aligned} &O_{ii} \cap O_{ij} = B_{ii} \cap B_{ij} = O_{ii} \cap V_{ij} = B_{ii} \cap V_{ji} = 0; \\ &O_{01} \cap V_{ik} = -\frac{1}{\sqrt{2}} O_{ii} \cap V_{\bar{i}k},\ B_{01} \cap V_{ik} = -\frac{1}{\sqrt{2}} B_{kk} \cap V_{i\bar{k}}; \\ &V_{ii} \cap V_{ii} = -\frac{1}{\sqrt{2}} O_{ii} \cap B_{\bar{i}i},\ V_{i\bar{i}} \cap V_{\bar{i}\bar{i}} = -\frac{1}{\sqrt{2}} B_{ii} \cap O_{i\bar{i}}; \qquad (5) \end{aligned}$$

$$V_{i\bar{i}} \cap V_{i\bar{i}} = -O_{ii} \cap B_{\bar{i}\bar{i}};$$

$$O_{01} \cap B_{01} = -\frac{1}{2}(V_{00} \cap V_{11} + \sqrt{3}\ T)$$

$$V_{01} \cap V_{10} = -\frac{1}{2}(V_{00} \cap V_{11} - \sqrt{3}\ T)$$

where $\bar{i} = 1$ if $i = 0$ and vice versa. It may further be shown that the function T is the only singlet one among the linear combinations of locally triplet functions (3). These products then have to be used in construction of linear combinations belonging to the irreducible representations of the group of symmetry operations which transform one ethylene molecule into the other. In our case even the C_{1h} (or C_2) group has this property. The functions V_{ik} are antisymmetrical with regard to the plane going though the centres of the ethylene bonds and perpendicular to the plane in which the ethylene molecules lie. Therefore, the functions of the $\{i, 1\}$ and $\{i, 3\}$ types are antisymmetrical with regard to this operation. Neglecting the differential overlap as usual [*22, 23*], the matrix elements of the Hamiltonian of the system in the representation of the "exciton" functions (2) $\langle \{ij\} | \boldsymbol{H} | \{kl\} \rangle$ may be derived easily (cf. Appendix).

The electron repulsion integrals of the Coulomb type

$$\gamma_{\mu\nu}^{\varkappa\lambda} = \int | \chi_\mu^\varkappa (1) |^2 \frac{1}{r_{12}} | \chi_\nu^\lambda (2) |^2 \, d\tau_{12} \tag{6}$$

were estimated according to Mataga and Nishimoto [*16*] (cf. also [*9*]). This estimate proved useful in the studies of spectra of aromatic hydrocarbons [*10, 11*] and of transannular interaction [*9, 20*].

As for the resonance integrals $\beta_{\mu\nu}^{\varkappa\lambda}$,

$$\beta_{\mu\nu}^{\varkappa\lambda} = \int \chi_\mu^\varkappa \, H_{core} \, \chi_\nu^\lambda \, d\tau \tag{7}$$

we took the value -2.430 eV for β_{01}^{00}, which gives agreement with experiment for the first excitation energy of ethylene as calculated in the approximation considering only monoexcited configurations. Moreover, we carried out the computations using the value of $\beta_{01}^{00} = -2.034$ eV, which gives agreement with experiment for ethylene when the doubly excited state is taken into consideration.

The remaining resonance integrals $\beta_{\mu\nu}^{01}$ were estimated by means of the relation

$$\frac{\beta_{\mu\nu}^{01}}{\beta_{12}^{00}} = \frac{S_{\mu\nu}^{01}}{S_{12}^{00}} \tag{8}$$

where

$$S_{\mu\nu}^{\varkappa\lambda} = \int \chi_\mu^\varkappa \, \chi^\lambda \, d\tau. \tag{9}$$

Atomic $2p_z$ orbitals $\chi_\mu^\varkappa$ according to Morse, Young and Haurwitz [*18*] with effective charge $\gamma = 1.51$ were used in the calculation of the overlap integrals $S_{\mu\nu}^{\varkappa\lambda}$.

Two orientations of the ethylene molecules were considered: in the first case, the nodal plane of all four p_z orbitals coincides with the plane of the four carbon nuclei (π-orientation), in the second one, the common nodal plane of two p_z orbitals belonging to the atoms of one of the ethylene molecules is perpendicular to the plane of the carbon nuclei (σ-orientation).

For both orientations, calculations were carried out for the distance a between the two ethylene molecules varying from 2.0 to 5.0 Å (at 0.5 Å intervals); for the

Table. *Comparison with* Craig*'s Calculations of Cyclobutadiene [1]. All energy date in eV*

M	This paper								Craig [1]			
	$\beta_{01}^{00} = -2.430$				$\beta_{01}^{00} = -2.034$				excluding 3-centre integrals		including 3-centre integrals	
	lowest energy of CWF*	lowest CCI energy	Δ (M)	$E_M - E_{B_{2g}}$	lowest energy of CWF*	lowest CCI energy	Δ (M)	$E_M - E_{B_{2g}}$	Δ (M)	$E_M - E_{B_{2g}}$	Δ (M)	$E_M - E_{B_{2g}}$
$^1B_{2g}$	-1.167	-2.288	1.121	0	-1.167	-2.441	1.274	0	2.38	0	2.42	0
$^1A_{1g}$	1.167	-0.589	1.756	1.699	1.167	-0.921	2.088	1.520	4.67	1.15	3.30	2.55
$^1B_{1g}$	1.167	0.997	0.170	3.285	1.167	0.970	0.197	3.411	0.18	3.32	0.14	5.67
^1E_u	4.317	3.618	0.699	5.906	3.926	3.146	0.780	5.587	—	—	—	—

* Configuration Wave Function

π-orientation, furthermore, for $a = 1.5$ Å and for the square configuration of cyclobutadiene ($a = 1.33$ Å).

The values of penetration integrals are not needed for the computation of excitation energies. On the other hand, they are essential for the evaluation of the ground state energy. Accordingly, a decrease in the contribution of the integrals $\beta_{\mu\nu}^{\varkappa\lambda}$ and $\gamma_{\mu\nu}^{\varkappa\lambda}$ to the ground state energy with diminishing a does not mean an increase in stability of the system of two interacting ethylene molecules.

The oscillator strengths were calculated in the usual manner (cf. [3]).

The results of the computations required for discussion are summarized in the table and on Figs. 2 — 6.

3. Discussion

a) A Comparison with Craig*'s Calculations of Cyclobutadiene by the Theoretical CCI Method in the π-Electron Approximation*

In his paper [1] on cyclobutadiene Craig evaluated the necessary integrals theoretically using $Z = 3.18$ as the effective charge of the p_z orbitals. He assumed the value of 1.40 Å for the distance between neighbour carbon atoms. Since our model for $a = 1.33$ Å (π-orientation) corresponds to the square configuration of cyclobutadiene, the result of the present paper for this distance of the ethylene molecules are a semiempirical counterpart of Craig's study [1]. As it is impossible to compare the values of integrals obtained theoretically and semiempirically directly, the difference in the assumed distances between the neighbour atoms is completely irrelevant.

The comparison is given in the table. The difference between the lowest energy of the configuration wave function of cyclobutadiene and the lowest energy of the state (resulting from CI) both belonging to the same representation M of the group D_{4h} are denoted by ΔM (the "depression" according to Craig's nomenclature [1]). The order of these quantities is the same as that given by Craig Δ $(^1A_{1g}) > \Delta$ $(^1B_{2g}) > \Delta$ $(^1B_{1g})$, the last value being rather small. Also the relative positions of the individual singlet states are quite close to the theoretical values neglecting three- and four-centre integrals. The values of resonance integrals and electronic repulsion integrals used in the theoretical and in the semiempirical methods being very different, the similarity of the results of both approaches is the more remarkable. Let us note, however, that the neglect of resonance integrals β_{01}^{01} (i.e. the tight binding approximation) would change the character of the calculated energy spectrum of cyclobutadiene significantly (e.g., the lowest excitation energy B_{3u}, cf. Fig. 2 and discussion in 3c.).

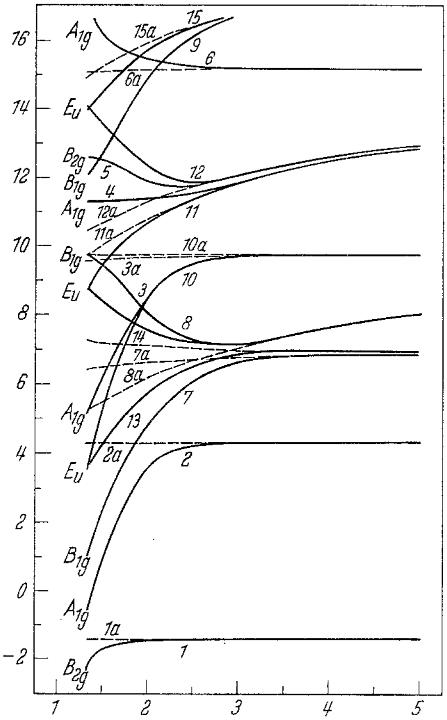

Fig. 2. Dependence of the energy (eV) of the individual singlet states on the distance a between the ethylene molecules for $\beta_{01}^{00} = -2.430$ eV. π-orientation. Curves 1—6 (A_{1g}), 7—9 (B_{1g}), 10—12 (B_{2u}), 13—15 (B_{3u}). Analogous curves resulting if β_{ij}^{01} is neglected are labelled 1a to 15a: 4a ≡ 11a, 5a ≡ 12a, 8a ≡ 14a, 9a ≡ 15a. Full (broken) lines; with (without) consideration of resonance integrals of the β_{ij}^{01} type. The notation of the cyclobutadiene terms is given on the left

b) Transannular Interaction; Effect of Higher Excited Configurations

In the studies of transannular interaction, the LCI method (Limited configuration interaction) including only monoexcited configurations of the system has been used up to now [*6, 9, 20, 30, 31*]. Only such distances of the interacting π-electron systems have been considered, that preclude the already mentioned crossing of or contact between levels arisen by splitting of energy levels of the frontier molecular orbitals of the isolated molecules. Such a crossing or contact makes the concept of a "molecule" in the system completely lose its significance and thus changes the classification of configurations according to the number of excited molecular orbitals. A limiting case of the system of two interacting ethylenes is the hypothetical cyclobutadiene, for which the notation of wave functions (2) obviously loses any physical sense, even though the functions can naturally still be used for the construction of the wave function of cyclobutadiene in CCI.

Every system in which transannular interaction has to be considered represents a transition between a system of non-interacting individual molecules and a system in which the interaction is so strong that we can no more distinguish the individual interacting molecules. These arguments make it clear that for models of transannular interaction it is particularly desirable to examine the influence of higher excited configurations on results obtained by CI. In view of the strong decrease in the energy of the ground state of an isolated ethylene molecule in our approximation due to interaction with the doubly excited configuration wave function B_{11} (cf. notation [3]) it is obvious that the results of the LCI and CCI methods obtained with the same values of the resonance and electron repulsion integrals cannot be compared quantitatively. We shall therefore focus attention on the qualitative influence of higher excited configurations on the character of the dependence of the individual excitation energies upon the distance a between the ethylene molecules.

Let us first notice that inclusion of certain configurations makes it necessary for some other configurations to be included into the CI as well, if the procedure is to be consistent. The function $\{0,2\}_1^+$ is the only one among the biexcited states which interacts in the limit $a \to \infty$ with the ground configuration $\{0,0\}$. If we wish to obtain the correct limit for the lowest excitation energy $B_{3u} \leftarrow A_{1g}$ when $a \to \infty$, we have to include into CI also the functions $\{0,3\}^+$ and $\{0,4\}$ in addition to the function $\{0,2\}_1^+$, i.e. all higher excited functions of the $\{0,j\}$ type containing B_{ii}.

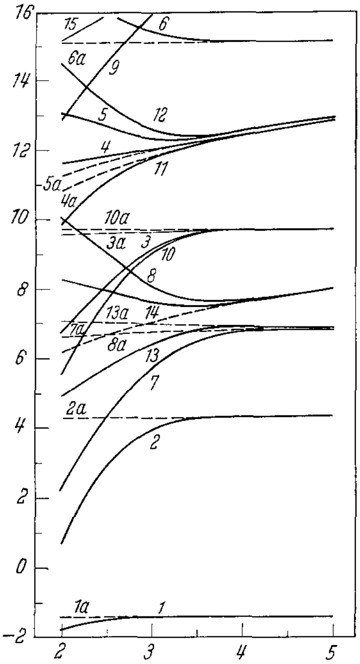

Fig. 3. Dependence of the energy (eV) of the individual singlet states on the distance a between the ethylene molecules for $\beta_{01}^{00} = -2.430$ eV. σ-orientation. Notation as in Fig. 2

Both LCI and CCI yield a qualitatively similar behaviour for the energies of the main states: the energies of the states B_{1g} and B_{3u} which for $a \to \infty$ pass into monoexcited states of isolated uncharged ethylene molecules are nearly constant above a certain distance a (let us call it a_M) and drop sharply with decreasing a for $a < a_M$. The energies of the states B_{1g} and B_{3u} which for $a \to \infty$ go over to states belonging to a pair of an isolated positive and negative ethylene ions in their ground states pass through a minimum as a decreases. The value a at which this minimum lies is close to a_M. This behaviour is due to the interaction of "uncharged" configuration functions of the $\{0,j\}$ type and "ionic" configuration functions of the $\{1,j\}$ type. For $a \to \infty$, the configuration wave functions of the $\{0,j\}$ type do not interact with the configuration wave functions of the $\{1,j\}$ type, which makes it possible, for $a > a_M$, to classify states as those excited without electron transfer from one ethylene molecule to the other (local excitation) and those of a system in which a transfer of an electron from one ethylene to the other has occured (charge transfer). For $a < a_M$, considerable interaction between the wave configuration functions of the $\{0,j\}$ and $\{1,j\}$ types admixes a significant amount of wave functions characteristic for the charge transfer to the states which for larger distances could be characterized as arising by local excitation.

Owing to the change in the character of a state when the distance of the ethylene molecules is reduced, the oscillator strength of the transition into the B_{3u} state which for $a \to \infty$ approaches a linear combination of configuration functions of the $\{0,j\}$ type diminishes in the vicinity of a_M. On the other hand, the oscillator strength of the transition into the B_{3u} state which for $a \rightarrow \infty$ passes into a function of the $\{1,j\}$ type grows in the same region of a.

For $a \rightarrow \infty$ the configuration wave functions of the $\{1,j\}$ type do not interact with each other, whereas the configuration wave functions of the $\{0,j\}$ type do. A corollary of this circumstance is an increase in the difference between the limiting values for $a \rightarrow \infty$ of the energies of the states of both types when passing from LCI to CCI. For every a, therefore, inclusion of higher excited states brings about a greater difference between the lowest energies of the "uncharged" and "ionic" states belonging to the same irreducible representation, i.e. B_{3u} or B_{1g}.

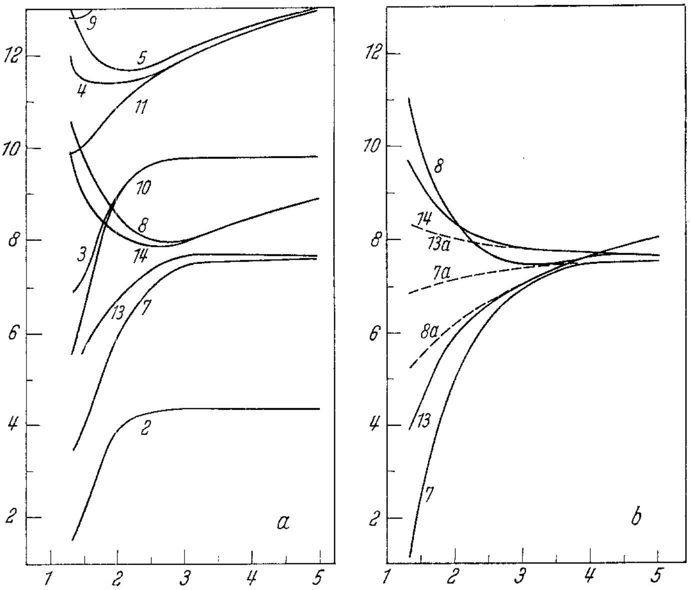

Fig. 4. Comparison of excitation energies (eV) of singlet states calculated by CCI for $\beta_{01}^{00} = -2.034$ eV (a) and by LCI for $\beta_{01}^{00} = -2.430$ eV (b). π-orientation. The labelling of excitation energies for the transition $M \leftarrow A_{1g}$ is the same as that of the terms M in Fig. 2

Now, let us consider a change in the resonance integrals β_{01}^{00} (and the associated change in other resonance integrals according to (8)) which leads to an agreement of the experimental excitation energy of the longest-wavelength absorption band of ethylene with the corresponding theoretical value computed by the CCI method. Such a change does not make it possible to obtain quantitative agreement of the dependence on a for the lowest energies B_{3u} and B_{1g} resulting from CCI using the resonance integral thus determined and of the corresponding energies resulting from LCI using the resonance integrals adjusted similarly within the framework of LCI (cf. Fig. 4). This result could have been expected in view of the larger difference in CCI between the energies of the "locally" excited and "ionic" states for $a \rightarrow \infty$. This larger difference in energies brings about a weakening of interaction between the configuration wave functions $\{0,j\}$ and $\{1,j\}$ and results therefore in a less sharp decrease in the excitation energies B_{3u} and B_{1g} with growing distance a in CCI than in LCI.

c) Comparison with Computations Neglecting Conjugation Effects between the Ethylene Molecules

Interaction of two ethylene molecules has been examined by the Pariser and Parr [*22*] and Pople [*23*] method by Nesbet [*19*]. In Nesbet's paper the resonance integrals between p_z orbitals belonging to different ethylene molecules are neglected. Contrary to the usual semiempirical LCI methods Nesbet takes into account the interaction between the $\{0,0\}$ ground configuration and the $\{0,2\}_0$ configuration.

To make possible a comparison with Nesbet's conclusions, we computed the interaction of two ethylene molecules using Nesbet's method and parameters adopted by us for the electron repulsion integrals (the σ and π orientations do not differ in this approximation).

The CCI method not considering the $\beta^{01}_{\mu\nu}$ integrals gives a similar behaviour for the main uncharged states as Nesbet's method: as the distance a diminishes the lowest energy of the B_{1g} state somewhat decreases and the lowest energy of the B_{3u} state increases slightly (cf. Fig. 2 and 3). The decrease in the energy of the ground state with diminishing a is very small (the difference between the energy of this state for $a = 2.0$ Å and that for $a \rightarrow \infty$ amounts to 0.0034 eV). All dependences of energies of the mentioned states on the distance a are less pronounced in CCI than in LCI (cf. Figs. 2 and 4b). Contrary to Nesbet, we do not find even a small reduction in oscillator strength of the $B_{3u} \leftarrow A_{1g}$ transition. Consequently, the hypochromic effect found by Nesbet is produced by the method adopted by him.

The sharp decrease in the lowest excitation energy of the $B_{1g} \leftarrow A_{1g}$ transition when the conjugation effect is taken into account is due exclusively to the consideration of the resonance integral β^{01}_{00} between the "nearest" neighbours. An analogously strong decrease in the lowest excitation energy of the $B_{3u} \leftarrow A_{1g}$ transition is obtained only if we ascribe the resonance integrals β^{01}_{01} values different from zero. Of course, the decrease in the oscillator strength of this transition is also due to the consideration of the resonance integrals β^{01}_{01}, which are, however, of the same order of magnitude as the integrals β^{01}_{00} owing to the geometry of the model.

d) General Features of the Interaction of Two π-Electron Systems with Consideration of Conjugation Effects

The LCI method neglecting higher than monoexcited configurations has shown that the effect of conjugation between π-electron systems on the properties of electronic absorption spectra is qualitatively the same for models of various systems in which transannular interaction plays a rôle [*2*, *12*] (e.g., transannular interaction between two double bonds in germacrol and bicyclo [1,2,2] heptadiene-(2,5), three double bonds in barrelene [*6*, *20*, *30*] and two benzene rings in (n,n)-paracyclophanes [*8*, *10*, *21*]). The present paper demonstrates that qualitatively similar effects of transannular interaction are to be expected also in the semiempirical CCI method.

Papers published hitherto make it very probable that the effect on the electronic spectrum of an interaction in which the conjugation effect between the π-electronic systems is important may be generalized in the following way:

1. For sufficiently large distances between the interacting molecules (more than about 4 Å), a distinction is possible between states arising by "local" excitation inside one molecule and those arising by charge transfer from one molecule to the other.

2. For smaller distances, mixing of the states of both types occurs.

3. In the cases considered thus far, this mixing splits off a forbidden band at the long-wavelength side of the absorption bands of the isolated molecules; starting from a certain critical distance a_1 between the molecules (3 to 4 Å), this band becomes pronounced.

4. The position of the main bands in the electronic absorption spectrum of the monomer does not change appreciably before a certain critical distance a_2 between the monomers is reached. At smaller distances these bands begin to shift strongly to longer wavelengths. a_2 is smaller than a_1, for electronic repulsion can at first cause a hypsochromic shift which at smaller distances is overcome by the bathochromic shift due to the interaction of the respective state with "charge transfer" states as the resonance effect makes itself felt (cf. [*26*], short-range and long-range forces).

5. Intensity of the longest-wavelength allowed band of the monomer decreases owing to a superposition of the respective state with the "charge transfer" state. The oscillator strengths of the transitions into these ionic states increase simultaneously. The distance between the monomers at which this hypochromic effect occurs is larger than a_2. This is so because the bathochromic effect appears only when the short-range forces prevail upon the long-range ones. On the other hand, hypochromism appears as soon as the short-range forces become appreciable.

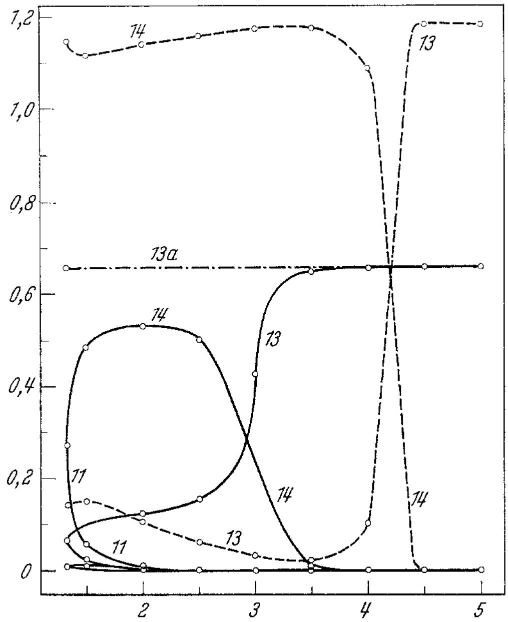

Fig. 5. Dependence on the distance a of absorption oscillator strengths f of the allowed transitions. π-orientation. The curves are labelled in the same way as the respective terms in Fig. 2 which combine with the ground state in the given transitions

6. As shown in the present work (cf. also [*21*] interaction between ionic and locally excited states is significant even if the energies of these states differ considerably (e.g. by 1—2 eV).

7. Paper [*21*] has shown that the nature of the effects mentioned is not changed by small mutual shifts of the interacting benzene nuclei. It may be inferred that smaller mutual shifts which lower the symmetry of the system of interacting monomers have no major effects on the general conclusions summarized under points 1—6.

e) The Possible Relation of Conjugation Effects to the Hypochromism of Polymers

The question about the connection between the conjugation effects and the hypochromism of helical polynucleotides has been raised already several times in the literature [*13, 14*]. However, the quantitative theory of the hypochromism of these substances considers only the potential of interaction between molecules in the "point-dipole" approximation [*5, 24, 27*]. In accordance with Nesbet [*19*], Rhodes [*24*] demonstrated that in this approximation hypochromism is not due to the fact that the excited wave function of the system of molecules has to be written in the form of a linear combination of functions representing the same local excitation $\alpha \leftarrow 0$ in the individual molecules of the system. Consequently, in this approximation hypochromism is caused only by the interaction of the transition moments of the $\alpha \leftarrow 0$ transition with other non-zero moments of the $\beta \leftarrow 0$ transitions. The quantitative agreement of the results of these theories with the experimentally found hypochromism of the absorption band in the region of 260 mμ (cf. [*15, 28, 29*]) should not be overestimated; the less so as the assumed interaction with the band near 215 mμ should result in hyperchromism in the region of this band. The hypochromism found in reality is usually explained by assuming a further hypothetical interaction with absorption bands at still shorter wavelengths [*24*].

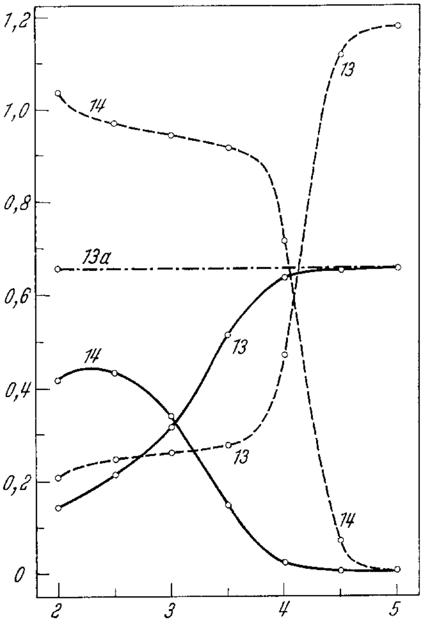

Fig. 6. Dependence of absorption oscillator strength of the individual allowed transitions on the distance *a*. σ-orientation. Notation as in Fig. 2

Let us note that the changes in absorption spectra of nucleic bases due to the formation of the helical polymer have properties similar to those expected on the basis of a model which takes into account conjugation effects.

The hypochromism of the band at 260 mμ (cf. [*15, 28, 29*]) may be related to point 5 of paragraph 3.d. A comparison of the electronic absorption spectrum of the monomer with that of the helical polynucleotide shows that the hypochromism is not accompanied by an observable shift of the maximum at 260 mμ. This circumstance agrees with point 4 of paragraph 3.d., ist being of course necessary to keep in view the complex structure of the band considered.

The long-wavelength side of the band with maximum at 260 mμ exhibits hyperchromism, ascribed by Rich and Kasha [*25*] to n-π^*transitions. This hyperchromism may also be related to the forbidden (or slightly allowed, with monomers of lower symmetry) band split off as described in point 3 of paragraph 3.d. The hypochromism of the band near 260 mμ need not bring about a hyperchromism of the allowed band at shorter wavelengths, but only a less pronounced hyperchromism of the originally forbidden band corresponding to the transition into the "ionic" state (cf. points 1,2 and 5 of paragraph 3.d). This band which exhibits hyperchromism may lie at quite short wavelengths (cf. point 6 of paragraph 3.d.). Similar considerations could be applied to the hypochromism of the absorption band near 215 mμ.

These considerations show that the phenomenon of hypochromism in helical polynucleotides may be connected also with conjugation effects between monomers, which are anyway quite probable at the distance of 3.36 Å between the monomers. The fact that according to this conception the hypochromism of helical polynucleotides would be related to superposition of configurations representing a charge transfer from one monomer to the other may prove interesting also in other connections [7].

In our simple models we were unable to compare the significance of interaction between locally excited and ionic configurations and of the TINOCO's interaction between transition moments of different transitions allowed in the monomer. Our models of monomers (ethylene and benzene) have only one allowed transition in the approximation used. The determination of the significance of the phenomenon studied in the present paper will no doubt be aided by a similar study of interaction between models of more complicated systems closer to the systems of nucleic bases.

We are indebted to Mr. VONDRA, Computation Centre of Kancelářské stroje, Praha, who carried out the numerical calculations on the National Elliott 803 B Computer.

Appendix

Matrix of the Hamiltonian in the Representation of Slater Determinants Constructed from the Ethylene Molecular Orbitals

According to definitions (3), function (2) may be expressed by means of SLATER determinants constructed from molecular orbitals of the individual ethylene molecules. The matrix elements of the Hamiltonian prove to be easily expressible in the representation of the said SLATER determinants even if the system may be considered a system of n interacting ethylene molecules. We write the normalized SLATER determinant in the form:

$$| q, m, p, \xi \rangle = | \overset{\alpha_1}{u}_{\mu_1} \eta_1, \overset{\alpha_2}{u}_{\mu_2} \eta_2, \cdots \overset{\alpha_{2n}}{u}_{\mu_{2n}} \eta_{2n} | \tag{A 1}$$

where $\overset{\alpha_i}{u}_{\mu_i}$ denotes the μ_i-th molecular orbital of the α_i-th ethylene molecule ($\mu_i = 0,1$ cf. Eq. [1]). $q \equiv (q_1, q_2 \cdots q_n)$, where q_k is the number of functions $u^k_{\mu_i}$ and $m \equiv (m_1, m_2 \cdots m_n)$, where m_k is the number of functions $u^k_1 \cdot p \equiv (p_1, p_2 \cdots p_n)$, where p_k is the number of spinorbitals $u^k_{\mu_i} \alpha \cdot \xi$ distinguishes functions with identical q, m and p. η_i is the spin part of the spinorbital. In the following, we consider only functions for which $\sum_{k=1}^{n} p_k = n$, which implies

$$\boldsymbol{S}_Z | q, m, p, \xi \rangle = 0. \tag{A 2}$$

We obtain the following expression for the matrix elements of the Hamiltonian in the representation of functions (A 1):

a) For the diagonal elements:

$$\langle q, m, p, \xi | \boldsymbol{H} | q, m, p, \xi \rangle - \langle q_0, m_0, p_0 | \boldsymbol{H} | q_0, m_0, p_0 \rangle$$

$$= -2\,P\,\beta_{01}^{11} - MB_{11} + NB^{11} + \frac{1}{2}\sum_{i}\sum_{\substack{j\\(i\neq j)}} (q_i\, q_j - 4)\; B^{ij} \tag{A 3}$$

where $q_0 = (2,2 \cdots 2)$ and $m_0 = (0,0 \cdots 0)$, $p_0 = (1,1 \cdots 1)$, and

$$P = \sum_{i=1}^{n} m_i,\; M = \frac{1}{2}\sum_{i=1}^{n} [p_i\,(p_i - 1) + (q_i - p_i)\,(q_i - p_i - 1)], \tag{A 4}$$

$$N = \frac{1}{2}\sum_{i=1}^{n} q_i\,(q_i - 1).$$

b) For the matrix elements between functions

$$\begin{aligned} |\, q_1, m_1, p_1, \xi_1 \,\rangle &= |\, u_{\varkappa}^{\varrho}\,\eta_1, u_{\mu_2}^{\alpha_2}\eta_2, \cdots \,| \\ |\, q_2, m_2, p_2, \xi_2 \,\rangle &= |\, u_{\lambda}^{\sigma}\,\eta_1, u_{\mu_2}^{\alpha_2}\eta_2, \cdots \,| \end{aligned} \tag{A 5}$$

which differ in one spinorbital:

$$\begin{aligned} \langle\, q_1, m_1, p_1, \xi_1 \,|\, \boldsymbol{H} \,|\, q_1, m_2, p_2, \xi_2 \,\rangle &= \sum_{i\neq\varrho} q_i\, B_{\varrho}^{i}; \\ \langle\, q_1, m_1, p_1, \xi_1 \,|\, \boldsymbol{H} \,|\, q_2, m_2, p_2, \xi_2 \,\rangle &= F^{\varrho\sigma}\,(\varkappa, \lambda),\; q_1 \neq q_2,\, \varrho \neq \sigma. \end{aligned} \tag{A 6}$$

c) For matrix elements between functions

$$\begin{aligned} |\, q_1, m_1, p_1, \xi_1 \,\rangle &= |\, u_{\varkappa}\,\eta_1, u^{\sigma}\,\eta_2, u_{\mu_3}^{\alpha_3}\eta_3 \cdots \,| \\ |\, q_2, m_2, p_2, \xi_2 \,\rangle &= |\, u_{\nu}^{\tau}\,\eta_1, u_{\pi}^{\omega}\,\eta_2, u_{\mu_3}^{\alpha_3}\eta_3 \cdots \,| \end{aligned} \tag{A 7}$$

which differ in two spinorbitals:

$$\langle\, q_1, m_1, p_1, \xi_1 \,|\, \boldsymbol{H} \,|\, q_2, m_2, p_2, \xi_2 \,\rangle = (\delta_{\varrho\tau}\,\delta_{\sigma\omega} - \delta_{\eta_1\,\eta_2}\,\delta_{\varrho\omega}\,\delta_{\tau\sigma})\; B_{\varrho\sigma}. \tag{A 8}$$

We introduced the following notation in these formulae:

$$F^{\varrho\sigma} = \frac{1}{2}\sum_{\mu,\nu=0}^{1} (-1)^{\mu k+\nu\lambda}\,\beta_{\mu\nu}^{\varrho\sigma},$$

$$B^{ij} = \frac{1}{4}\sum_{\mu,\nu=0}^{1} \gamma_{\mu\nu}^{ij},\; B_{ij} = \frac{1}{4}\sum_{\mu,\nu=0}^{1} (-1)^{\mu+\nu}\,\gamma_{\mu\nu}^{ij},$$

$$B_{j}^{i} = \frac{1}{4}\sum_{\mu,\nu=0}^{1} (-1)^{\nu}\,\gamma_{\mu\nu}^{ij}.$$

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