

Direct conversion **3** → **1**. 1 g (0.005 mol) **3** was electrolyzed in 320 ml acetonitrile or 50% aqueous tetrahydrofuran in the presence of 30 ml 40% tetrabutylammonium hydroxide as base and supporting electrolyte. In tetrahydrofuran under the same experimental conditions as in methanol 130 mg (13%) **1** are obtained after workup and recrystallization. In acetonitrile the current intensity decreased during the electrolysis so that the voltage had to be risen to 80 V. The yield was similar as in THF ($\approx 10\%$).

REFERENCES

- [1] J. E. Heller, A. S. Dreiding, B. R. O'Connor, H. E. Simmons, G. L. Buchanan, R. A. Raphael & R. Taylor, *Helv. 56*, 272 (1973).
- [2] B. Belleau & N. L. Weinberg, *J. Amer. chem. Soc.* **85**, 2525 (1963).
- [3] P. Margaretha & P. Tissot, *Org. Synth.* submitted for publication.
- [4] N. L. Weinberg in *Techniques of Organic Chemistry*, vol. V, (Techniques of Electroorganic Synthesis), p. 259, A. Weissberger Editor, John Wiley, New York, 1974.
- [5] A. A. Ponomarev & I. A. Markushina, *Ž. Obšč. Chim.* **33**, 3955 (1963). *J. Gen. Chem. USSR*, **33**, 3892 (1963).
- [6] C. K. Mann & K. K. Barnes, *Electrochemical Reactions in Nonaqueous Systems*, p. 163, M. Dekker, New York, 1970.

105. A Quantitative Assessment of "Through-space" and "Through-bond" Interactions. Application to Semi-empirical SCF Models

by Edgar Heilbronner and Andreas Schmelzer

Physikalisch-chemisches Institut der Universität Basel, Klingelbergstr. 80, CH-4056 Basel

(6. II. 75)

Summary. The scheme of 'through-space' and 'through-bond' interaction of (semi)localized orbitals, originally proposed by Hoffmann, is reexamined in terms of SCF many-electron treatments. It is shown that the two types of interaction can be characterized by examining the corresponding off-diagonal matrix elements of the *Hartree-Fock* matrices of the localized or the symmetry adapted localized orbitals and of the partially diagonalized *Hartree-Fock* matrices referring to 'precanonical orbitals'.

The procedure outlined is applied to three practical examples using the semiempirical many-electron treatments SPINDO, MINDO/2 and CNDO/2:

a) A reassessment of 'through-space' and 'through-bond' interaction in norbornadiene indicates, that the latter type of interaction is also of importance for the orbital based mainly on the antisymmetric combination of the localized π -orbitals. The differences in the predictions derived from the three models are critically examined.

b) The competition between 'through-space' and 'through-bond' interaction in the series of bicyclic dienes from norbornadiene to bicyclo[4.2.2]-deca-7,9-diene and in cyclohexa-1,4-diene, *i.e.* their dependence on the dihedral angle ω is reexamined. It is found that the rationalization for the orbital crossing near $\omega = 130^\circ$ deduced from PE. spectroscopic data can not be as simple as originally suggested and that the 'relay' orbitals responsible for 'through-bond' interaction affecting both the symmetric and the antisymmetric combination of the π -orbitals extend over the whole CC- σ -system of the six membered ring.

c) 'Through-bond' interaction of the two lone pair orbitals in 1,4-diazabicyclo[2.2.2]octane is found to be large for their symmetric and the antisymmetric linear combination.

The analysis quoted, draws attention to some of the dangers involved in using semiempirical treatments for the interpretation of PE. data in terms of Koopmans' theorem, without due caution.

1. Introduction. - In the wake of the *Woodward-Hoffmann* rules [1] numerous new concepts have found their way into molecular orbital theory, concepts which in turn have led to heuristically useful rules of thumb for the systematization and prediction of physical and chemical properties of molecules [2]. Among these, two of the most widely accepted notions are those of 'through-space' and 'through-bond' interaction between localized or semi-localized basis orbitals, originally introduced by *Hoffmann* [3]. They are traditionally used either qualitatively or in the framework of an independent-electron treatment, e.g. the *Hückel*-MO or the EHT-model [4] (EHT = Extended *Hückel* Theory), and are defined as follows:

'*Through-space*' interaction. Two basis orbitals χ_a, χ_b are said to interact 'through-space' if their overlap integral $S_{ab} = \langle \chi_a | \chi_b \rangle$ and thus their interaction matrix element $H_{ab} = \langle \chi_a | \mathbf{H} | \chi_b \rangle \propto -S_{ab}$ differ significantly from zero. (\mathbf{H} is the *Hückel* hamiltonian).

It should be noted that in the HMO- or EHT-model the interaction element H_{ab} is a resonance integral. For positive (negative) overlaps S_{ab} the matrix element H_{ab} becomes negative (positive). If $H_{ab} < 0$, the orbital energy ϵ_- of the resulting semi-localized linear combination $\eta_- = a\chi_a - b\chi_b$ (i.e. the one that takes the node) lies above ϵ_+ , i.e. the orbital energy of $\eta_+ = a'\chi_a + b'\chi_b$ ($a, b, a', b' > 0$). We call this the 'natural' sequence of orbitals. If χ_a and χ_b are related by symmetry, then η_+ is symmetric, η_- antisymmetric with respect to the discriminating symmetry operation.

'*Through-bond*' interaction. Consider first the case in which χ_a and χ_b do not overlap significantly ($S_{ab} \approx 0$). Under these circumstances one can form linear combinations $\chi_+ = (\chi_a + \chi_b)/\sqrt{2}$, $\chi_- = (\chi_a - \chi_b)/\sqrt{2}$ which are of same orbital energy even if the energies of the basis orbitals χ_a, χ_b differ ($\epsilon_a \neq \epsilon_b$). 'Through-bond' interaction between χ_a and χ_b occurs if both orbitals χ_a, χ_b overlap significantly with at least one other basis orbital χ_c of the molecule. The resulting interaction matrix elements H_{ac}, H_{bc} (which in HMO or EHT are again resonance integrals) lead to

$$\begin{aligned} H_{c+} &= \langle \chi_c | \mathbf{H} | \chi_+ \rangle = (H_{ac} + H_{bc})/\sqrt{2} \propto -(S_{ac} + S_{bc})/\sqrt{2} \\ H_{c-} &= \langle \chi_c | \mathbf{H} | \chi_- \rangle = (H_{ac} - H_{bc})/\sqrt{2} \propto -(S_{ac} - S_{bc})/\sqrt{2} \end{aligned} \quad (0)$$

The matrix elements H_{c+} and H_{c-} differ in size, thus lifting the (almost) degeneracy of χ_+ and χ_- . Usually it will be found that χ_c lies below χ_+ and χ_- in energy and that $|\epsilon_+ - \epsilon_c| \approx |\epsilon_- - \epsilon_c|$ is large compared to H_{c+} and H_{c-} . Under these circumstances the 'through-bond' induced shifts τ_+, τ_- of the orbital energies $\epsilon_+ = \langle \chi_+ | \mathbf{H} | \chi_+ \rangle$, $\epsilon_- = \langle \chi_- | \mathbf{H} | \chi_- \rangle$ can then be evaluated by a second-order perturbation treatment as follows:

$$\tau_+ = H_{c+}^2/(\epsilon_+ - \epsilon_c) \quad \tau_- = H_{c-}^2/(\epsilon_- - \epsilon_c) \quad (1)$$

An important consequence is that, depending on the relative sizes of H_{c+} and H_{c-} , one can have either $\tau_+ < \tau_-$ or $\tau_+ > \tau_-$. Whereas the former relationship leads again to the 'natural' sequence of the perturbed orbitals, χ'_- above χ'_+ , an inverted sequence is obtained in the latter case, i.e. χ'_+ above χ'_- .

In general 'through-space' and 'through-bond' interactions will occur simultaneously in a given molecule. It should be noted that the relevant interaction matrix

elements (H_{ab} and H_{c+} or H_{c-}) can be of the same or of opposite sign, so that the two effects can either reinforce, cancel or over-compensate each other. Obviously, only their resultant, *i.e.* their sum or difference can, if at all, be correlated with the observed data. For a more detailed discussion the reader is referred to [3].

Photoelectron (PE.) spectroscopic investigations of a variety of model systems [5-8] have provided data, which, at first sight, seem to be direct evidence for the 'existence' and the interplay of these two types of orbital interaction.

In particular the following observations are relevant for the analysis presented in this paper:

1. It has been shown that the PE. spectroscopic data of the series norbornadiene (1), bicyclo[2.2.2]octadiene (2) [5], bicyclo[3.2.2]nona-6,8-diene (3) [9], bicyclo[4.2.2]deca-7,9-diene (4) [10] and cyclohexa-1,4-diene (5) [5] can be rationalized by assuming that the two highest occupied molecular orbitals, both dominantly π in character, are $b_2(\pi)$ above $a_1(\pi)$ in 1 [7] and 2 [11], but $a_1(\pi)$ above $b_2(\pi)$ in 3, 4 [12] and 5 [11], [12].



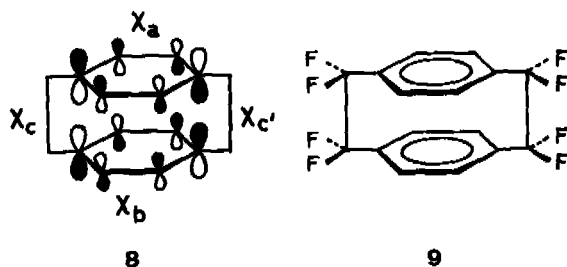
2. In 1,4-diazabicyclo[2.2.2]octane (6) [6] (DABCO) it has been postulated that the molecular orbital $a_1'(n_+)$, based on the linear combination $n_+ = (n_1 + n_4)/\sqrt{2}$, lies above $a_2''(n_-)$ which is based on $n_- = (n_1 - n_4)/\sqrt{2}$. This has been explained as being



due to the dominating 'through-bond' interaction between n_1 and n_4 via the three CC- σ -orbitals of the bonds 2,3; 5,6 and 7,8 [11].

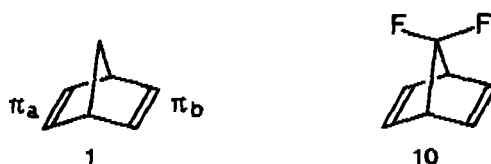
3. In those cases where the 'through-space' interaction of a particular basis orbital χ_a with lower lying orbitals is prohibited for reasons of symmetry (*e.g.* in 7-oxanorbornane (7) [13] of the oxygen lone-pair orbital $n \equiv \chi_a$ with the σ -'ribbon'-orbitals of the six-membered ring [14]) electron ejection from χ_a is predicted to lead to a higher ionization energy [15] than expected on the basis of the usual 'inductive-effect' arguments.

Recently we have shown [16] for [2,2]paracyclophane 8 that the assumption of a 'through-bond' interaction between the benzene orbitals χ_a and χ_b , via the CC- σ -orbitals χ_c , $\chi_{c'}$, is supported by the experimental findings derived from the PE. spectra of 8 [17] and of its octafluoro-derivative 9. Fluorination of the methylene groups considerably lowers $\epsilon_c = \epsilon_{c'}$, which leads to an increase of $\epsilon_+ - \epsilon_c$. As can be



seen from (1) this necessarily entails a diminution of τ_i in **9**. Indeed, an analysis of the photoelectron spectra of **8** and **9** shows clearly that with respect to the model we have $\tau_+(8) \gg \tau_+(9)$, thus proving the presence of appreciable ‘through-bond’ interaction in **8** [18], or more precisely in its radical cation **8⁺**.

Trying to apply the same technique [19] to the pair norbornadiene (**1**) and 7,7-difluoronorbornadiene (**10**) it has been observed that both π -bands in the PE. spectrum



of **1**, *i. e.* the bands assigned to the molecular orbitals dominated by the linear combinations $\pi_+ = (\pi_a + \pi_b)/\sqrt{2}$ and $\pi_- = (\pi_a - \pi_b)/\sqrt{2}$ are shifted by equal amounts towards higher ionization energies on fluorination of the methylene bridge [20]. This unexpected result has led us to reexamine the problem by applying orbital localization techniques to semi-empirical many-electron models of **1**. In addition this seemed also of interest in connection with a detailed investigation [21] of the applicability of semi-empirical SCF treatments for the rationalization of PE. spectroscopic results.

2. Theoretical. – We shall now reformulate the ‘through-bond’, ‘through-space’ interaction scheme in the framework of a many-electron SCF treatment, keeping as close as possible to the original concepts of *Hoffmann* [3].

A. Canonical Molecular Orbitals (CMO). – Consider a closed shell molecule with $2N$ electrons occupying N canonical molecular orbitals (CMO) φ_j by pairs with anti-parallel spin. The CMOs are obtained by solving the *Hartree-Fock* equations

$$\mathcal{F}\varphi_j = \varepsilon_j \varphi_j \quad ; \quad j = 1, 2, \dots, N \quad (2)$$

where \mathcal{F} is the *Fock*-operator and ε_j the molecular orbital energy. In practice (2) will be solved most of the time within a semi-empirical treatment, *e.g.* MINDO/2 [22], CNDO/2 [23], SPINDO [24] *etc.* [25]. The solutions of (2), which satisfy the relationship

$$\mathbf{F}_\varphi = (\langle \varphi_i | \mathcal{F} | \varphi_j \rangle) = (\varepsilon_i \delta_{ij}) \quad (3)$$

are collected into a column vector

$$\varphi = \begin{pmatrix} \varphi_1 \\ \vdots \\ \varphi_j \\ \vdots \\ \varphi_N \end{pmatrix} \equiv (\varphi_1 \dots \varphi_j \dots \varphi_N)^T, \quad (4)$$

the upper index \top meaning the transposed matrix.

B. Localized Molecular Orbitals (LMO). – The N CMOs φ can be transformed according to

$$\mathbf{L} \varphi = \lambda \quad (5)$$

into a set of localized molecular orbitals (LMO) λ_j

$$\lambda = (\lambda_1 \dots \lambda_j \dots \lambda_N)^T \quad (6)$$

by choosing the unitary transformation matrix \mathbf{L} in agreement with a preselected localization procedure, e.g. the intrinsic localization criterion of *Edmiston & Ruedenberg* [26],

$$\sum_{j=1}^N \left[\iint \lambda_j(1) \lambda_j(2) \frac{e^2}{r_{12}} \lambda_j(1) \lambda_j(2) \, dv_1 \, dv_2 \right] = \text{Maximum}. \quad (7)$$

The resulting *Hartree-Fock* matrix becomes

$$\mathbf{F}_\lambda = (\langle \lambda_i | \mathcal{F} | \lambda_j \rangle) = \mathbf{L} \mathbf{F}_\varphi \mathbf{L}^T. \quad (8)$$

Note that \mathbf{F}_λ is now a full matrix.

C. Symmetry-adapted Semi-localized Molecular Orbitals (SLMO). – If the molecule belongs to a symmetry group \mathcal{G} with irreducible representations $\Gamma^{(1)} \dots \Gamma^{(r)} \dots \Gamma^{(s)}$ one can form symmetry-adapted, semi-localized molecular orbitals (SLMO) ϱ_j according to

$$\varrho = \mathbf{R} \lambda. \quad (9)$$

Without loss of generality the unitary transformation matrix \mathbf{R} can always be chosen in such a way that the SLMOs ϱ_j are ordered in the column vector ϱ according to the conventional sequence of the irreducible representations $\Gamma^{(r)}$ to which they belong. (This sequence will usually be the one adopted universally in character tables):

$$\varrho = (\underbrace{\varrho_1 \dots \varrho_n}_{\Gamma^{(1)}}; \dots; \underbrace{\varrho_i \dots \varrho_n}_{\Gamma^{(r)}}; \dots; \underbrace{\varrho_s \dots \varrho_N}_{\Gamma^{(s)}}) = (\varrho^{(1)\top}; \dots \varrho^{(r)\top}; \dots \varrho^{(s)\top}). \quad (10)$$

Under this condition the *Hartree-Fock* matrix

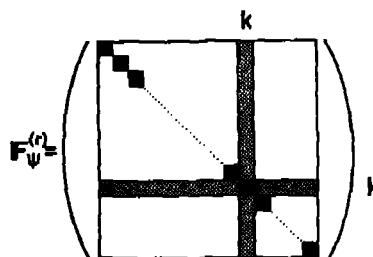
$$\mathbf{F}_\varrho = (\langle \varrho_i | \mathcal{F} | \varrho_j \rangle) = \mathbf{R} \mathbf{F}_\lambda \mathbf{R}^T \quad (11)$$

is blocked out in submatrices \mathbf{F}_ρ ($\Gamma^{(\nu)} \equiv \mathbf{F}_\rho^{(\nu)}$) belonging to the different irreducible representations $\Gamma^{(\nu)}$ of \mathcal{G} :

$$\mathbf{F}_\rho = \mathbf{F}_\rho^{(1)} \oplus \mathbf{F}_\rho^{(2)} \oplus \dots \mathbf{F}_\rho^{(r)} \oplus \dots \oplus \mathbf{F}_\rho^{(s)}. \quad (12)$$

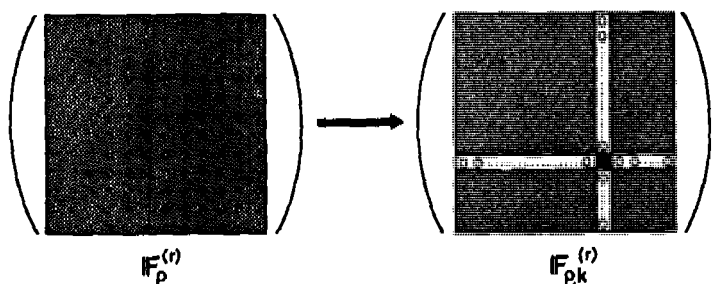
If the molecule has no symmetry (*i.e.* belongs to C_1), then the SLMOs are identical with the LMOs. However, it may still be convenient to choose two (or more) LMOs (*e.g.* the π -LMOs λ_a, λ_b of a diene) and to transform them into semi-localized molecular orbitals (*e.g.* $\rho_+ = (\lambda_a + \lambda_b)/\sqrt{2}$; $\rho_- = (\lambda_a - \lambda_b)/\sqrt{2}$). All other LMOs λ_j ($j \neq a, b$) remain unchanged ($\lambda_j \equiv \rho_j$). The resulting matrix \mathbf{F}_ρ , which obviously is not blocked out, will be the one used in the next step D.

D. *Precanonical Molecular Orbitals (PCMO)*. ... In the following we restrict our discussion to the subset $(\rho_1 \dots \rho_k \dots \rho_n) = \boldsymbol{\rho}^{(\nu)\top}$ of SLMOs belonging to the irreducible representation $\Gamma^{(\nu)}$ (see (10)). (The extension to the full set $\boldsymbol{\rho}$ is trivial.) To simplify the discussion we assume that we are interested only in the behaviour of a single preselected SLMO ρ_k of the set $\boldsymbol{\rho}^{(\nu)}$ in relation to the remaining $(n - 1)$ SLMOs ρ_j ($j \neq k$). The neatest way of achieving this comparison consists in forming orthonormal linear combinations ψ_j from the $(n - 1)$ SLMOs ρ_j ($j \neq k$) in such a way that all interaction matrix elements $\langle \psi_i | \mathcal{F} | \psi_j \rangle = 0$ for $i \neq j$ and $i, j \neq k$. We call such orbitals ψ_j 'precanonical orbitals' (PCMO). Obviously the cross terms $\langle \psi_j | \mathcal{F} | \rho_k \rangle$ will differ from zero, so that the resulting submatrix $\mathbf{F}_\psi^{(\nu)}$ is of the form:



(13)

To compute $\mathbf{F}_\psi^{(\nu)}$ we first delete all off-diagonal elements in row k and column k of the matrix $\mathbf{F}_\rho^{(\nu)}$ generating $\mathbf{F}_{\rho,k}^{(\nu)}$:



(14)

Diagonalization of $\mathbf{F}_{\rho,k}^{(\nu)}$ yields

$$\mathbf{P}_k^{(\nu)} \mathbf{F}_{\rho,k}^{(\nu)} \mathbf{P}_k^{(\nu)\top} = (\epsilon_i^{\text{PCMO}} \delta_{ij}) \quad (15)$$

with $\epsilon_k^{\text{PMCO}} = F_{\rho, \text{kk}}^{(r)}$. The corresponding set of orbitals

$$\psi^{(r)} = (\psi_1 \dots \psi_{k-1}, \rho_k, \psi_{k+1} \dots \psi_N)^T \quad (16)$$

obtained by the transformation

$$\psi^{(r)} = \mathbf{P}_k^{(r)} \rho^{(r)} \quad (17)$$

is the set of precanonical molecular orbitals (PCMO) ψ_j . Note that $\psi_k \equiv \rho_k$. Finally we calculate the matrix (13) according to

$$\mathbf{F}_\psi^{(r)} = \mathbf{P}_k^{(r)} \mathbf{F}_\rho^{(r)} \mathbf{P}_k^{(r)\dagger}. \quad (18)$$

As shown diagrammatically in (13) all off-diagonal elements $F_{\psi, ij}^{(r)}$ are zero, with the exception of the elements $F_{\psi, jk}^{(r)}$ and $F_{\psi, kj}^{(r)}$ in column k and row k . These elements link the SLMO $\rho_k \equiv \psi_k$ to the set of PCMOs ψ_j ($j \neq k$).

We are now in a position to recast the concepts of 'through-space' and 'through-bond' interaction in the framework of a many-electron SCF-model.

'Through-space'-Interaction. - Two LMOs λ_a, λ_b are said to interact 'through-space' if their matrix element $F_{\lambda, ab}$ of the Hartree-Fock matrix \mathbf{F}_λ differs significantly from zero.

In general all $F_{\lambda, ab}$ will be different from zero. For practical reasons it is therefore necessary to set lower limits to the values of $|F_{\lambda, ab}|$, below which 'through-space' interaction between λ_a and λ_b is no longer considered to be significant. These limits will not only depend on the type of problem to be discussed, but also on the ratio $|F_{\lambda, ab}|^2 / |F_{\lambda, aa} - F_{\lambda, bb}|$ where $F_{\lambda, aa}, F_{\lambda, bb}$ are the self-energies of λ_a, λ_b .

'Through-bond'-Interaction. - If two LMOs λ_a, λ_b are related by symmetry, then the SLMOs $\rho_k^{(r)} = (\lambda_a + \lambda_b)/\sqrt{2}$ and $\rho_l^{(s)} = (\lambda_a - \lambda_b)/\sqrt{2}$ belong necessarily to two different irreducible representations of the group \mathbf{G} , e.g. to $\Gamma^{(r)}$ and to $\Gamma^{(s)}$. If we apply the transformation (18) to $\mathbf{F}_\rho^{(r)}$ and to $\mathbf{F}_\rho^{(s)}$ we obtain $\mathbf{F}_\psi^{(r)}$ and $\mathbf{F}_\psi^{(s)}$.

Two LMOs λ_a and λ_b are said to interact 'through-bond' if at least one of the matrix elements $F_{\psi, kj}^{(r)}$ ($j \neq k$) and/or $F_{\psi, li}^{(s)}$ ($i \neq l$) differs significantly from zero.

A few comments are in order. In the above statement the indices $j(i)$ refer to the PCMO $\psi_j(\psi_i)$ belonging to the same irreducible representation $\Gamma^{(r)}$ ($\Gamma^{(s)}$) as $\psi_k \equiv \rho_k$ ($\psi_l \equiv \rho_l$). As before all matrix elements $F_{\psi, kj}^{(r)}$ ($F_{\psi, li}^{(s)}$) will be different from zero so that it will be again necessary to set a lower limit to the absolute values $|F_{\psi, kj}^{(r)}|$ ($|F_{\psi, li}^{(s)}|$) below which the particular 'through-bond' interaction between λ_a and λ_b involving the PCMO $\psi_j(\psi_i)$ as a 'relay'-orbital will be neglected. This limit will differ from one relay-orbital to another because the size of the perturbation τ_{kj} (τ_{li}) suffered by λ_a and λ_b or more precisely by their linear combinations ρ_k (ρ_l) depends not only on $F_{\psi, kj}^{(r)}$ ($F_{\psi, li}^{(s)}$) but according to

$$\begin{aligned} \tau_{kj} &= (F_{\psi, kj}^{(r)})^2 / (F_{\psi, kk}^{(r)} - F_{\psi, jj}^{(r)}) \\ \tau_{li} &= (F_{\psi, li}^{(s)})^2 / (F_{\psi, li}^{(s)} - F_{\psi, ii}^{(s)}) \end{aligned} \quad (19)$$

also on the differences between the diagonal elements, i.e. $F_{\psi, kk}^{(r)} - F_{\psi, jj}^{(r)}$ and $F_{\psi, li}^{(s)} - F_{\psi, ii}^{(s)}$ respectively. This will be discussed in connection with the examples given below.

Finally it should be recalled that in molecules without symmetry (*i.e.* $G \cong C_1$) all of the above statements still hold true, with the added simplification that $\lambda_j \equiv \varrho_j$ *i.e.* $F_\lambda \equiv F_\rho$. However, it is usually convenient to form linear combinations of the type ϱ_+ and ϱ_- , as indicated at the end of paragraph C.

Concluding Remarks. - For practical purposes, *i.e.* the qualitative or semiquantitative rationalization of observed results or for the formulation of general rules of thumb, it is not only desirable but indeed necessary that the interaction scheme based on the 'through-space', 'through-bond' concept can be discussed in terms of simple first- and/or second-order perturbation treatments (*cf.* formulae (0), (1) and (19)). This is *not* possible on the LMO or SLMO level because most, if not all the off-diagonal matrix elements $F_{\lambda,ij}$ of F_λ or $F_{\varrho,ij}^{(r)}$ of $F_\varrho^{(r)}$ are usually large compared to the corresponding differences $|F_{\lambda,ii} - F_{\lambda,jj}|$ or $|F_{\varrho,ii}^{(r)} - F_{\varrho,jj}^{(r)}|$ between the diagonal elements. The reason is that LMOs (and thus SLMOs) fall necessarily into a narrow range of energies. Consequently the transformation into PCMOs is a necessary step, if a heuristically useful scheme is required.

The procedure proposed does yield a description of orbital interactions as close as possible to *Hoffmann's* original proposal. Although this scheme appeals to the chemist's intuition, it must nevertheless be stated explicitly that *this separation into two types of interactions is artificial and closely tied to the underlying SCF model*. In particular it will emerge that the relative sizes of 'through-space' and 'through-bond' interaction between two LMOs λ_a, λ_b depend critically on the particular SCF model chosen. Finally, it should be remembered that the interaction matrix elements $F_{\lambda,ab}$ and $F_{\varrho,ij}^{(r)}$ are anything but simple in their theoretical build-up and in their physical origin.

3. Applications. - We shall now demonstrate the application of the method outlined above to three examples. It will emerge that the procedure embodied in steps A to D is in fact much simpler and straightforward than might be inferred from the theoretical formalism described in section 2.

In this context an important point, briefly mentioned above, must be emphasized. This point, which will be developed in greater detail in a forthcoming publication [21], concerns the adequacy and/or reliability of the widely used semiempirical SCF models for the calculation of one-electron properties, *e.g.* properties that can be related to the construct of an individual CMO φ_j and its associated orbital energy ϵ_j . It will be seen that such models differ considerably in their assessment of the two postulated effects, so much so that a judicious choice of a particular model will already determine by itself the proof or disproof of a postulated effect. Or, to put it more crudely: We can 'justify' a preconceived idea about the relative importance of 'through-space' *vs.* 'through-bond' interaction by 'objectively' performing a calculation, using an appropriately chosen standard SCF-procedure without tampering with its original parametrization!

From the large number of semi-empirical SCF-procedures available (*e.g.* from QCPE = Quantum Chemistry Program Exchange) we have chosen three, which are widely used and which embody three different points of view of calibration:

1. CNDO/2 [23] which has been parametrized to mimic *ab initio* calculations;

2. MINDO/2 [22] which has been parametrized to yield optimum agreement between calculated and observed enthalpies (or energies) of formation;

3. SPINDO [24] (a modified INDO [25] [27] treatment), which has been parametrized to yield optimum agreement between calculated and observed ionization energies (usually taken from PE. spectroscopic data), assuming the validity of *Koopmans'* theorem [28], i.e. $I_{v,j} = -\epsilon_j$ ($I_{v,j}$ = vertical ionization energy).

Example 1: 'Through-space' and 'Through-bond' Interaction in Norbornadiene (1). - In the following calculations the experimentally determined interatomic distances and bond angles of **1** (symmetry C_{2v}) [29] have been used.

This first example will be worked out in full detail to demonstrate the procedure proposed in section 2. With regard to the particular problem answers are sought to the following questions:

a) how do 'through-space' and 'through-bond' interactions between the orbitals π_a and π_b compare in their relative importance in determining the orbital energies of the CMOs $a_1(\pi)$ and $b_2(\pi)$;

b) which of the σ -orbital(s) is (are) the important relay-orbital(s) for 'through-bond' interaction between π_a and π_b ;

c) how does the choice of a particular semi-empirical SCF model (SPINDO, MINDO/2, CNDO/2) influence the conclusions drawn concerning the question a) and b).

Step A. The orbital energies ϵ_j of the 18 bonding CMOs φ_j of **1** (valence shell only) are given in Tab. 1. They belong to the irreducible representations $\Gamma^{(1)} \equiv A_1$, $\Gamma^{(2)} \equiv A_2$, $\Gamma^{(3)} \equiv B_1$ and $\Gamma^{(4)} \equiv B_2$ of the group $G \equiv C_{2v}$. The two highest occupied CMOs are φ_7 and φ_{18} . According to SPINDO and MINDO/2 $\varphi_{18} \equiv b_2(\pi)$ lies above $\varphi_7 \equiv a_1(\pi)$

Table 1. Orbital energies ϵ_j of the canonical molecular orbitals (CMO) φ_j of norbornadiene (**1**). All energies are given in eV. Molecular symmetry C_{2v} . The discriminating mirror plane (xz) contains the carbon atoms 1, 4 and 7.

$\Gamma^{(r)}$	j	SPINDO	MINDO/2	CNDO/2
A ₁	1	-27.47	-42.79	-58.62
	2	-21.61	-26.91	-35.70
	3	-18.41	-19.60	-29.36
	4	-17.12	-17.71	-27.84
	5	-13.02	-12.78	-21.04
	6	-12.77	-10.88	-15.36
	7	-10.13	-9.40	-12.04
A ₂	8	-17.87	-19.41	-26.99
	9	-11.56	-10.22	-14.74
B ₁	10	-21.85	-27.81	-36.68
	11	-16.50	-16.95	-24.38
	12	-13.04	-11.76	-16.85
	13	-11.91	-10.80	-15.84
B ₂	14	-23.07	-29.47	-39.05
	15	-15.73	-15.67	-26.77
	16	-14.11	-12.36	-18.67
	17	-12.35	-10.87	-15.89
	18	-9.57	-9.26	-12.40

whereas CNDO/2 predicts the reverse sequence. If *Koopmans'* theorem is accepted the former result, *i.e.* $b_2(\pi)$ above $a_1(\pi)$ corresponds to the photoelectron spectroscopic finding [7]. Note that $a_1(\pi)$ is mainly $(\pi_a + \pi_b)/\sqrt{2}$ in character and $b_2(\pi)$ mainly $(\pi_a - \pi_b)/\sqrt{2}$.

Steps B and C. The CMOs φ_j are transformed into LMOs λ_j according to (5), *i.e.* using the localization criterion (7) [26]. Then the symmetry-equivalent LMOs are combined into SLMOs ϱ_j by the transformation (9). The corresponding *Hartree-Fock* matrix \mathbf{F}_ρ is blocked out into four submatrices

$$\begin{aligned} \mathbf{F}_\rho &= \mathbf{F}_\rho^{(1)} \oplus \mathbf{F}_\rho^{(2)} \oplus \mathbf{F}_\rho^{(3)} \oplus \mathbf{F}_\rho^{(4)} \\ \Gamma^{(r)} & \begin{array}{cccc} A_1 & A_2 & B_1 & B_2 \end{array} \\ \text{Order: } & 7 \times 7 \quad 2 \times 2 \quad 4 \times 4 \quad 5 \times 5 \end{aligned} \quad (20)$$

The order of each submatrix $\mathbf{F}_\rho^{(r)}$ is equal to the number of CMOs φ_j belonging to $\Gamma^{(r)}$, as shown in Tab. 1.

In Tab. 2 are given the four submatrices $\mathbf{F}_\rho^{(r)}$. The headings of the rows and columns are schematic representations of the SLMOs ϱ_j the basis energies of which are the diagonal elements $F_{\varrho_i, \varrho_j}^{(r)}$. The off-diagonal elements $F_{\varrho_i, \varrho_j}^{(r)}$ describe the interaction between ϱ_i and ϱ_j . As mentioned before these matrix elements are as large and sometimes larger than the differences between the basis energies of the interacting SLMOs. This precludes the application of simple perturbation arguments at this level.

Our main interest concerns the interaction of the π -orbitals π_a and π_b in **1**. For the LMOs $\lambda_a \equiv \pi_a$ and $\lambda_b \equiv \pi_b$ the following matrix elements F_{λ_i, λ_j} of \mathbf{F}_λ had been obtained (in eV):

	SPINDO	MINDO/2	CNDO/2	
$F_{\lambda, aa} = F_{\lambda, bb}:$	-10.44	-10.70	-16.41	(21)
$F_{\lambda, ab}:$	- 0.54	- 0.78	- 2.09	

According to the definition given in section 2, the matrix element $F_{\lambda, ab}$ measures the 'through-space' interaction between $\lambda_a \equiv \pi_a$ and $\lambda_b \equiv \pi_b$.

The transformation (9) yields the SLMOs

$$\begin{aligned} \varrho_7 &= (\lambda_a + \lambda_b)/\sqrt{2}; (A_1) \\ \varrho_{18} &= (\lambda_a - \lambda_b)/\sqrt{2}; (B_2) \end{aligned} \quad (22)$$

which do no longer interact for reasons of symmetry. Their energies are (in eV):

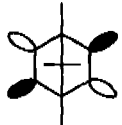
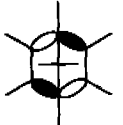
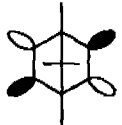
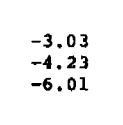
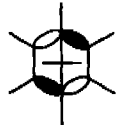
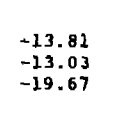
	SPINDO	MINDO/2	CNDO/2	
$F_{\varrho, 7, 7}^{(1)}:$	-10.98	-11.47	-18.50	
$F_{\varrho, 18, 18}^{(4)}:$	- 9.90	- 9.92	-14.32	(23)
Split:	1.08	1.55	4.18	

Note that $F_{\varrho, 18, 18}^{(4)} - F_{\varrho, 7, 7}^{(1)} = -2 F_{\lambda, ab}$.

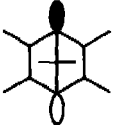
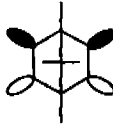
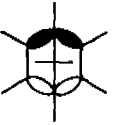

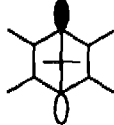
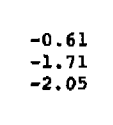
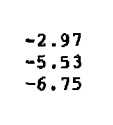
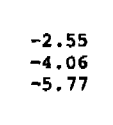
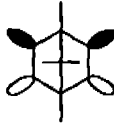
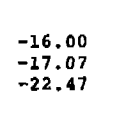
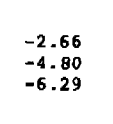
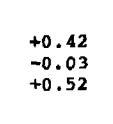

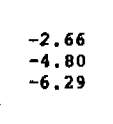
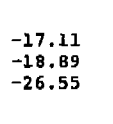
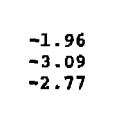
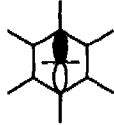
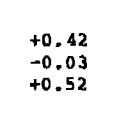
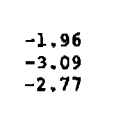
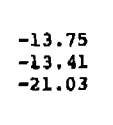
Table 2. Submatrices $F_{ij}^{(1)}$ of *norbornadiene 1*. The four submatrices $F_{ij}^{(1)}$ are those listed in (20). The headings of rows and columns are qualitative, schematic representations of the SLMOs ϕ_i . All matrix elements $F_{ij}^{(1)}$ are in eV. The three values given for each $F_{ij}^{(1)}$ correspond from top to bottom to the results obtained from the SPINDO, MINDO/2 and CNDO/2 model (in this order)

	ρ_1	ρ_2	ρ_3	ρ_4	ρ_5	ρ_6	ρ_7	
$F_{ij}^{(1)}$								$\Gamma^{(1)} \equiv A_1$
ρ_1	-20.08 -23.04 -32.55	+0.85 +0.03 +3.12	-3.37 -7.13 -6.55	-4.00 -9.08 -11.99	-1.87 -4.65 -8.16	-0.29 -1.18 -0.39	+0.15 +0.84 +1.38	
ρ_2	+0.85 +0.03 +3.12	-16.64 -18.00 -24.21	-1.01 -1.87 -2.67	-2.74 -5.33 -4.45	-1.39 -3.37 -1.95	-0.84 -2.28 -2.45	-0.50 -0.66 -1.62	
ρ_3	-3.37 -7.13 -6.55	-1.01 -1.87 -2.67	-17.23 -19.65 -26.61	-0.89 -3.30 -0.93	+0.81 +0.30 +3.13	-0.19 -0.38 -0.27	+0.06 +0.27 -0.16	
ρ_4	-4.00 -9.08 -11.99	-2.74 -5.33 -4.45	-0.89 -3.30 -0.93	-19.46 -24.44 -38.49	-4.07 -8.32 -13.35	+0.05 -1.60 -0.18	+1.09 +1.75 +4.37	
ρ_5	-1.87 -4.65 -8.16	-1.39 -3.37 -1.95	+0.81 +0.30 +3.13	-4.07 -8.32 -13.35	-18.00 -21.27 -32.15	-4.00 -7.63 -8.24	-1.14 -1.71 -4.64	
ρ_6	-0.29 -1.18 -0.39	-0.84 -2.28 -2.45	-0.19 -0.38 -0.27	+0.05 -1.60 -0.18	-18.15 -22.21 -27.47	-18.15 -22.21 -27.47	-0.33 -0.89 -1.27	
ρ_7	+0.15 +0.84 +1.38	-0.50 -0.66 -1.62	+0.06 +0.27 -0.16	+1.09 +1.75 +4.37	-1.14 -1.71 -4.64	-0.33 -0.89 -1.27	-10.98 -11.47 -18.50	

$\Gamma^{(2)} \equiv A_2$

	ρ_8	ρ_9
$\mathbb{F}_\rho^{(2)}$		
ρ_8	 -15.62 -16.59 -22.07	 -3.03 -4.23 -6.01
ρ_9	 -3.03 -4.23 -6.01	 -13.81 -13.03 -19.67

$\Gamma^{(3)} \equiv B_1$

	ρ_{10}	ρ_{11}	ρ_{12}	ρ_{13}
$\mathbb{F}_\rho^{(3)}$				
ρ_{10}	 -16.44 -17.94 -23.71	 -0.61 -1.71 -2.05	 -2.97 -5.53 -6.75	 -2.55 -4.06 -5.77
ρ_{11}	 -0.61 -1.71 -2.05	 -16.00 -17.07 -22.47	 -2.66 -4.80 -6.29	 +0.42 -0.03 +0.52
ρ_{12}	 -2.97 -5.53 -6.75	 -2.66 -4.80 -6.29	 -17.11 -18.89 -26.55	 -1.96 -3.09 -2.77
ρ_{13}	 -2.55 -4.06 -5.77	 +0.42 -0.03 +0.52	 -1.96 -3.09 -2.77	 -13.75 -13.41 -21.03

	ρ_{14}	ρ_{15}	ρ_{16}	ρ_{17}	ρ_{18}	$\Gamma^{(4)} \equiv B_2$
$F_p^{(4)}$						
ρ_{14}	-19.26 -20.44 -28.19	-3.51 -7.00 -7.54	-2.68 -4.99 -5.71	-0.61 -1.44 -2.29	-0.36 -0.79 -1.96	
ρ_{15}	-3.51 -7.00 -7.54	-16.98 -19.26 -26.05	-1.28 -2.85 -2.29	+0.03 -0.38 +0.16	-0.02 -0.27 -0.36	
ρ_{16}	-2.68 -4.99 -5.71	-1.28 -2.85 -2.29	-15.10 -14.66 -24.37	-1.65 -2.45 -5.58	-1.14 -1.69 -4.74	
ρ_{17}	-0.61 -1.44 -2.29	+0.03 -0.38 +0.16	-1.65 -2.45 -5.58	-13.59 -13.35 -19.83	-0.92 -1.23 -2.79	
ρ_{18}	-0.36 -0.79 -1.96	-0.02 -0.27 -0.36	-1.14 -1.69 -4.74	-0.92 -1.23 -2.79	-9.90 -9.92 -14.36	

Step D. As the questions to be answered concern only those orbitals which are predominantly π in character, we limit ourselves to the matrices $F_p^{(1)}$ and $F_p^{(4)}$ which contain the relevant linear combinations ρ_7 and ρ_{18} (see Tab. 2). To transform the SLMOs into the PCMOs ψ_j we remove the last lines and columns from $F_p^{(1)}$ ($k = 7$) and $F_p^{(4)}$ ($l = 18$) and diagonalize the remaining matrices of order 6 and 4, as summarized in the formulae (13) to (17). Transforming $F_p^{(1)}$ and $F_p^{(4)}$ as indicated in (18) yields the matrices $F_{\psi,7}^{(1)}$ and $F_{\psi,18}^{(4)}$ listed in Tab. 3.

The headings of the columns are schematic representations of the PCMOs ψ_j in order of increasing energy, with $\psi_7 \equiv \rho_7$ and $\psi_{18} \equiv \rho_{18}$ in the last rows and columns. These diagrams indicate the relative phases of the LMOs λ_j which occur in the linear combinations ψ_j and qualitatively the size of the coefficients with which they are affected. Attention is drawn to the fact that the PCMOs of same index calculated according to SPINDO, MINDO/2 and CNDO/2 do not always exhibit the same phase-relationships but that they can differ noticeably from one another in this respect.


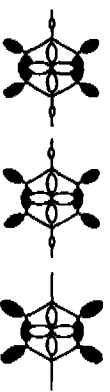
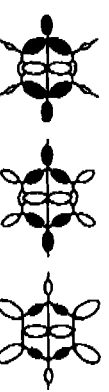

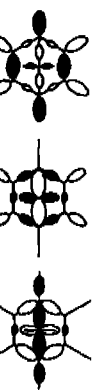
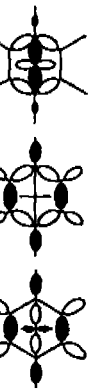
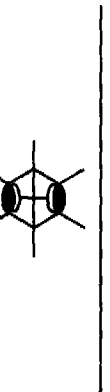
The entries in the last row and column of $F_{\psi,7}^{(1)}$ and $F_{\psi,18}^{(4)}$ are the matrix elements $F_{\psi,7}^{(1)}$ and $F_{\psi,18}^{(4)}$ which link the relay σ -PCMOs ψ_j to the π -SLMOs $\psi_7 \equiv \rho_7$, $\psi_{18} \equiv \rho_{18}$.

i.e. those describing the 'through-bond' interaction according to the rule given in section 2.

The magnitude of the individual contributions $\tau_{7j}^{(1)}$ and $\tau_{18i}^{(4)}$ to the 'through-bond' interaction of π_a and π_b depends on two quantities (see (19)), namely

1. the size of the matrix elements $F_{\psi,7j}^{(1)}$ or $F_{\psi,18i}^{(4)}$ and
2. the differences between the diagonal terms $F_{\psi,7,7}^{(1)} - F_{\psi,jj}^{(1)}$ and $F_{\psi,18,18}^{(4)} - F_{\psi,ii}^{(4)}$.

Table 3. Hartree-Fock matrices $F_{\psi}^{(1)}$ and $F_{\psi}^{(4)}$ of the PCMOs acting as relay orbitals for 'through-bond' interaction between $\lambda_a \equiv \pi_a$ and $\lambda_b \equiv \pi_b$. All matrix elements in eV. The headings of the columns are qualitative, schematic representations of the PCMOs ψ_j . The three values given for each $F_{\psi,j}^{(1)}$ and $F_{\psi,18}^{(4)}$ correspond from top to bottom to the results obtained from the SPINDO, MINDO/2 and CNDO/2 model (in this order).

	ψ_1	ψ_2	ψ_3	ψ_4	ψ_5	ψ_6	ρ_7	$\Gamma^{(1)} \equiv A_1$
$F_{\psi}^{(1)}$								
ψ_1	-27.47 -42.79 -58.61	0	0	0	0	0	0.02 0.31 0.75	
ψ_2	0	-21.52 -26.63 -34.66	0	0	0	0	0.95 2.07 3.92	
ψ_3	0	0	-18.38 -19.55 -28.78	0	0	0	0.54 0.65 2.49	
ψ_4	0	0	0	-17.10 -17.67 -27.72	0	0	0.34 0.52 1.48	
ψ_5	0	0	0	0	-12.79 -11.19 -16.47	0	-0.14 1.47 -4.51	
ψ_6	0	0	0	0	0	-12.30 -10.78 -15.23	-1.24 -0.85 1.45	
ρ_7	0.02 0.31 0.75	0.95 2.07 3.92	0.54 0.65 2.49	0.34 0.52 1.48	-0.14 1.47 -4.51	-1.24 -0.85 1.45	-10.98 -11.47 -18.50	

ψ_{14}

ψ_{15}

ψ_{16}

ψ_{17}

ρ_{18}

$\Gamma^{(4)} \equiv B_2$

$F_{\psi}^{(4)}$					
ψ_{14}	-23.02 -29.35 -38.26	0	0	0	-0.80 -1.51 -4.33
ψ_{15}	0	-15.48 -15.24 -25.72	0	0	+1.18 +1.58 +3.86
ψ_{16}	0	0	-14.07 -12.31 -18.62	0	-0.48 -0.41 -0.63
ψ_{17}	0	0	0	-12.35 -10.60 -15.85	-0.04 +0.36 +0.42
ρ_{18}	-0.80 -1.51 -4.33	+1.18 +1.58 +3.86	-0.48 -0.41 -0.63	-0.04 +0.36 +0.42	-9.90 -9.92 -14.36

If these differences are large relative to the corresponding cross-terms, then the total 'through-bond' destabilizations $\tau^{(1)}$, $\tau^{(4)}$ can be calculated by a second order approximation:

$$\tau_k^{(r)} \approx \sum_j^{(r)} \tau_{kj}^{(r)} = \sum_j^{(r)} (F_{\psi, kj}^{(r)})^2 / (F_{\psi, kk}^{(r)} - F_{\psi, jj}^{(r)}) \quad (24)$$

with $r = 1$, $k = 7$ (irreducible representation $\Gamma^{(1)} \equiv A_1$) and $r = 4$, $k = 18$ (irreducible representation $\Gamma^{(4)} \equiv B_2$). On the other hand, if the cross-terms $F_{\psi, kj}^{(r)}$ are large compared to $F_{\psi, kk}^{(r)} - F_{\psi, jj}^{(r)}$ then (19) and (24) can not be applied. In this case only a diagonalization of $F_{\psi}^{(r)}$ will yield the desired insight into the extent of 'through-bond' interaction.

In Tab. 4 are summarized the results obtained according to (19) from the data given in Tab. 3.

Discussion. - From the calculated results the following conclusions can be drawn:

1. In Fig. 1 are displayed the self-energies $\varepsilon_a = \varepsilon_b$ of the LMOs $\lambda_a = \lambda_b = \lambda_{\psi}$, the self-energies $F_{\rho, 7, 7}^{(1)} \equiv F_{\psi, 7, 7}^{(1)}$ and $F_{\rho, 18, 18}^{(4)} \equiv F_{\psi, 18, 18}^{(4)}$ of the SLMOs ρ_7 , ρ_{18} and the orbital

energies ϵ_7 and ϵ_{18} of the CMOs $\varphi_7 \equiv a_1(\pi)$ and $\varphi_{18} \equiv b_2(\pi)$ as obtained by the three semi-empirical SCF procedures. The 'through-space' interaction corresponds to the step from the LMOs to the SLMOs (see (23)), whereas the one from the SLMOs to the CMOs includes the total 'through-bond' contributions $\tau_7^{(1)}$ and $\tau_{18}^{(4)}$. It is immediately obvious that the three models differ significantly in their assessment of the size of these contributions (in eV):

	SPINDO	MINDO/2	CNDO/2	
$A_1: \tau_7^{(1)}$	0.85	2.07	6.46	
$B_2: \tau_{18}^{(4)}$	0.34	0.66	1.96	(25)
$\tau_7^{(1)} - \tau_{18}^{(4)}$	0.51	1.41	4.50	

Table 4. Second-order 'through-bond' shifts $\tau_j^{(1)}$ and $\tau_{18j}^{(4)}$ due to interaction of the π -SLMOs $\psi_7 \equiv \varrho_7$ and $\psi_{18} \equiv \varrho_{18}$ with the PCMOs ψ_1 of same symmetry. Values calculated according to (19) in eV. The three values given for each j refer from top to bottom to SPINDO, MINDO/2 and CNDO/2 respectively. a = second order treatment not applicable.

ψ_j	$\Gamma^{(1)} \equiv A_1$			ψ_j	$\Gamma^{(4)} \equiv B_2$		
	$F_{\psi, 7, 7}^{(1)} - F_{\psi, jj}^{(1)}$	$F_{\psi, 7j}^{(1)}$	$\tau_{7j}^{(1)}$		$F_{\psi, 18, 18}^{(4)} - F_{\psi, jj}^{(4)}$	$F_{\psi, 18j}^{(4)}$	$\tau_{18j}^{(4)}$
1	16.49	0.02	0.00	14	13.12	-0.80	0.05
	31.32	0.31	0.00		19.43	-1.51	0.12
	40.11	0.75	0.01		23.90	-4.33	0.78
2	10.54	0.95	0.09	15	5.58	1.18	0.25
	15.16	2.07	0.28		5.32	1.58	0.47
	16.16	3.92	0.95		11.36	3.86	1.31
3	7.40	0.54	0.04	16	4.17	-0.48	0.06
	8.08	0.65	0.05		2.39	-0.41	0.07
	10.28	2.49	0.60		4.26	-0.63	0.09
4	6.12	0.34	0.02	17	2.45	-0.04	0.00
	6.20	0.52	0.04		0.88	0.36	0.15
	9.22	1.49	0.24		1.49	0.42	0.12
5	1.81	-0.14	0.01				
	-0.28	1.47	a				
	-2.03	-4.51	a				
6	1.32	-1.24	a				
	-0.69	-0.85	a				
	-3.27	1.45	a				

We note that the 'through-bond' interaction predicted for the $b_2(\pi)$ orbital is by no means negligible. The difference between the shifts suffered by the symmetric and the antisymmetric SLMOs, as predicted by CNDO/2, is almost a power of ten larger than by SPINDO, MINDO/2 taking an intermediate position. Furthermore $\tau_7^{(1)}$ derived from the CNDO/2 model is so large that it leads to an inverted order of the $a_1(\pi)$ and $b_2(\pi)$ CMO orbital energies, a result which is in contradiction with PE spectroscopic results [5] if *Koopmans'* approximation is accepted. However, both the 'correct' and the reversed order predicted by MINDO/2 and CNDO/2 respectively must be considered as accidental, because the resulting difference $|\epsilon(b_2(\pi)) - \epsilon(a_1(\pi))|$

is smaller by a factor of 10 to 20 than the individual 'through-space' and 'through-bond' contributions. As we shall see in the next example, the calculated order depends critically on small changes in the assumed molecular geometry.

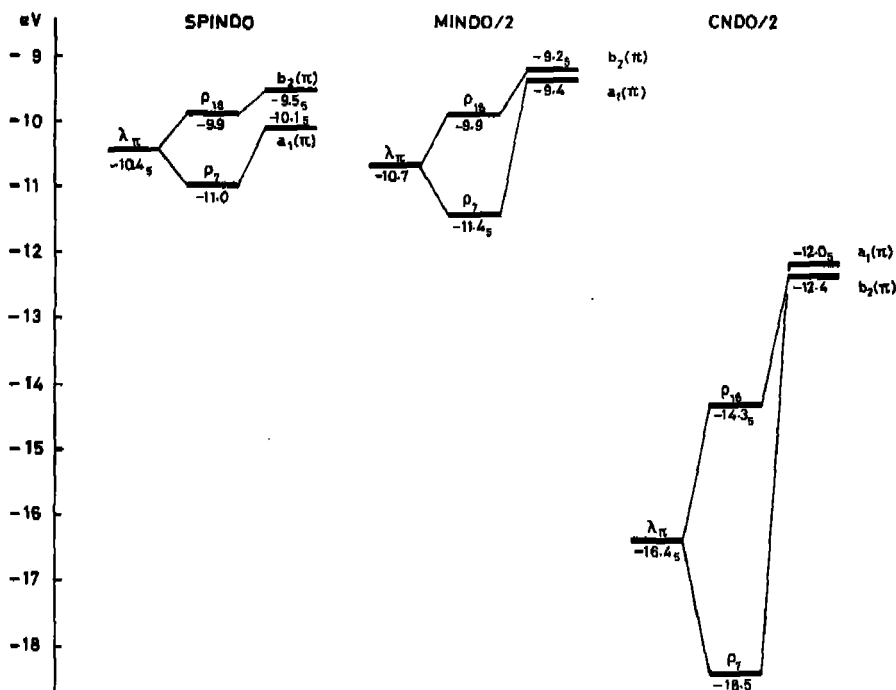
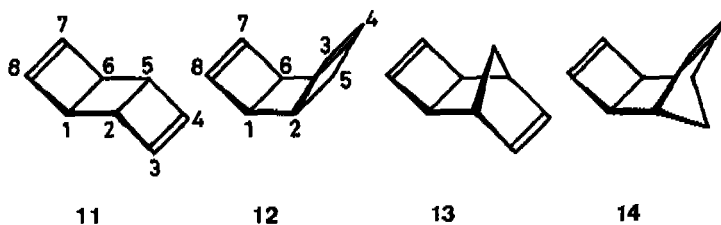


Fig. 1. Correlation diagram for 'through-space' and 'through-bond' interaction of π_a and π_b in norbornadiene (1) (See 'Discussion' of Example 1 in section 3)

A typical example for this type of difficulty is provided by the analysis of the PE. spectra of *anti*- (11) and *syn*-tricyclo[4.2.0.0^{2,5}]octadiene (12) [30].



Correlation techniques based on the experimentally observed ionization energies of 11 and 12, their hydrogenated derivatives and of related systems such as *exo*-13 [31] and *endo*-tricyclo[4.2.1.0^{2,5}]nona-3,7-diene (14) [32] suggest that the two highest occupied orbitals in 11 and 12 are $9a_g(\pi_+)$ (-8.96 eV), $8b_u(\pi_-)$ (-9.93 eV) and $9a_1(\pi_+)$ (-9.08 eV), $8b_g(\pi_-)$ (-9.44 eV) respectively.

Recently 11 and 12 have been reexamined theoretically by two independent groups [33], [34] both using the same MINDO/2 procedure. (The latter group has also

reexamined the PE. spectra of **11** and **12** [34]). In both cases the molecular geometries of these two molecules have been optimized by minimizing the total energy of the systems within the theoretical model chosen.

Whereas the interatomic distances and bond-angles obtained by *Bodor et al.* [34] (values without brackets) agree closely with those expected on the basis of previous experience, *Iwamura et al.* [33] calculate parameters which differ slightly, albeit significantly (values in brackets): **11**, $R_{12} = 1.533$ (1.505), $R_{16} = 1.528$ (1.55), $R_{23} = 1.487$ (1.48), $R_{34} = 1.324$ (1.33) Å, dihedral angle 120.4° (116°); **12**, $R_{13} = 1.542$ (1.50), $R_{16} = 1.521$ (1.55), $R_{23} = 1.476$ (1.48), $R_{34} = 1.330$ (1.33) Å, dihedral angle 119.2° (119°). (Presumably the true energy minimum has not been reached by *Iwamura et al.*). Although the differences in the structural parameter are small (<0.04 Å; $<4.4^\circ$ in **11**) the orbital sequences presented are completely at variance. Whereas *Bodor et al.* give (in descending order) $9a_g(\pi)$, $6a_u(\sigma)$, $8b_u(\sigma)$, $7b_u(\pi)$ for **11** and $8a_1(\pi)$, $8b_2(\sigma)$, $5a_2(\sigma)$, $6b_1(\sigma)$, $7b_2(\pi)$ for **12** [34], *Iwamura et al.* come to the conclusion that 'the highest (occupied) molecular orbitals (are) devoid of any ethylenic π -character' and that they belong to the irreducible representations B_u (**11**) and B_g (**12**) respectively [33]. (Note that the latter representation is B_1 in [33], due to an exchange of the x- and y-axes). The origin for such dramatic discrepancies within the same theoretical model is the extreme sensitivity of the difference and the sum of 'through-space' and 'through-bond' interactions with respect to small changes in geometry. This is evident from the analysis summarized in Fig. 1 for **1**.

It might be mentioned that the occurrence of high lying σ -orbitals is typical for MINDO/2, which has proved to be an unrealistic model for the prediction of ionization energies of small-ring compounds [35], a property shared by MINDO/3 [36]. *Ab-initio* calculations by *Lehm & Wipff* [37] seem to confirm the previously proposed order of the π -orbitals in **11** but the reverse order for **12**, without interspersed σ -dominated orbitals in both cases. Also more recent PE. spectroscopic results on systems related to the hydrocarbons **11** to **14** [38] indicate that the assignments derived by a simple correlation technique [31] or obtained from the *ab-initio* calculations [37] are at least heuristically useful and presumably a safer guide for the interpretation of PE. spectra than semi-empirical calculations. Needless to say that this does not reflect on the usefulness of such models with respect to the properties for which they have been parametrized, e.g. heats of formation in the case of MINDO/2 or MINDO/3.

2. An analysis of the PE. spectra of the hydrocarbons **1** to **5** has led to the conclusion [12] that $\tau_7^{(2)} - \tau_{18}^{(4)} \approx 1.6$ eV. This value agrees best with the one derived from the MINDO/2 model (see (25)), whereas the difference obtained by SPINDO seems to be too small and by CNDO/2 too large by a factor of 3. However, the 'experimental' value has been derived under simplifying assumptions which make a direct comparison somewhat doubtful.

3. As expected the lower lying PCMOs ψ_j are necessarily close in energy to the corresponding CMOs ϕ_j , as can be seen by comparing the entries ϵ_j and $F_{\nu, j}^{(n)}$ in Tab. 1 and 3 (hence the name 'precanonical').

An important feature is that both MINDO/2 and CNDO/2 yield, within the irreducible representation A_1 , two PCMOs ψ_5 and ψ_6 which lie above the SLMO $\phi_7 \equiv \psi_7$, i.e. the symmetry adapted linear combination of the π -LMOs λ_a , λ_b . In

contrast, $\varphi_7 \equiv \psi_7$ is the highest PCMO of symmetry A_1 in SPINDO, a result more in keeping with PE. spectroscopic experience. (Indeed, as mentioned before, the two former methods have a pronounced tendency to yield high-lying σ -CMOs, from which one would infer that a corresponding number of σ -bands should be observed in the π -band region of the PE. spectrum. However, in most cases studied so far this does not seem to be the case.) As a consequence the differences $F_{\psi,77}^{(1)} - F_{\psi,ji}^{(1)}$ for $j = 5$ or 6 are small relative to $F_{\psi,7j}^{(1)}$ (see Tab. 4), so that formula (24) can not be applied even in a crude approximation in the case of the PCMOs belonging to the irreducible representation A_1 , in contrast to those belonging to B_2 .

4. Diagonalization of the matrices $F_{\psi}^{(1)}$ and $F_{\psi}^{(4)}$ given in Tab. 3 leads back to the CMOs φ_j belonging to $\Gamma^{(1)} \equiv A_1$ and $\Gamma^{(4)} \equiv B_2$, which are now expressed as linear combinations over the PCMOs ψ_k :

$$\varphi_j = \sum_k C_{kj} \psi_k \quad (26)$$

The C_{kj} for the highest occupied CMOs φ_7 and φ_{18} of the irreducible representation $\Gamma^{(1)} \equiv A_1$ and $\Gamma^{(4)} \equiv B_2$ are found to be:

$$\varphi_7 \equiv 7a_1(\pi) \quad (27)$$

k =	1	2	3	4	5	6	7		
$C_{k,7}$	{	0.00	0.07	0.06	0.04	-0.05	-0.49	0.86	SPINDO
		0.01	0.08	0.04	0.04	0.57	-0.43	0.69	MINDO/2
		0.01	0.11	0.10	0.06	-0.67	0.30	0.66	CNDO/2

k =	14	15	16	17	18		
$C_{k,18}$	{	-0.06	0.19	-0.10	-0.01	0.97	SPINDO
		-0.07	0.24	-0.12	0.21	0.93	MINDO/2
		-0.16	0.27	-0.09	0.11	0.94	

Whereas in the framework of the SPINDO model, the CMO $\varphi_7 \equiv 7a_1(\pi)$ is essentially π in character, we observe that it is dominated by the σ -components ψ_5 and ψ_6 in both the MINDO/2 and CNDO/2 approximation. This is particularly apparent from Tab. 5 in which the squared coefficients $C_{kj}^2 \cdot 100$ are listed, *i.e.* the percent contributions of the individual PCMOs ψ_k to the CMO φ_j . Both in MINDO/2 and in CNDO/2 the CMOs φ_7 and φ_5 have practically the same π -character, although φ_5 lies 3.4 eV or 9.0 eV below φ_7 and also below φ_6 which is a pure σ -type orbital.

On the other hand all three treatments agree in making $\varphi_{18} \equiv 5b_2(\pi)$ a strongly π -dominated CMO. It is noteworthy that the relatively small contribution of the σ -PCMOs $\psi_{14}, \dots, \psi_{17}$ (see (27)) leads to a sizeable 'through-bond' shift $\tau_{18}^{(4)}$ as indicated in (25) and in Fig. 1. This perhaps surprising result, namely that a minor admixture of σ -PCMOs has such a large effect on the orbital energy, is nothing but another

confirmation of *Pauling's* well known adage that 'a little hybridization goes a long way'.

5. To conclude the discussion of this example we wish to comment on the shape of those σ -PCMOs which are the important relay orbitals for the 'through-bond' interaction in the CMOs $\varphi_7 \equiv 7a_1(\pi)$ and $\varphi_{18} \equiv 5b_2(\pi)$. According to (27) and to Tab. 5 these are

	SPINDO	MINDO/2	CNDO/2	
$\varphi_7 \equiv 7a_1(\pi)$	ψ_6	ψ_5 and ψ_6	ψ_5	(28)
$\varphi_{18} \equiv 5b_2(\pi)$	ψ_{15}	ψ_{15} and ψ_{17}	ψ_{15}	

Table 5. Build-up of the CMOs φ_j belonging to the irreducible representations A_1 and B_2 from the PCMOs ψ_k . The numbers given are the percent contribution of the PCMO ψ_k to the CMO φ_j , i.e. the square of the coefficients C_{kj} in the expansion $\varphi_j = \sum_k C_{kj} \psi_k$. (see (26)).

		CMO		PCMO						
		φ_j	ϵ_j	ψ_1	ψ_2	ψ_3	ψ_4	ψ_5	ψ_6	$\psi_7 \equiv \rho_7$
SPINDO	φ_7	-10.13	0	1	0	0	0	24	74	
	φ_6	-12.77	0	0	0	0	91	8	1	
	φ_5	-13.02	0	0	0	0	9	68	24	
MINDO/2	φ_7	-9.40	0	1	0	0	32	19	48	
	φ_6	-10.88	0	0	0	0	26	72	1	
	φ_5	-12.78	0	1	0	1	41	9	48	
CNDO/2	φ_7	-12.04	0	1	1	0	45	9	43	
	φ_6	-15.36	0	0	0	0	11	88	1	
	φ_5	-21.04	0	4	5	2	43	3	44	
		φ_j	ϵ_j	ψ_{14}	ψ_{15}	ψ_{16}	ψ_{17}	$\psi_{18} \equiv \rho_{18}$		
SPINDO	φ_{18}	-9.57	0	4	1	0	95	0		
	φ_{17}	-12.35	0	0	0	100	0			
MINDO/2	φ_{18}	-9.26	0	6	2	5	87			
	φ_{17}	-10.87	0	1	0	95	4			
CNDO/2	φ_{18}	-12.40	2	7	1	1	88			
	φ_{17}	-15.89	0	0	0	99	1			

Note that PCMOs of same index may have different phase-relationships between the LMOs from which they are built (see Tab. 3) depending on the theoretical model used. From Tab. 3 we see that all the PCMOs listed in (28) are heavily localized on the CH-bonds of the bridging methylene group and on the CC-bonds 1,2; 1,6; 3,4 and 4,5. This becomes even more apparent if the CMOs φ_7 and φ_{18} are expressed in terms of the SLMOs ϱ_1 according to

$$\varphi_j = \sum_1 c_{1j} \varrho_1, \quad (29)$$

the ϱ_1 being defined as in Tab. 2. The coefficients c_{17} and c_{118} are:

		$\varphi_7 \equiv 7a_1(\pi)$							
i =		1	2	3	4	5	6	7	
		-0.06	-0.16	-0.02	0.32	-0.32	0.15	0.86	SPINDO
c_{i7}		-0.10	-0.20	-0.05	0.45	-0.47	0.21	0.69	MINDO/2
		0.06	-0.15	-0.15	0.38	-0.55	0.26	0.66	CNDO/2
		$\varphi_{18} \equiv 5b_2(\pi)$							(30)
i =		14	15	16	17	18			
		0.01	0.02	-0.16	-0.16	0.97			SPINDO
c_{i18}		0.09	0.01	-0.32	-0.12	0.93			MINDO/2
		0.00	0.03	-0.33	-0.11	0.94			CNDO/2

Thus the π -orbitals $\lambda_a \equiv \pi_a$ and $\lambda_b \equiv \pi_b$ 'see' mainly the CH- σ -orbitals of the methylene group and the sp^3 - sp^2 CC- σ -orbitals of the six-membered ring in both φ_7 and in φ_{18} . A necessary consequence is, that the replacement of the methylene group in position 7 by a difluoromethylene group will lower the orbital energies of $\varphi_7 \equiv 7a_1(\pi)$ and of $\varphi_{18} \equiv 18b_2(\pi)$, in essential agreement with the photoelectron-spectroscopic observation mentioned at the beginning [20].

Example 2: Dependence of 'Through-space' and 'Through-bond' Interactions on the Dihedral Angle in 1,4-Cyclohexadiene and its Bridged Derivatives. - This problem has been discussed qualitatively, based on simple HMO-type models [11] [12] and by *Bischof* using the MINDO/2 procedure [39], in view of explaining the trend observed in the first two ionization energies of the series of hydrocarbons 1 to 5.

Since then, some doubt has been cast on the experimentally determined dihedral angle $\omega = 163^\circ$ [40] that had been assumed for 1,4-cyclohexadiene (5) (see [12]).

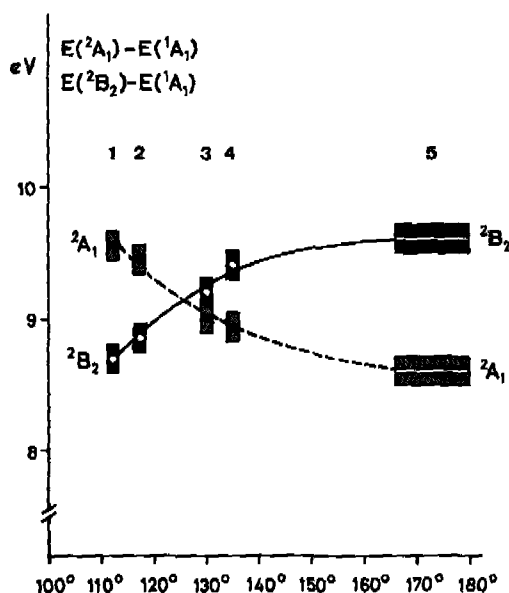


Fig. 2. Dependence of the energy of the radical cation states 2A_1 and 2B_2 of the dienes 1 to 5 on the dihedral angle ω

More recent investigations suggest that this molecule is planar ($\omega = 180^\circ$) [41]. However, as can be seen from Fig. 2, this uncertainty does not affect our argument. This Figure shows the dependence of the energies of the 2A_1 and 2B_2 states of the radical cations 1^+ to 5^+ , relative to the 1A_1 ground-state of the parent hydrocarbons, as a function of ω . The assignment of symmetries to the radical cation states rests on the method described previously [9] [10] [12]. The important result is that the two radical cation states, which correspond to the removal of an electron from one or the other of the two highest π -CMOs $a_1(\pi)$ and $b_2(\pi)$ cross for $\omega \approx 130^\circ$. In orbital language (*i.e.* assuming the validity of *Koopmans'* theorem) this means that $b_2(\pi)$

Table 6. *Semi-empirical CMO orbital energies ($\epsilon(\varphi_i)$), LMO and SLMO selfenergies ($F_{\lambda,\pi}$ and $F_{\rho,++}$, $F_{\rho,--}$) for a hypothetical cyclohexa-1,4-diene (5) with dihedral angle $\omega = 180^\circ, 150^\circ, 120^\circ$. All values in eV. For $\omega = 180^\circ$ the system exhibits D_{2h} symmetry; nevertheless the C_{2v} labels for the CMOs have been kept for sake of convenience.*

		$\omega = 180^\circ$	$\omega = 150^\circ$	$\omega = 120^\circ$
SPINDO	$\epsilon(a_1(\pi))$	- 9.58	- 9.72	-10.16
	$\epsilon(b_2(\pi))$	-10.29	-10.12	- 9.47
	$F_{\lambda,\pi}$	-10.46	-10.44	-10.41
	$F_{\rho,++}$	-10.62	-10.69	-11.07
	$F_{\rho,--}$	-10.29	-10.19	- 9.74
MINDO/2	$\epsilon(a_1(\pi))$	- 9.09	- 9.29	- 9.89
	$\epsilon(b_2(\pi))$	-10.29	- 9.95	- 8.90
	$F_{\lambda,\pi}$	-10.62	-10.63	-10.64
	$F_{\rho,++}$	-10.95	-11.10	-11.64
	$F_{\rho,--}$	-10.29	-10.16	- 9.63
CNDO/2	$\epsilon(a_1(\pi))$	-11.99	-12.40	-13.57
	$\epsilon(b_2(\pi))$	-15.29	-14.26	-11.12
	$F_{\lambda,\pi}$	-16.54	-16.63	-17.64(!)
	$F_{\rho,++}$	-17.79	-18.12	-19.66
	$F_{\rho,--}$	-15.29	-15.13	-15.62

lies above $a_1(\pi)$ in 1 and 2, but below $a_1(\pi)$ in 3, 4 and 5. The observed splits $\epsilon(b_2(\pi)) - \epsilon(a_1(\pi))$ are 0.8₅, 0.6, -0.2, -0.3₅ and -1.0 eV for 1, 2, 3, 4 and 5 respectively (see [9] [10] [12]).

To investigate the relative importance of 'through-space' and 'through-bond' interaction in such molecules we have again carried out semi-empirical calculations, within the three models used above for hypothetical 1,4-cyclohexadienes (5) with dihedral angles $\omega = 180^\circ, 150^\circ$ and 120° , keeping all other parameters constant, *i.e.* $R_{C=C} = 1.34 \text{ \AA}$, $R_{C-C} = 1.50 \text{ \AA}$, $R_{C-H} = 1.10 \text{ \AA}$, $\sphericalangle(C-C-C) = 123^\circ$, $\sphericalangle(H-C-H) = 109\frac{1}{2}^\circ$. The results obtained are summarized in Tab. 6 and in Fig. 3. For simplicity, the following abbreviations have been used: $F_{\lambda,\pi}$ stands for the selfenergies of the LMOs $\lambda_a \equiv \pi_a$ and $\lambda_b \equiv \pi_b$, $F_{\rho,++}$ and $F_{\rho,--}$ for selfenergies of the π -SLMOs ρ_+ ($\equiv \rho_a$) and ρ_- ($\equiv \rho_{1a}$) belonging to the irreducible representations $\Gamma^{(1)} \equiv A_1$ and $\Gamma^{(6)} \equiv B_2$.

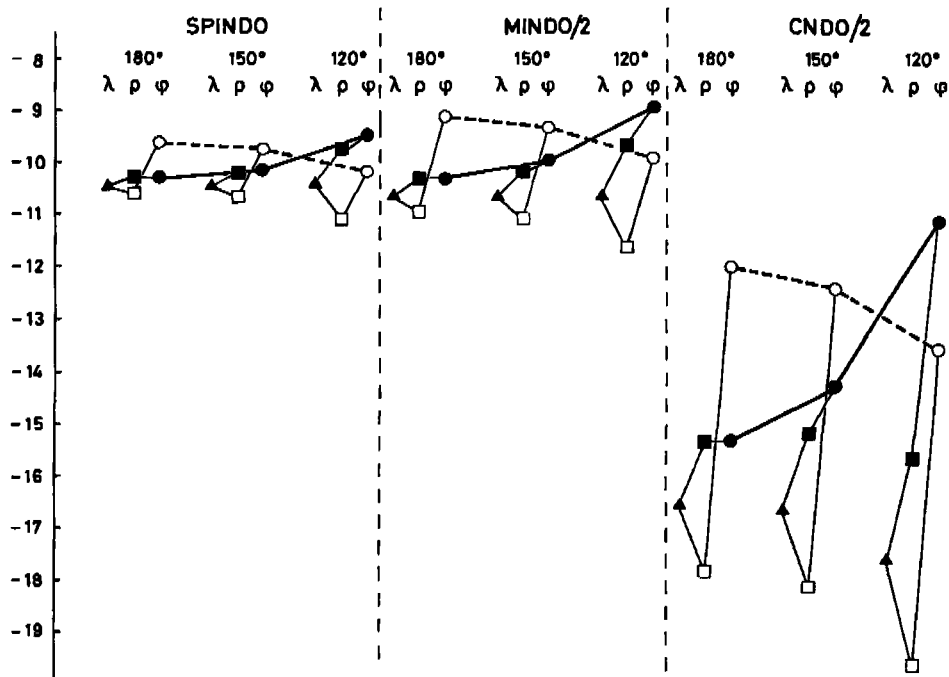


Fig. 3. Orbital energies of the LMOs ($\lambda_a \equiv \pi_a$, $\lambda_b \equiv \pi_b$), the SLMOs (ρ_+ , ρ_-) and the CMOs ($\varphi_6 \equiv a_1(\pi)$, $\varphi_{16} \equiv b_2(\pi)$) of **5** as a function of the dihedral angle ω ; \blacktriangle = LMO energies; \square , \blacksquare = SLMO energies; \circ , \bullet = CMO energies. Open squares and circles refer to orbitals of A_1 symmetry, full squares and circles to orbitals of B_2 symmetry.

It is gratifying to observe that all three semi-empirical treatments (SPINDO, MINDO/2 and CNDO/2) agree in predicting a crossing of the π -CMOs $\varphi_6 \equiv a_1(\pi)$ and $\varphi_{16} \equiv b_2(\pi)$ near $\omega \approx 130^\circ$. On the other hand the three models differ considerably with regard to the quantitative aspects of the 'through-space' and 'through-bond' interactions, as shown in the following comparison, in which 'through-space-Split' stands for the difference $F_{\rho,-} - F_{\rho,+}$ of the selfenergies of the SLMOs ρ_- and ρ_+ , and τ_+ , τ_- for the 'through-bond' destabilizations, as defined previously (all values in eV):

	ω	180°	150°	120°	
SPINDO	through-space-Split	0.33	0.50	1.33	
	τ_+	1.04	0.97	0.91	
	τ_-	0.00	0.07	0.27	
MINDO/2	through-space-Split	0.66	0.94	2.01	
	τ_+	1.86	1.81	1.75	(31)
	τ_-	0.00	0.21	0.73	
CNDO/2	through-space-Split	2.50	2.99	4.04	
	τ_+	5.80	5.72	6.09	
	τ_-	0.00	0.87	4.50	

As in the first example the 'through-space' and 'through-bond' interactions calculated by the CNDO/2 procedure are larger by almost an order of magnitude than those derived from the SPINDO model. Again MINDO/2 assumes an intermediate position. As a consequence the CMO $a_1(\pi)$ has a rather low π -character according to both MINDO/2 and CNDO/2 and even $b_2(\pi)$ tends to be rather mixed with decreasing dihedral angle ω :

		π -character (in percent)		
		SPINDO	MINDO/2	CNDO/2
$a_1(\pi)$	180°	81	70	58
	150°	82	69	57
	120°	82	63	49
$b_2(\pi)$	180°	100	100	100
	150°	98	92	87
	120°	94	83	65

(32)

Comparing these results to the rules of thumb derived empirically from the photoelectron spectra of unsaturated hydrocarbons, one comes to the conclusion that MINDO/2, and certainly CNDO/2 exaggerate the amount of σ/π -mixing in such systems.

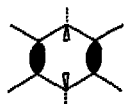
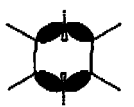
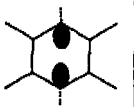
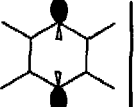
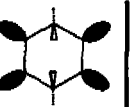
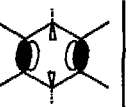


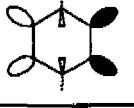

If one disregards the quantitative aspects, all three models agree in yielding the same rationalization for the experimentally observed crossing of the radical-cation states 2A_1 and 2B_2 shown in Fig. 3. As expected, the 'through-space' interaction between the LMOs $\lambda_a \equiv \pi_a$ and $\lambda_b \equiv \pi_b$ decreases with increasing ω , proportional to the overlap integral $S_{ab} = \langle \pi_a | \pi_b \rangle$, whereas the 'through-bond' induced shift τ_+ of the π -orbital belonging to the representation A_1 is almost independent of ω . Surprisingly enough, the major reason for the observed crossing of $a_1(\pi)$ and $b_2(\pi)$ is the unexpected large increase of τ_- with decreasing angle ω . The latter 'through-bond' contribution has usually been assumed to be negligibly small in qualitative discussions, because the methylene groups lie on the nodal plane of the orbital $b_2(\pi)$ for all values of ω and are thus not available for hyperconjugative 'through-bond' interaction within this orbital. It is therefore worthwhile to analyse the lack of dependence of τ_+ on ω and the origin of τ_- for $\omega < 180^\circ$ in more detail. To this end we shall concentrate our attention on the SPINDO model, this being obviously the model most appropriate for the rationalization of photoelectron spectroscopic results.

In Tab. 7 are shown qualitative representations of the SLMOs ϱ_1 to ϱ_6 (belonging to $\Gamma^{(2)} \equiv A_1$) and ϱ_{13} to ϱ_{16} (belonging to $\Gamma^{(4)} \equiv B_2$) of **5** ($\omega = 180^\circ, 150^\circ, 120^\circ$) which have been obtained according to steps A to C, using the SPINDO procedure. As before the $F_{\varrho_i}^{(r)}$ ($r = 1, 4$) are the selfenergies of the SLMOs ϱ_i . The coefficients c_{16} and c_{116} are those, which according to (29) define the CMOs $\varphi_6 \equiv a_1(\pi)$ and $\varphi_{16} \equiv b_2(\pi)$:

$$\varphi_6 = \sum_{i=1}^6 c_{i6} \varrho_i; \quad \varphi_{16} = \sum_{i=13}^{16} c_{i16} \varrho_i \quad (33)$$

In the totally symmetrical CMO $\varphi_8 \equiv a_1(\pi)$ the π -SLMO $\varrho_8 \equiv \varrho_+$ interacts out-of-phase with the pseudo- π -orbitals of the two methylene groups, which for $\omega = 180^\circ$ can be written as $(\varrho_3 - \varrho_4)/\sqrt{2}$. This particular 'through-bond' interaction is usually termed hyperconjugation. With decreasing ω the interaction of ϱ_8 with the SLMO ϱ_4 is getting smaller, *i.e.* with the SLMO of those CH-bonds which assume an equatorial position for $\omega < 180^\circ$. However, the associated loss in hyperconjugation of $\varphi_8 \equiv a_1(\pi)$ is compensated by the increase in mixing with the CC- σ -SLMO ϱ_2 as

Table 7. SLMO selfenergies $F_{\varrho_i, j}^{(1)}$ and $F_{\varrho_i, j}^{(4)}$ and coefficients of the CMOs in terms of the SLMOs for **5** with dihedral angles $\omega = 180^\circ, 150^\circ$ and 120° , as calculated by the SPINDO method

$\Gamma^{(1)} \equiv A$		ρ_1	ρ_2	ρ_3	ρ_4	ρ_5	ρ_6
							
$F_{\rho_i, j}^{(1)}$	180°	-20.17	-19.07	-16.32	-16.32	-17.25	-10.62
	150°	-20.24	-19.23	-16.45	-16.38	-17.24	-10.69
	120°	-20.59	-19.68	-16.72	-16.53	-17.24	-11.07
c_{j6}	180°	0.00	0.00	-0.31	0.31	0.00	0.90
	150°	0.03	0.09	-0.35	0.23	-0.05	0.90
	120°	0.01	0.18	-0.35	0.16	-0.08	0.90
$\Gamma^{(4)} \equiv B_2$		ρ_{13}	ρ_{14}	ρ_{15}	ρ_{16}		
							
$F_{\rho_i, j}^{(4)}$	180°	-19.60	-15.24	-17.14	-10.29		
	150°	-19.51	-15.00	-17.08	-10.19		
	120°	-19.10	-14.34	-16.91	-9.74		
c_{j16}	180°	0.00	0.00	0.00	1.00		
	150°	0.00	-0.13	0.04	0.99		
	120°	-0.07	-0.21	0.08	0.97		

sociated with the four sp^2 - sp^3 CC-single bonds emanating from the two double bonds. As a consequence τ_+ remains practically constant.

For symmetry reasons there is no hyperconjugative contribution from the two methylene groups to the 'through-bond' interaction τ_- affecting the energy of the CMO $\varphi_{16} \equiv b_2(\pi)$. However, for $\omega < 180^\circ$ one notices a strong increase of the interaction of the CC- σ -SLMO ϱ_{14} with the π -SLMO $\varrho_{16} \equiv \varrho_-$. Again, as in the case of ϱ_8 , ϱ_{14} is built from the LMOs of the four sp^2 - sp^3 CC-bonds.

Thus the previously used qualitative picture which assumed that only the CMO $a_1(\pi)$ is strongly affected by an ω -dependent 'through-bond' interaction ($\tau_+ = \tau_+(\omega)$), whereas $b_2(\pi)$ is completely devoid of this type of destabilizing contribution ($\tau_- = 0$) has to be modified. With increased bending, *i.e.* with decreasing dihedral ω , the LMOs π_a and π_b 'see' more and more of the σ -LMOs of the two sp^3 - sp^3 CC-single bonds on the other side of the molecule. In fact, it is this contribution which is responsible for the observed orbital crossing near $\omega = 130^\circ$.

For the development of qualitative arguments it is of some interest to visualize the important relay orbitals responsible for the 'through-bond' interaction between the LMOs $\lambda_a \equiv \pi_a$ and $\lambda_b \equiv \pi_b$. As explained in section 2, the best way of achieving this, consists in calculating the relevant PCMOs. In Tab. 8 are given the energy gaps $F_{\psi,6,6}^{(1)} - F_{\psi,jj}^{(1)}$ and $F_{\psi,16,16}^{(4)} - F_{\psi,jj}^{(4)}$ between the selfenergies of the PCMOs $\psi_6 \equiv \varrho_6 \equiv \varrho_+$ or $\psi_{16} \equiv \varrho_{16} \equiv \varrho_-$ and the other PCMOs belonging respectively to the irreducible representations A_1 or B_2 . The $F_{\psi,6}^{(4)}$ and $F_{\psi,16j}^{(4)}$ are the cross terms which link the PCMOs $\psi_1 \dots \psi_5$ to $\psi_6 \equiv \varrho_6$ and $\psi_{13}, \dots \psi_{16}$ to $\psi_{16} \equiv \varrho_{16}$. From these, one calculates the second order contributions to τ_+ and τ_- according to (19). It is immediately obvious that the main relay PCMO for 'through-bond' interaction in $a_1(\pi)$ is ψ_4 , yielding a contribution $\tau_{6,4}^{(1)}$ of ~ 1 eV to τ_+ . The decrease in $\tau_{6,4}^{(1)}$ with decreasing ω is compensated by the increase in $\tau_{6,5}^{(1)}$ due to 'through-bond' interaction of $\psi_6 \equiv \varrho_6$ with the PCMO ψ_5 . On the other hand the 'through-bond' interaction which occurs in $b_2(\pi)$ when $\omega < 180^\circ$ involves mainly the PCMO ψ_{15} .

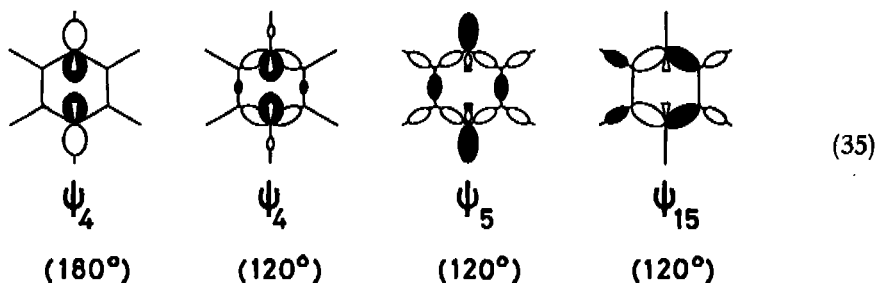
Table 8. PCMO selfenergy differences ($F_{\psi,6,6}^{(1)} - F_{\psi,jj}^{(1)}$, $F_{\psi,16,16}^{(4)} - F_{\psi,jj}^{(4)}$), cross terms ($F_{\psi,6}^{(4)}$, $F_{\psi,16j}^{(4)}$) and second order perturbation contributions ($\tau_{6,j}^{(1)}$, $\tau_{16,j}^{(4)}$) for the 'through-bond' interaction of $\lambda_a \equiv \pi_a$ and $\lambda_b \equiv \pi_b$. All values in eV. The values of $\tau_{6,j}^{(1)}$ and $\tau_{16,j}^{(4)}$ have been computed according to the second order approximation (19), except those given in brackets which were obtained by solving the corresponding secular determinant of order 2. The corresponding second order results would have been for $\omega = 180^\circ, 150^\circ, 120^\circ$: $\tau_{6,j}^{(1)} = 1.36, 1.19, 1.03$ eV.

ω	ψ_j	$F_{\psi,6,6}^{(1)} - F_{\psi,jj}^{(1)}$	$F_{\psi,6j}^{(1)}$	$\tau_{6j}^{(1)}$	ψ_j	$F_{\psi,16,16}^{(4)} - F_{\psi,jj}^{(4)}$	$F_{\psi,16j}^{(4)}$	$\tau_{16j}^{(4)}$
180°	1	15.30	0.00	0.00	13	12.75	0.00	0.00
150°		15.33	0.21	0.00		12.73	-0.22	0.00
120°		15.35	0.48	0.02		12.73	-0.90	0.06
180°	2	9.72	0.00	0.00	14	4.83	0.00	0.00
150°		9.85	0.22	0.01		4.80	0.22	0.01
120°		9.36	0.15	0.00		4.87	0.03	0.00
180°	3	5.82	0.00	0.00	15	3.51	0.00	0.00
150°		5.90	-0.18	0.01		3.49	-0.44	0.06
120°		5.79	-0.11	0.00		3.51	-0.90	0.23
180°	4	3.41	-2.15	(1.04)				
150°		3.40	-2.01	(0.93)				
120°		3.31	-1.85	(0.83)				
180°	5	1.79	0.00	0.00				
150°		1.80	0.31	0.05				
120°		1.60	0.44	0.12				

These PCMOs can be given as linear combinations in terms of the SLMOs displayed in Tab. 7:

$$\begin{aligned}
 \omega = 180^\circ \quad \psi_4 & \equiv & & 0.71 \varrho_3 - 0.71 \varrho_4 \\
 \omega = 150^\circ \quad \psi_4 & = 0.09 \varrho_1 - 0.36 \varrho_2 + 0.84 \varrho_3 - 0.39 \varrho_4 + 0.08 \varrho_5 \\
 \omega = 120^\circ \quad \psi_4 & = 0.19 \varrho_1 - 0.56 \varrho_2 + 0.80 \varrho_3 - 0.11 \varrho_5 + 0.08 \varrho_5 \\
 \omega = 120^\circ \quad \psi_5 & = 0.45 \varrho_1 - 0.34 \varrho_2 - 0.21 \varrho_3 + 0.65 \varrho_4 - 0.46 \varrho_5 \\
 \omega = 120^\circ \quad \psi_{15} & = 0.10 \varrho_{13} + 0.84 \varrho_{14} - 0.54 \varrho_{15}
 \end{aligned} \tag{34}$$

Their phase relationship can be represented qualitatively as follows:



The PCMOs ψ_4 and ψ_5 are closely related to the so-called 'ribbon-orbital' of A_1 symmetry [14].

Example 3: 'Lone-pair Interaction' in 1,4-Diazabicyclo[2.2.2]octane (6). - The photoelectron spectrum of **6** [6], if interpreted in terms of *Koopmans'* theorem, leads to the conclusion that the interaction of the lone-pair basis orbitals n_1 and n_4 is almost exclusively 'through-bond', placing the totally symmetric CMO $a_1'(n)$ above the antisymmetric CMO $a_2''(n)$. More precisely, the photoelectron spectrum indicates that the state ${}^2A_1'(n)$ of the radical cation 6^+ (*i.e.* corresponding to the ejection of the photoelectron from the CMO $a_1'(n)$) is more stable by 2.1 eV than the state ${}^2A_2''(n)$ (ejection from $a_2''(n)$). We shall not be concerned with the interpretation of the photoelectron spectrum of **6**, but rather with the question, how the interaction between n_1 and n_4 is described by a particular semi-empirical SCF procedure *viz.* by MINDO/2. We chose this model because it was used previously by *Dewar & Wasson* [42] who confirmed the qualitative and EHT results [3] [43] concerning the n_1, n_4 -interaction. The geometry assumed for **6** is, under strict D_{3h} symmetry: $R(CC) = 1.52 \text{ \AA}$, $R(CN) = 1.47 \text{ \AA}$, $R(CH) = 1.09 \text{ \AA}$ and all angles tetrahedral.

For the valence shell of **6** a set of 23 CMOs φ_i is obtained. They distribute over the irreducible representations of D_{3h} as follows:

$$(4 \times A_1') + A_2' + (4 \times E') + A_1'' + (3 \times A_2'') + (3 \times E'') \tag{36}$$

Of these the two 'lone-pair' CMOs are $\varphi_1 \equiv a_1'(n)$; $\varepsilon_1 = -8.56 \text{ eV}$ and $\varphi_{15} \equiv a_2''(n)$; $\varepsilon_{15} = -10.36 \text{ eV}$, *i.e.* $\varepsilon_1 - \varepsilon_{15} = 1.80 \text{ eV}$. (The CMOs φ_i are numbered from top to bottom within the sequence (36) of irreducible representations). In the following we shall limit the discussion exclusively to the corresponding irreducible representations A_1' and A_2'' .

The lone-pair LMOs $\lambda(n_1)$ and $\lambda(n_4)$ are obtained according to (5), (6) and (7). Their phases are chosen in such a way that they transform into each other under D_{3h} according to A'_1 . The corresponding matrix elements of F_λ are $F_{\lambda, n_1, n_1} = F_{\lambda, n_4, n_4} = -14.22$ eV and $F_{\lambda, n_1, n_4} = 0.14$ eV. It is of interest that the latter matrix element is positive, so that 'through-space' interaction between $\lambda(n_1)$ and $\lambda(n_4)$ will already place the symmetric SLMO $\varrho_+ = (\lambda(n_1) + \lambda(n_4))/\sqrt{2}$ above the anti-symmetric SLMO $\varrho_- = (\lambda(n_1) - \lambda(n_4))/\sqrt{2}$. This is not what one would have predicted from the usual overlap criterion. If n_1 and n_4 of **6** are assumed to be pure Slater-type sp^3 orbitals with exponents of 1.95, separated by a distance of 2.4 to 2.6 Å and pointing away from each other, then a positive overlap integral S_{14} of 0.016 to 0.011 is calculated. This leads to a small but negative resonance integral, e.g. within the EHT model, and thus to the natural sequence of ϱ_- above ϱ_+ . Obviously this is not the case if the LMOs $\lambda(n_1)$ and $\lambda(n_4)$ are used and if the cross-term includes electron-electron repulsion. It follows that for small or vanishing overlaps it is not always possible to deduce the sign of the 'through-space' interaction between LMOs by qualitative arguments and that it will depend rather critically on the type of model and/or the geometry assumed.

The 'lone-pair' SLMOs obtained according to (9) from the LMOs $\lambda(n_1)$, $\lambda(n_4)$ will be designated by $\varrho_1 \equiv \varrho_+$ and $\varrho_{15} \equiv \varrho_-$ belonging respectively to $\Gamma^{(1)} \equiv A'_1$ and $\Gamma^{(5)} \equiv A'_2$. Their orbital energies are $F_{\varrho_+, +}^{(1)} = -14.08$ eV, $F_{\varrho_-, -}^{(5)} = -14.36$ eV. The remaining SLMOs are also completely determined by symmetry and can be characterized as follows:

$$\Gamma^{(1)} \equiv A'_1: \varrho_2 = \varrho^{(1)}(\text{CC}), \varrho_3 = \varrho^{(1)}(\text{CH}), \varrho_4 = \varrho^{(1)}(\text{CN});$$

$$\Gamma^{(5)} \equiv A'_2: \varrho_{16} = \varrho^{(5)}(\text{CH}), \varrho_{17} = \varrho^{(5)}(\text{CN}).$$

The PCMO matrices $F_\psi^{(1)}$ and $F_\psi^{(5)}$ derived according to (18) from the SLMO matrices $F_\varrho^{(1)}$ and $F_\varrho^{(5)}$ are for $\Gamma^{(1)} \equiv A'_1$,

$F_\psi^{(1)}$	ψ_1	ψ_2	ψ_3	ψ_4	
ψ_1	- 12.75			- 3.93	
ψ_2		- 21.92		3.11	(37)
ψ_3			- 43.60	- 6.26	
ψ_4	- 3.93	3.11	- 6.26	- 14.08	

with

$$\begin{aligned} \psi_1 &= -0.87 \varrho^{(1)}(\text{CC}) + 0.43 \varrho^{(1)}(\text{CH}) + 0.24 \varrho^{(1)}(\text{CN}) \\ \psi_2 &= 0.14 \varrho^{(1)}(\text{CC}) + 0.69 \varrho^{(1)}(\text{CH}) - 0.71 \varrho^{(1)}(\text{CN}) \\ \psi_3 &= 0.47 \varrho^{(1)}(\text{CC}) + 0.58 \varrho^{(1)}(\text{CH}) + 0.66 \varrho^{(1)}(\text{CN}) \\ \psi_4 &= \varrho^{(1)}(n_1 + n_4) \end{aligned} \quad (38)$$

and for $\Gamma^{(5)} \equiv A'_2$,

$F_{\psi}^{(5)}$	ψ_{15}	ψ_{16}	ψ_{17}
ψ_{15}	-16.91		1.87
ψ_{16}		-29.72	-8.19
ψ_{17}	1.87	-8.19	-14.36

(39)

with

$$\begin{aligned} \psi_{15} &= -0.59 \rho^{(5)}(\text{CH}) + 0.80 \rho^{(5)}(\text{CN}) \\ \psi_{16} &= 0.80 \rho^{(5)}(\text{CH}) + 0.59 \rho^{(5)}(\text{CN}) \\ \psi_{17} &= \rho^{(5)}(n_1 - n_4). \end{aligned} \quad (40)$$

To keep the format used in the previous examples $\rho_1 \equiv \rho_+$ and $\rho_{15} \equiv \rho_-$ have been moved into the last columns and rows of $F_{\psi}^{(1)}$ and $F_{\psi}^{(5)}$, i. e. $\psi_4 \equiv \rho_1 \equiv \rho_+$ and $\psi_{17} \equiv \rho_{15} \equiv \rho_-$.

Fig. 4 shows on the left the orbital energy levels of the PCMOs (37), (38) and on the right those of the PCMOs (39) and (40). The two central levels are those of the CMOs $\varphi_1 \equiv a'_1(n)$ and $\varphi_{15} \equiv a''_2(n)$. The values in circles are the crossterms between the

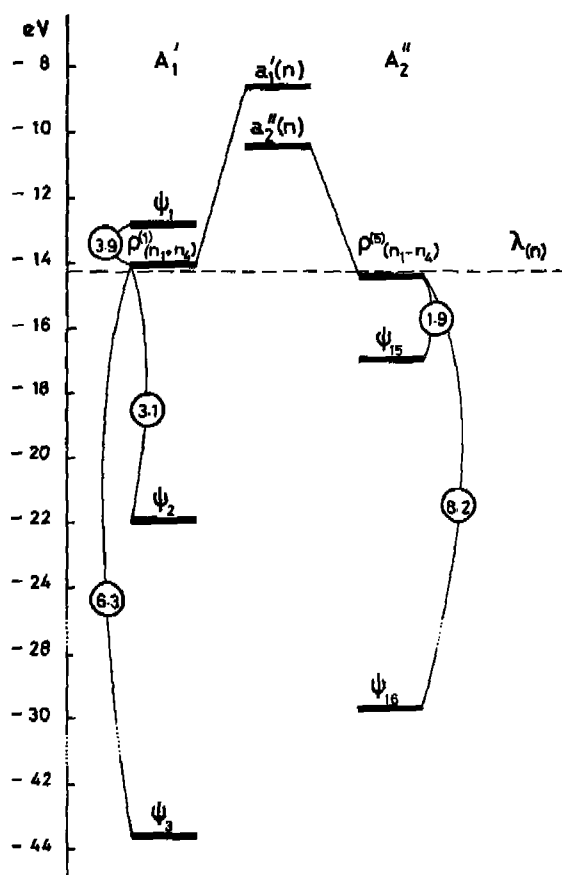


Fig. 4. Orbital energies of the PCMOs (left A_1' , right A_2'') and the two highest CMOs $a'_1(n)$, $a''_2(n)$ of 1,4-diazabicyclo[2.2.2]octane 6

PCMOs, as given in (37) and (39). It is obvious that the second order approximation (19) is not appropriate for the calculation of the 'through-bond' shifts τ_+ and τ_- because of the large size of the interaction elements. Nevertheless the diagram is rather useful for gaining a qualitative insight into the way in which the SLMOs $\varrho_+ \equiv \psi_4$ and $\varrho_- \equiv \psi_{17}$ will respond to 'through-bond' interaction via the relay orbitals ψ_1, ψ_2, ψ_3 or ψ_{15}, ψ_{16} . The result obtained by diagonalizing the matrices $F_{\psi}^{(1)}$, (37) and $F_{\psi}^{(5)}$, (39) is shown in the central part of Fig. 4, as far as the highest occupied CMO of each irreducible representation A_1' and A_2'' is concerned.

A first noteworthy feature is that both ϱ_+ and ϱ_- are strongly affected by 'through-bond' interaction and that the positive displacements $\tau_+ = 5.52$ eV and $\tau_- = 4.00$ eV are much larger than the 'through-space' contributions (0.14 eV) which can be neglected. Thus the previous assumption [3] [6] that the SLMO $\varrho_- = (\lambda(n_1) - \lambda(n_4))/\sqrt{2}$ is not affected by 'through-bond' interaction via lower lying σ -orbitals or even depressed by interaction with antibonding σ^* -orbitals of same symmetry ($\tau_- = 0$ or $\tau_- < 0$) is not correct within the framework of the MINDO/2 treatment and presumably in the framework of any other similar SCF model.

The CMOs $a_1'(n)$ and $a_2''(n)$ can be expressed as follows:

$$\begin{aligned} a_1'(n) &= 0.67 \psi_1 - 0.17 \psi_2 + 0.13 \psi_3 - 0.71 \psi_4 \\ &= -0.54 \varrho^{(1)}(\text{CC}) + 0.25 \varrho^{(1)}(\text{CH}) + 0.37 \varrho^{(1)}(\text{CN}) \\ &\quad - 0.71 \varrho_+(n_1 + n_4) \\ a_2''(n) &= 0.25 \psi_{15} - 0.38 \psi_{16} + 0.89 \psi_{17} \\ &= -0.02 \varrho^{(5)}(\text{CH}) - 0.45 \varrho^{(5)}(\text{CN}) + 0.89 \varrho_-(n_1 - n_4) \end{aligned} \quad (41)$$

It is found that the important relay SLMOs for ϱ_+ are not only $\varrho^{(1)}(\text{CC})$ but also $\varrho^{(1)}(\text{CH})$ and in particular $\varrho^{(1)}(\text{CN})$, *i.e.* the one built from the same LMOs as $\varrho^{(5)}(\text{CN})$ which serves as relay SLMO for ϱ_- .

4. Concluding Remarks. – It has been shown that it is easy to incorporate the heuristically very useful and chemically appealing concepts of 'through-space' and 'through-bond' interactions proposed by *Hoffmann* [3] into a many electron SCF model. The results so obtained will lead in some cases to a reassessment of which orbitals are the really important relay orbitals for a postulated 'through-bond' interaction. This in turn will provide a safer basis for qualitative discussions.

In this paper the treatment described in section 2 was applied to semiempirical SCF treatments. The reason was twofold:

1. Such models are widely used for checking and supporting qualitative arguments coached in orbital language. It is therefore of interest to see how the qualitative concepts, *e.g.* the *Hoffmann*-scheme, reflect in such treatments and whether some of the assumptions made in qualitative arguments are valid within the SCF models used to support them.

2. Independent of the agreement or lack of agreement with qualitative models, the type of analysis proposed yield a reinterpretation of the results obtained through such semiempirical treatments in 'chemical' terms and through these a transparent characterization of their underlying concept, which is otherwise obscured by the complicated interrelationship of the many parameters on which they depend.

In particular it was found that SPINDO goes easy on 'through-bond' interaction and leaves to π -orbitals their local individuality. MINDO/2 yields rather too high-lying σ -orbitals, if the photoelectron spectroscopic results are a guide-line, which mix rather extensively with π and/or lone-pair orbitals. Finally CNDO/2 tends to give dramatic 'through-bond' interactions, which dominate 'through-space' interactions and results in, presumably, exaggerated 'hyperconjugative' contributions. With the possible exception of SPINDO, the small differences in energy of some of the CMOs obtained from these semiempirical treatments are found to be the resultant of the sums and differences of large 'through-space' and 'through-bond' contributions. This suggests that the orbital sequence so derived may well be accidental for close lying CMOs, because of the sensitivity of the contributions to small changes in geometry and/or the underlying parameters. It must be emphasized that this does in no way detract from the usefulness of such semiempirical models with respect to the prediction of such properties for which they were designed and calibrated.

As far as photoelectron spectroscopy is concerned, one might expect that the CMO energies derived from semiempirical SCF treatments are adequate for predicting or rationalizing the essential features of the PE. spectra of medium size organic molecules containing first and second row elements, assuming the validity of *Koopmans'* approximation. This seems to be true for SPINDO which has been calibrated on such spectra. On the other hand MINDO/2 and certainly CNDO/2 are much poorer models for this particular purpose. The application of simple correlation techniques to PE. spectra of sets of related molecules strongly suggest that the orbital schemes 'observed' follow much simpler rules than suggested by either MINDO/2 or CNDO/2 and that some of the orbital sequences predicted are hardly compatible with the PE. spectra observed. In view of the analysis given above, the almost religious belief of some authors in the reliability of the semiempirical treatment they happen to use for the interpretation of their photoelectron spectra is, more often than not, unfounded.

We wish to thank Prof. *Ruben Pauncz* for his interest and many valuable suggestions.

This work is part of project No. 2.159.74 of the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung*. Support by *Ciby-Geigy S.A.*, *F. Hoffmann-La Roche & Cie S.A.* and *Sandoz S.A.* (Basel) is gratefully acknowledged.

A.S. thanks the *Studienstiftung des Deutschen Volkes* for a fellowship.

BIBLIOGRAPHY

- [1] *R. B. Woodward & R. Hoffmann*, J. Amer. chem. Soc. **87**, 395, 2511 (1965); *R. Hoffmann & R. B. Woodward*, *ibid.* **87**, 2046 (1965); *R. B. Woodward & R. Hoffmann*, *Angew. Chem.* **81**, 797 (1969).
- [2] *M. J. S. Dewar*, *Angew. Chem.* **83**, 859 (1971).
- [3] *R. Hoffmann, A. Imamura & W. J. Hehre*, J. Amer. chem. Soc. **90**, 1499 (1968); *R. Hoffmann*, *Accounts chem. Res.* **4**, 1 (1971); *R. Gleiter*, *Angew. Chem.* **86**, 770 (1974); and references given therein.
- [4] *R. Hoffmann*, J. chem. Physics **39**, 1397 (1963); **40**, 2745, 2474, 2480 (1964); *Tetrahedron* **22**, 521, 539 (1966).
- [5] *P. Bischof, J. A. Hashmall, E. Heilbronner & V. Hornung*, *Helv.* **52**, 1745 (1969); *Tetrahedron Letters* **1970**, 1033.
- [6] *P. Bischof, J. A. Hashmall, E. Heilbronner & V. Hornung*, *Tetrahedron Letters* **1969**, 4025; *E. Heilbronner & K. A. Muszkat*, J. Amer. chem. Soc. **92**, 3818 (1970).

- [7] E. Heilbronner & H.-D. Martin, *Helv.* **55**, 1490 (1972).
- [8] Summarized in e.g.: H. Bock & G. B. Ramsey, *Angew. Chem.* **85**, 773 (1973); J. H. D. Eland, *Photoelectron Spectroscopy*, Butterworths, London, 1974.
- [9] M. J. Goldstein, S. Natowsky, E. Heilbronner & V. Ilornung, *Helv.* **56**, 294 (1973).
- [10] E. Heilbronner, XXIIIrd International Congress of Pure and Applied Chemistry, Butterworths, London, 1971, Vol. 7, p. 9.
- [11] R. Hoffmann, E. Heilbronner & R. Gleiter, *J. Amer. chem. Soc.* **92**, 706 (1970).
- [12] E. Heilbronner, *Israel J. Chemistry* **10**, 143 (1972).
- [13] A. D. Bain, J. C. Bünzli, D. C. Frost & L. Weiler, *J. Amer. chem. Soc.* **95**, 291 (1973).
- [14] R. Hoffmann, Ph. D. Mollère & E. Heilbronner, *J. Amer. chem. Soc.* **95**, 4860 (1973).
- [15] J. C. Bünzli, D. C. Frost & L. Weiler, *J. Amer. chem. Soc.* **95**, 7880 (1973).
- [16] E. Heilbronner & J. P. Maier, *Helv.* **57**, 151 (1974).
- [17] S. Pignataro, V. Mancini, J. N. A. Ridyard & H. J. Lempha, *Chem. Commun.* **1971**, 142; R. Boschi & W. Schmidt, *Angew. Chem.* **83**, 408 (1973).
- [18] R. Gleiter, *Tetrahedron Letters* **1969**, 4453.
- [19] W. Schmidt & B. T. Wilkins, *Tetrahedron* **28**, 5649 (1972).
- [20] E. Heilbronner & C. W. Jefford, unpublished results.
- [21] E. Heilbronner, R. Pauncz & A. Schmelzer, to be published.
- [22] M. J. S. Dewar & E. Haselbach, *J. Amer. chem. Soc.* **92**, 590 (1970); N. Bodor, M. J. S. Dewar, A. Harget & E. Haselbach, *ibid.* **92**, 3854 (1970); M. J. S. Dewar, E. Haselbach & S. D. Worley, *Proc. Roy. Soc. A* **315**, 431 (1970); M. J. S. Dewar, *The Molecular Orbital Theory of Organic Chemistry*, McGraw-Hill Book Company, New York, 1969.
- [23] J. A. Pople, D. P. Santry & G. A. Segal, *J. chem. Physics* **43**, S 129 (1965); J. A. Pople & G. A. Segal, *ibid.* **43**, S 136 (1965) and subsequent papers; J. A. Pople & D. L. Beveridge, *Approximate Molecular Orbital Theory*, McGraw-Hill Book Company, New York 1970.
- [24] L. Åsbrink, C. Fridh & E. Lindholm, *J. Amer. chem. Soc.* **94**, 5501 (1972); C. Fridh, L. Åsbrink & E. Lindholm, *Chem. Physics Letters* **15**, 282 (1972).
- [25] J. N. Murrell & A. J. Harget, *Semiempirical Self-consistent-field Molecular-orbital Theory of Molecules*, Wiley-Interscience, London 1972.
- [26] C. Edmiston & K. Ruedenberg, *Rev. mod. Physics* **35**, 457 (1963); *J. Chem. Physics* **43**, 597 (1965); K. Ruedenberg, *Modern Quantum Chemistry*, Academic Press, New York, 1965, Vol. I, p. 85; W. England, L. S. Salmon & K. Ruedenberg, *Fortschr. chem. Forsch.* **23**, 31 (1971).
- [27] J. A. Pople, D. L. Beveridge & P. A. Dobosh, *J. chem. Physics* **47**, 2026 (1967).
- [28] T. Koopmans, *Physica* **1**, 104 (1934).
- [29] G. Dallinga & L. H. Toneman, *Rec. Trav. chim. Pays-Bas* **87**, 805 (1968).
- [30] R. Gleiter, E. Heilbronner, M. Hekman & H.-D. Martin, *Chem. Ber.* **106**, 28 (1973).
- [31] F. Brogli, W. Eberbach, E. Haselbach, E. Heilbronner, V. Hornung & D. M. Lemal, *Helv.* **56**, 1933 (1973).
- [32] H.-D. Martin, S. Kagabu & R. Schwesinger, *Chem. Ber.* **107**, 3130 (1974).
- [33] H. Iwamura, H. Kihara, K. Morio & T. L. Kunii, *Bull. chem. Soc. Japan* **46**, 3248 (1973).
- [34] N. Bodor, B. H. Chen & S. D. Worley, *J. Electron Spectrosc.* **4**, 65 (1974).
- [35] D. C. Clary, A. A. Lewis, D. Morland, J. N. Murrell & E. Heilbronner, *J. chem. Soc. Faraday II*, **70**, 1889 (1974).
- [36] M. J. S. Dewar & P. Bischof, private communication.
- [37] J. M. Lehn & G. Wipff, private communication; G. Wipff, *Thèse*, Université Louis Pasteur de Strasbourg, 1974.
- [38] H.-D. Martin & R. Schwesinger, *Chem. Ber.* **107**, 3143 (1974); H.-D. Martin, *Habilitationschrift*, Universität Freiburg i. Br., 1974.
- [39] P. Bischof, *thesis*, Universität Basel, 1971.
- [40] G. Dallinga & L. H. Toneman, *J. mol. Structure* **1**, 11 (1967–68).
- [41] L. A. Carreira, R. O. Carter & J. R. Durig, *J. chem. Physics* **59**, 812 (1973); P. W. Rubideau & J. W. Paschal, *J. Amer. chem. Soc.* **96**, 272 (1974).
- [42] M. J. S. Dewar & J. S. Wasson, private communication.
- [43] W. Adam, *Jerusalem Symp. Quantum Chem. Biochem.* (Israel Acad. Sci. and Humanities) **2**, 118 (1970); W. Adam, A. Grimison & R. Illoffmann, *J. Amer. chem. Soc.* **91**, 2590 (1971).