Occupation Numbers of Natural Orbitals as a Criterion for Biradical Character. Different Kinds of Biradicals

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Abstract: The existence of two natural orbital occupation numbers (NOON) appreciably different from the values zero and two can be considered as an appropriate criterion of the biradical character of a molecular system under consideration. More generally, the values of NOONs can be used as the quantitative measure of the biradicaloid character. The classification of the biradicals into different classes according to their topological or symmetrical properties has been made using a model Hamiltonian which allows us to consider the correlation effects completely. The relative position of the lowest triplet and singlet states of the biradicals belonging to different classes can be easily understood.

I. Introduction

The amount of biradical character is an important property of a molecular system which is connected with its stability, magnetic properties, and multiplicity of its ground state.[1] If the considered system is a model for an intermediate in a thermal concerted reaction, the absence of biradical character is a possible criterion for the probability of the proposed reaction path. Many photochemical and some pyrolytic reactions are supposed to occur via biradical intermediates (e.g., the ring-opening and isomerization reactions of small rings[2] and the dimerization of allenes[3]). Examples of "more or less" stable compounds with a biradical ground state are the hydrocarbons of Schlenk type and twisted Tschitschibabin hydrocarbons. Some reactive biradicaloids have been investigated after trapping them in noble-gas matrices, e.g., trimethylenemethane and 1,8-naphthoquinodimethanes.

Although the concept of a biradical is broadly used, the definition and characterization of a biradical are nevertheless not unique (cf. ref 1). For example, a very narrow gap between the lowest triplet and the lowest singlet state is evidently a sign of a biradical-like character but this criterion is not specific enough and it is too phenomenological. It does not give therefore sufficient insight into the structural reasons for the biradical behavior of a molecule. The energy difference between the lowest triplet and singlet state is not suitable as a quantitative criterion of biradicaloid properties because even pronounced biradicals can have the singlet-triplet energy sequence different. Moreover, more precise measurements and more exact (or just methodically different) calculations lead, very often, to the reversal of the singlet-triplet sequence for biradicals which is evidently a very sensitive property of these molecular systems.

Wilson and Wang[4] have already pointed out that the values of occupation numbers of natural orbitals (NOs) may be useful for predicting a concerted reaction pathway. Dewar[5] and Zimmermann[6] have emphasized the importance of the aromaticity and antiaromaticity of the π-electron systems "isoconjugated" with the transition states relevant for concerted reactions using Hückel-approach-like arguments. Flynn and Michl[7] have used the natural orbital occupation numbers (NOONs) in PPP models with limited CI as a measure of the biradical character of quinodimethanes. The usefulness of various instabilities of the HF solutions, as a quantitative measure of the biradical character, was studied extensively in a series of papers by Yamaguchi, Fueno, and Fukutome.[8]

In this contribution, the rules for the occurrence of biradical or biradicaloid species which should be essentially independent of approximate treatment used are formulated employing the

concept of natural orbitals. The properties of NO occupation numbers of the lowest singlet state are systematically investigated for model hydrocarbons of more or less expressed biradical character, using for sake of illustration the full CI PPP approach.[9,10] The advantage of this approach is the use of a simplified, well-defined π-electron Hamiltonian for which the eigenproblem is exactly soluble so that the correlation among the considered π electron can be completely taken into account. If desired, these model compounds, containing one or two π-electron subsystems,[13] can be considered as π-electron systems "isoconjugated" with the reaction intermediates.[5] The independence of the conclusions from the model is documented with some relevant ab initio results.

II. Biradicals and NO Occupation Numbers

The natural orbitals (NOs) are the eigenvectors and the corresponding occupation numbers (NOONs) are the eigenvalues of the one-electron density matrix belonging to the wave function in which the electronic correlation effects are treated completely within the framework of the approach used.
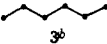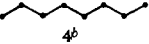
The expectation value $\bar{A}$ of any one-electron property A (to which the operator $\hat{A}$ is assigned) in the many-electron state $|\psi\rangle$ is

$$\bar{A} = \langle\psi|\hat{A}|\psi\rangle = \sum_i n_i \langle n_i|\hat{A}|n_i\rangle \tag{1}$$

where $|n_i\rangle$ is the NO with the corresponding NOON n_i. The NOs of "normally" behaving (diamagnetic) molecules can be divided into two groups with occupation numbers having values either near to zero or two, respectively (compare, for example, the PPP results for compounds **1–14** in Table I and the ab initio results for ethylene and butadiene in Figure 5). If two NOs $|n\rangle$ and $|n'\rangle$ exist for which the approximate relations $n \simeq 1$ and $n' \simeq 1$ are valid, these two NOs contribute to the expectation value of an arbitrary one-electron property A with the amount $1\cdot\langle n|\hat{A}|n\rangle + 1\cdot\langle n'|\hat{A}|n'\rangle$. Such contributions can be expected from a pair of noninteracting electrons. Consequently, the existence of two NOONs appreciably different from both zero and two can be considered as a sign of the existence of two more or less unpaired electrons in a molecule, i.e., of biradicaloid character. If a pair of NOs have two occupation numbers for the ground state (n, n') very close to one, we call this species a pronounced biradical. In this paper we shall use, very often, for convenience, the name biradical in a more restrictive (and therefore model dependent) sense when $n = n' = 1$.

The well-known chemical instability of *o*- and *p*-quinodimethane (**13** and **14**) under usual laboratory conditions and the relative lability of longer *n*-polyenes illustrate the usefulness and sensibility of the NOONs as a measure of biradical character (compare PPP results, Table I).

Table I. Examples of Hydrocarbons with Nonexpressed Biradical Character[a]

sym	1[b] D_{2h}	2[b] C_{2h}	3[b] C_{2h}	4[b] C_{2h}	5 C_{2v}	6 D_{6h}	7 C_{2v}
n	0.0431	0.0612	0.0732	0.0814	0.0370	0.0410	0.0503
n'	1.9569	1.9388	1.9268	1.9186	1.9624	1.9590	1.9549
E_S	−4.31	−9.34	−14.40	−19.47	−16.38	−15.66	−20.37
E_T	0.00	−6.14	−11.74	−17.09	−13.34	−11.74	−18.22

sym	8 C_{2v}	9 C_{2v}	10 C_{2v}	11 C_{2v}	12 D_{3h}	13 C_{2v}	14 D_{2h}
n	0.0967	0.0976	0.1021	0.1144	0.1212	0.2349	0.2677
n'	1.8714	1.9257	1.8979	1.8856	1.9137	1.7651	1.7323
E_S	−19.02	−14.17	−13.75	−13.05	−13.91	−18.34	−18.25
E_T	−17.86	−12.67	−11.63	−11.03	−11.69	−17.37	−17.32

[a] Dots in the formulas denote carbon atoms. E_S and E_T are the energies of the lowest singlet and the lowest triplet state, respectively (in units of eV); n and n' denote the two NOONs with values closest to 1.0. [b] The bond lengths are $r_o = 1.35$ Å and $r_e = 1.45$ Å.

In the LCAO approach with the orthogonal AOs (which is the case for the PPP model) the determination of NOs and corresponding NOONs is equivalent to the diagonalization of the bond order matrix **P**. In the PPP model of an alternant hydrocarbon n labels the largest NOON satisfying the inequality $0 < n \leq 1$ and n' labels the smallest NOON satisfying the inequality $1 \leq n' < 2$. The NOON $n_j = 1 + x_j$ are the roots of the determinantal equation

$$D(x) = \det(\mathbf{P} - (1 + x)\cdot\mathbf{I}) = \det(\mathbf{R} - x\cdot\mathbf{I}) = 0 \quad (2)$$

where **I** is the unity matrix and **P** is the bond order matrix. In general, if two rows of the determinant $D(0)$ for a conjugated system are exactly linearly dependent, at least one of the NOONs is equal to one. If the rank of the matrix **R** is lower by two than its dimension, the molecule is an expressed biradical. More generally, the magnitude of the determinant $D(0)$ can be considered as an equivalent measure of the biradical character.

For the exact solutions $|\Psi\rangle$ of an alternant system in the PPP model the bond order matrix $\mathbf{P} = (p_{ij})$[14] and consequently the NOs and the corresponding occupation numbers exhibit pairing properties.[15] The bond order matrix elements

$$P_{ij} = \frac{1}{2} \langle \Psi | \hat{E}_{ij} + \hat{E}_{ji} | \Psi \rangle \quad (3)$$

are zero if i and j label different centers belonging to the same class.[16] Quantities $\hat{E}_{ij} = \hat{a}_i{}^+\hat{a}_j$ are basic symmetry or transfer operators from the orbital $|j\rangle$ to the orbital $|i\rangle$,[17] where $\hat{a}_i{}^+$ and $\hat{a}_j$ are the creation and annihilation operator of orbitals i and j, respectively. In an alternant system to each NO corresponds a second NO which is obtained by interchanging the signs of the LCAO coefficients of AOs belonging to the unstarred carbon atoms and leaving the LCAO coefficients of AOs of starred atoms unchanged. The sum of the NOONs assigned to paired NOs is equal to two. It follows from the pairing properties of alternant hydrocarbons with an even number of π electrons that generally an even number (including zero) of NOONs is equal to one.

Already Longuet-Higgins[18] has pointed out the importance of the rank of the adjacency (topological) matrix **A** for the existence of biradical character in the framework of Hückel theory. If no Kekulé structure can be drawn for an alternant hydrocarbon, the rank of the matrix **A** is smaller than its dimension and at least two nonbonding molecular orbitals (NBMOs) are present.[19] There exists an analogy between the NOs with $n = n' = 1$ and the NBMOs of the Hückel approximation: the matrix **R** related to the bond order matrix has the same bloc form as the adjacency matrix **A**.

$$\mathbf{R} = \begin{pmatrix} \mathbf{o} & \mathbf{r} \\ \tilde{\mathbf{r}} & \mathbf{o} \end{pmatrix} \qquad \mathbf{A} = \begin{pmatrix} \mathbf{o} & \mathbf{a} \\ \tilde{\mathbf{a}} & \mathbf{o} \end{pmatrix} \quad (4)$$

Moreover, (in the ground state) the largest matrix elements of **R** and of the adjacency matrix **A** are situated at the same positions. Consequently, the consideration of Hückel NBMOs is useful for an estimation of biradical properties as was shown by Borden and Davidson[20] with the help of perturbation MO analysis. The present contribution shows more fundamental reasons for the acceptability of the properties of the NBMOs to diagnose the biradical character of hydrocarbons.

III. Conjugated Hydrocarbons Containing One π-Electron System

On the basis of the classification of conjugated hydrocarbons into alternant and nonalternant species combined with the consideration of the properties of the bond order matrix **P** we divide the biradicals into the following various classes (see also Baumgartner et al.[21a,b]).

1. Alternant Topological Biradicals with $m^* \neq m^0$. If the number of starred atoms m^* and unstarred atoms m^0 is different in a system with an even number of centers ($m^* > m^0$), at least two NOs have occupation numbers equal to one because the matrix **R** contains no quadratic bloc matrices[16] and therefore the determinant $D(0)$ is equal to zero, independent of the values of the matrix elements in the submatrix r. In this case geometrical changes of the molecular system cannot destroy the biradical character which is a consequence of topology (compare, for example, biradicals **15** and **15a**). Examples of several topological biradicals are given in Table II.

It is worth mentioning that the lowest state of these molecules is a triplet state. This property has been experimentally confirmed for trimethylenemethane[2,22] (**15**), Schlenk's hydrocarbon[23a] (**23**), and 1,8-naphthoquinodimethane[23b] as well as for the related bridged system **24a** and **24b**.[23c] It can be easily shown that for topological biradicals of this class ($m^* \neq m^0$) the NOs with NOONs $n = n' = 1$ cannot be chosen in such a way that each of them has only contributions from one of the two disjoint groups of centers. Notice that the NOs of the lowest triplet state have in general qualitatively the same properties as the NOs of the lowest singlet state for all birad-

Table II. Examples of Conjugated Alternant Topological Biradicals with $m^* > m^0$ [a]

sym	15[d] D_{3h}	15a[b] C_s	16 D_{2h}	17 C_s	18 C_{2v}	19 C_{2v}	20 C_{2v}
E_S	-5.8351	-5.8363	-11.84	-11.29	-16.49	-16.07	-17.25
E_T	-6.7210	-6.7211	-12.55	-11.79	-16.89	-16.09	-17.64

sym	21 C_{2v}	22 C_s	23[c]	24[c] C_{2v}	24a[c] C_{2v}	24b[c] C_{2v}
E_S	-16.37	-16.56				
E_T	-16.74	-16.86				

[a] For notation see Table I. [b] The angles are 119, 120, and 121°. [c] The calculations have not been carried out for this compound. [d] The lowest singlet state is degenerate.

Table III. Examples of Conjugated Alternant Topological Biradicaloids with $m^* = m^0$

sym	25 D_{2h}	26 D_{2h}	27 C_s	28 C_s
n	0.9757	0.9980	0.9828	0.9567
n'	1.0243	1.0020	1.0172	1.0433
E_S	-11.50	-16.18	-16.59	-16.54
E_T	-11.41	-16.13	-16.53	-16.46

Table IV. Examples of Conjugated Alternant Symmetrical Biradicals

sym	29 D_{4h}	29a[a] D_{2h}	30 C_{2v}	31 D_{8h}	32 D_{2h}	33a[b] C_{2v}
E_S	-8.04	-8.06	-12.91	-18.81	-17.73	-17.75
E_T	-7.75	-7.79	-12.66	-18.43	-17.49	-17.52

[a] The smaller angle in the rhomb is 60°. [b] The angle in the vinyl group is 120°.

icals considered here. The analogy can be drawn between the properties of the NOs with NOONs $n = n' = 1$ and the properties of the Hückel-type NBMOs and their connection with the relative position of the triplet and singlet states for this class of alternant biradicals.[20] Ovchinnikov[21c] has also shown that the Heisenberg Hamiltonian predicts the lowest triplet state with a lower energy than the lowest singlet state of the alternant conjugated hydrocarbon in the PPP picture if $m^* \neq m^0$.

Any even alternant conjugated system which is obtained by adding two methylene groups or methylene-like rests ($-CR_2$) with an odd number of AOs to the centers which belong to the same class of the original conjugated system is a topological biradical (cf. Table II). The well-known Schlenk's hydrocarbon (**23**), other hydrocarbons of Schlenk type,[24] and 1,8-naphthoquinodimethane (**24**)[25] can serve as illustrations of this rule. The same situation arises if two methylene (-like) groups are attached to a single center (as, e.g., the compounds **15, 17, 19, 21,** and **22**).

2. Alternant Topological Biradicals with $m^* = m^0$ and with No Kekulé Structure. The other class of alternant topological biradicals is characterized by the fact that no Kekulé structure can be drawn for them, but they contain an equal number of starred and unstarred atoms ($m^* = m^0$) (Table III) in contrast to the class discussed in section III1. Because of the nonexistence of Kekulé structures, these hydrocarbons have (at least) two NBMOs, and two NOs with occupation numbers n and n' only nearly equal to one owing to nonvanishing values of the bond orders among the atoms which are not nearest neighbors.

For example, compound **25** has slightly different bond orders between terminal atoms in the matrix $\mathbf{R}$ ($p_{15} = p_{26} \neq p_{16} = p_{25}$) which cause a small deviation from the linear dependency of rows or columns of the submatrix r. Even smaller deviation of n and n' from the value one is expected in the case of biradicaloid **26**. For this class of alternant biradicaloids topology is of paramount importance compared with geometrical

properties, as illustrated by comparison of compounds **27** and **28**.

The appropriate linear combinations of the NOs with $n \simeq n' \simeq 1$ can be formed in such a way that each of them can be confined to the subspace spanned exclusively by starred or unstarred centers only. The same properties have also the NBMOs for the compounds of this class. These properties of NOs indicate that the lowest triplet should lie slightly above the lowest singlet state (cf. Table III).

3. Alternant Symmetrical Biradicals. Not only topology but also symmetry can cause a linear dependency of rows in the matrix $\mathbf{R}$. As a consequence of symmetry the bond orders between symmetrically equivalent centers take the same values. If the symmetry brings about the linear dependency of two rows in the matrix r, then, owing to the bloc form of the matrix $\mathbf{R}$ for alternant systems, there exist two NOs with $n = n' = 1$. Some symmetrical alternant pronounced biradicals ($n = n' = 1$) for which at least one Kekulé structure can be drawn are listed in Table IV.

In contrast to topological biradicals, geometrical deformations lowering the symmetry can change the pronounced biradical character into a biradicaloid one or erase it completely. The NOONs n and n' of the alternant symmetrical biradicaloids obtained from the symmetrical biradicals by geometrical changes (which can, for example, simulate consequences of the Jahn-Teller effect) show deviations from the value one which can be considered as a sign of an increased stability (cf. compounds **29, 29b, 30, 30a, 32,** and **32b** in Tables IV and V). Whether the symmetrical biradical retains its character or not after geometrical deformation depends on the kind of symmetry subgroups of the original symmetry group which remain. Therefore, the lowering of symmetry does not necessarily always have to change the biradical character into the biradicaloid one, as the comparisons between **29** and **29a** as well as between **32** and **32a** demonstrate. From the above-mentioned analysis of the corresponding bond order matrices assigned to **29** and **29a** (cf. also **42** and **42b**) the behavior of

Table V. Examples of Conjugated Alternant Symmetrical Biradicaloids

sym	29b[a] D_{2h}	30a C_s	32b C_{2h}
n	0.4155	0.9879	0.9744
n'	1.5845	1.0121	1.0256
E_S	−7.69	−12.92	−17.75
E_T	−7.20	−12.68	−17.51

[a] The longer bond in the rectangle is 1.45 Å, the shorter one 1.40 Å.

Table VI. Alternant Hydrocarbons Containing Möbius-Type Arrays[a]

sym	33 D_{4h}	34 C_s	35 D_{8h}	36 D_{6h}
n	0.0223	0.0597	0.0640	1.0000
n'	1.9777	1.9403	1.9360	1.0000
E_S	−11.41	−15.98	−20.18	−13.65
E_T	−5.76	−12.84	−17.26	−13.30

[a] One of the annular resonance integrals has positive value.

these compounds can be easily understood as a consequence of the combined symmetry and alternancy properties. The NOs of compounds **29-32a** with NOONs $n = n' = 1$ are linear combinations of AOs belonging to different classes, and therefore the energy of the lowest singlet state is below the energy of the lowest triplet state.

As illustrative examples of symmetrical biradicals may serve the $4m$-membered annulenes **29** and **31**, containing $4m$ electrons ($m \in$ N).[26] In this case the sum of the NOONs belonging to the two-dimensional representation of D_{4mh} is equal to two ($n = n' = 1$).

If the molecular symmetry exists, then the properties of NOs and Hückel MOs have analogical features. For example, for annulenes with $4m$ electrons the transition from a Hückel-type array to a corresponding Möbius-type array causes a change in the values of NOONs, describing a transition from biradical to normal molecular situation. Annulenes with $(4m + 2)$ electrons show the opposite behavior. This is also valid for other symmetrical biradicaloids (**30, 32**), containing the corresponding rings (see compounds **33-36** in Table VI).

The ground state of the symmetrical biradicals is a singlet, due to the localization properties of NOs with NOONs n and n'.

4. Nonalternant Biradicaloids. The nonalternant biradicaloids can be formally derived from topological or symmetrical biradicals (or biradicaloids) by introducing bonds between centers belonging to the same class in the original alternant conjugated system (cf. Table VII). Generally, the introduction of such an alternancy violating bond tends to diminish the biradicaloid character of the conjugated system, which does not need to proceed in a continuous way. For example, the strengthening of the transannular bond in the cyclooctatetraene, leading to the pentalene, shows a discontinuity in the NOONs n and n' caused by crossing of the lowest singlet states (Figure 1). Similarly, the transition from cyclobutadiene to bicyclobutadiene via strengthening of the transannular bond (simulated by increasing of the absolute value of the resonance integral $|\beta_{ij}|$ between the corresponding centers) leads to the crossing of the two lowest singlet states. This crossing causes a sudden change of the biradicaloid character to a nearly "normal" one and can be understood as due to the strengthening of the bond between two carbon atoms which in the original alternant cyclobutadiene have belonged to the same class. Analogous behavior of the two lowest singlet states was found for the H_4 system with an ab initio method by Gerhartz et al.[27] The strengthening of the diagonal bond gives a driving force for a cross-bond creation in the photochemical isomerization of butadiene and related compounds.[28]

Ab initio SCF and CEPA calculations for Li_4 clusters yield for the stable geometrical arrangement the rhombic form and not the biradicaloid square form.[29] The structure **42b** can be considered as a "hydrocarbon analogue" of the Li_4 rhombus. The sudden development of the quasi-normal molecular character from the pure biradical one of **42a** with change of the rhomb angle as well as the sudden changes in the atomic charges (compare Figure 2) can be easily understood as a consequence of the crossing between the two lowest singlet states. Keeping in mind the evident difference between the Li_4 rhombus and the "hydrocarbon" rhombus, two important similarities could be noticed: first, both rhombs are stable and both square conformations are unstable biradicals. The stable "hydrocarbon" rhombus has positive charges at the centers lying on the shorter diagonal in complete analogy to the Li_4 rhombus obtained using the above-mentioned more sophisticated methods.

The other subgroup of nonalternant biradicaloids is the odd-membered annulenes with $4m$ ($m \in$ N) electrons (cf. Table VIII). For these compounds our calculations yield two lowest singlet states which are degenerate and lie above the lowest triplet state;[30] the corresponding NOs are not localized on different centers. Two NOONs for each of the lowest degenerate singlet states have values near to one. In spite of the arbitrariness in selection of the degenerate state the odd-membered annulenes with $4m$ electrons can be considered as biradicaloids invoked by molecular symmetry.

5. Weakening of the Kekulé Double Bonds in Polyenic Chains. A conjugated bond can be weakened either by stretching or by rotation. Experimental evidence exists for both kinds of bond weakening.[31,32] In this section we investigate the stretching of an essential double bond[18,21b] according to the Kekulé structure. Generally, the weakening of a double bond

Table VII. Examples of Nonalternant Biradicaloids

sym	37 C_{2v}	38 C_{2v}	39 C_s	40a C_{2v}	41b C_{2v}	42c D_{2h}	43c D_{2h}	42a_d D_{4h}	42b_e D_{2h}
n	0.3307	0.9696	0.2857	0.9414	0.0660	0.0609	0.1156	1.0000	0.0921
n'	1.6677	1.0402	1.7121	1.0580	1.9110	1.9364	1.9016	1.0000	1.9047
E_S	−12.03	−17.43	−17.11	−18.02	−19.68	−9.46	−19.97	−8.04	−9.20
E_T	−12.41	−17.66	−17.55	−18.39	−19.10	−8.01	−19.26	−7.75	−8.00

For the meaning of the symbols n and n' compare the description of Table I. The resonance integral for the transannular bond has the values [a] $\beta = -0.2711$ eV; [b] $\beta = -2.60$ eV; [c] $\beta = -2.60$ eV; [d] $\beta = -0.7234$ eV; [e] $\beta_{13} = -0.2711$ eV; $\beta_{24} = -2.60$ eV; the smaller angle in the rhomb is 60°.
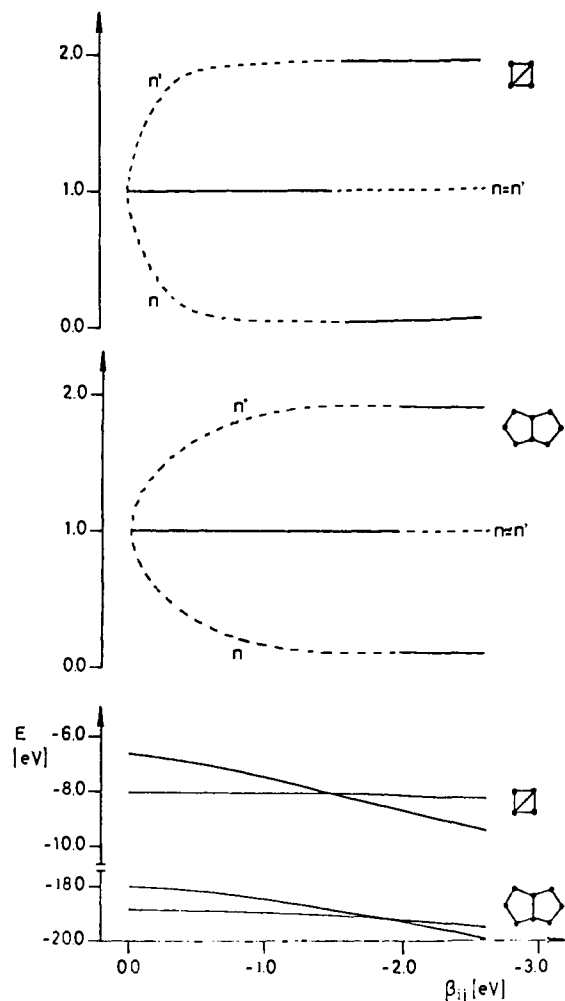
Figure 1. NO occupation numbers n and n' for the two lowest singlet states of bicyclobutadiene and bicyclo[3.3.0]octatetraene (pentalene) as a function of the resonance integral β assigned to the transannular bond. The full and broken lines denote n and n' for the lowest and energetically next lying singlet state, respectively. The energies of the two corresponding singlet states of both compounds are given in the lower part of the figure.

Figure 2. Atomic charges $\bar{q} = (q - 1)$ of centers 1 and 2 for the lowest two singlet states (S_0, S_1) of the nonalternant rhombus **42b** as a function of the angle ϑ.

in the only Kekulé structure of a hydrocarbon can be considered as a smooth transition to a hydrocarbon without a Kekulé structure which is a biradicaloid as already discussed in previous sections. As an example we have investigated the weakening of all essential double bonds in the linear polyenes. This bond stretching tends to create isolated radical centers at the end of the chain. The tendency to exhibit biradical features increases with the length of the polyenic chain. The biradical character appears in the long polyenic chains even for small deviations from the geometry, predicted by the Kekulé structure (i.e., small Δr). This corresponds to the well-known fact that the long n-polyenes are not too stable (Figure 3).

The development of the biradicaloid character runs parallel with the strange behavior of the one-electron approximation, i.e., the appearance of triplet instabilities and the nonuniqueness of the HF solutions mentioned in the literature.[33]

The NOs of a polyene with n and n' near to one behave like the linear combination of Shockley end states in semiinfinite linear atomic chains and similarly to the Shockley surface states in a semiinfinite crystal.[34] In these NOs for longer polyenes the AO coefficients of even centers (counted from the nearest chain end) are nearly equal to zero and the coefficients of the odd AOs alternate in sign and decrease in absolute value going from the polyenic ends toward the middle of the chain. The analogous behavior of the linear combinations
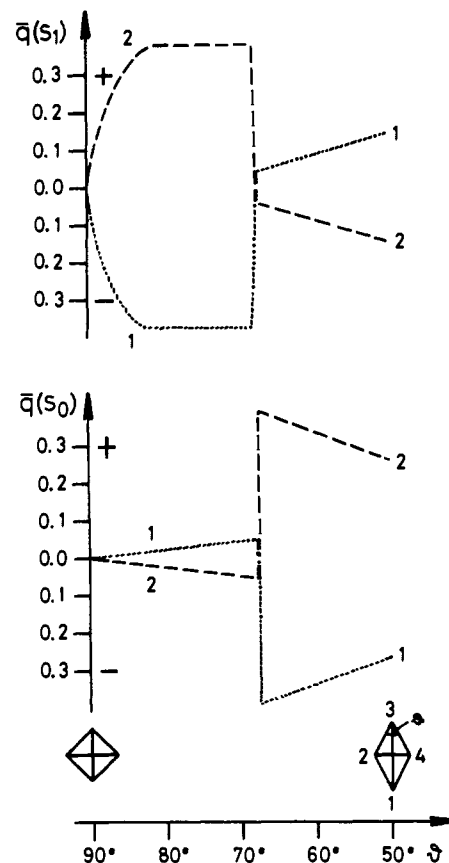
of these NOs, which are approximately localized at the ends of the polyenic chain, and the Shockley one-electron states indicate that the interpretation of Shockley surface states as symptoms of the dangling bonds is confirmed in this theory which respects completely the electron correlation effects.

IV. Biradicals Which Can Be Described by a Model Containing Two π-Electron Subsystems

Some intermediates which are assumed to be important for photochemical reaction paths result from a rotation around an essential double bond.[18,21b,35] In the model described here, we focus our attention on the AOs which form the π-electron system in the molecule before the relaxation following the excitation takes place. If the relaxation includes the rotation around a conjugated bond, the original π-electron system gives rise to two π-electron subsystems which in the π-electron PPP model interact through the Coulomb forces in a semiclassical manner.[13,36] Another type of interaction is assumed to take place through the resonance integral β of the rotated bond, of course. The rotation around one essential double bond produces two odd π-electron subsystems for $\vartheta = 90°$ and, according to the general theory of the PPP approach, the state resulting from the CI treatment is a linear combination of electronic configurations with a fixed number of electrons in both subsystems.[13] Therefore, for a 90° twist two NOs equal to one must exist. Figure 4 shows for several compounds the smooth transition from the normal behavior to the biradical one when the twist around a formal double bond increases.

The values of NOONs in Figure 5 are determined with the ab initio MRD–CI procedure[39] with AO basis of double ζ quality and configurations built up from triplet SCF molecular orbitals. The comparison of Figures 4 and 5 demonstrates closely analogical changes in values of NOONs n and n' as a

Table VIII. Odd-Membered Annulenes with $4m$ Electrons Containing Hückel- and Möbius-Type Arrays[a]

sym	H D_{3h}	M D_{3h}	H D_{5h}	M D_{5h}	H D_{7h}	M D_{7h}
n	0.9731	0.0200	0.9994	0.0228	1.0005	0.0437
n'	1.0276	1.9900	0.9993	1.9721	1.0005	1.9609
E_S	0.14	−4.92	−6.86	−9.95	−12.75	−14.95
E_T	−0.76	1.84	−7.25	−4.80	−12.98	−11.03

[a] H and M denote Hückel-type and Möbius-type arrays, respectively. For the meaning of the symbols n and n' compare the description of Table I.
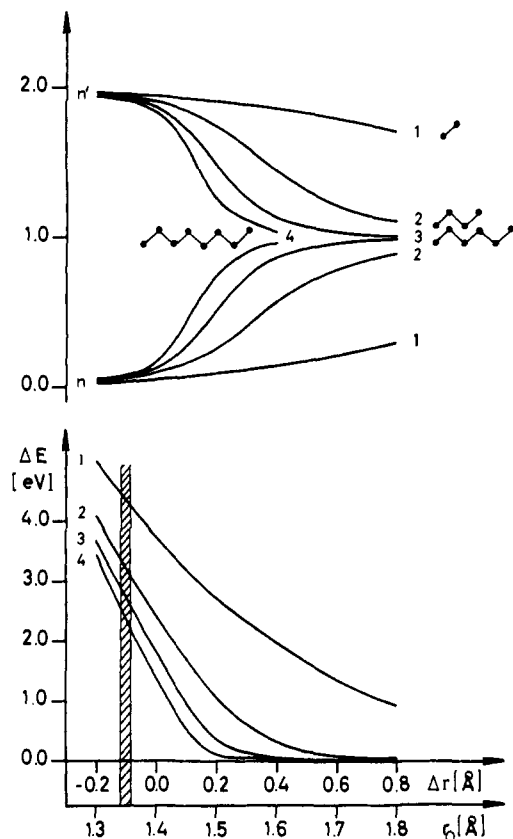

Figure 3. NO occupation numbers n and n' of the singlet ground state for ethylene (1), *trans*-butadiene (2), *all-trans*-hexatriene (3), and *all-trans*-octatetraene (4), and energy differences between the lowest triplet and the lowest singlet $\Delta E = E_T - E_S$ as a function of the bond length difference $\Delta r = r_o - r_e$. The sum of the odd (r_o) and even (r_e) bond length is kept constant ($r_o + r_e = 2.8$ Å). Vertical shaded region denotes experimentally found ground-state geometry.

Figure 4. NO occupation numbers n and n' of the lowest lying singlet states for ethylene (1), styrene (2), butadiene (3), and hexatriene (4) as functions of the twist angle ϑ around the double bond denoted by an arrow.

Figure 5. The MRD-CI natural orbital occupation numbers n and n' for ethylene, butadiene, and trimethylenemethane (TMM) as a function of the twist angle ϑ around the bond denoted by an arrow. The AO basis is of double ζ quality for ethylene and 4-31G[42] for butadiene and trimethylenemethane. The one-electron functions in the configurations are the triplet SCF-MOs. The thresholds in the MRD-CI selection procedure are 5 μhartrees with respect to three main configurations for ethylene,[43] 10 μhartrees for butadiene[44] (eight mains), and 10 μhartrees for trimethylenemethane[45] (three mains).

consequence of the twist of an essential double bond in polyenes. The values of NOONs n and n', calculated for trimethylenemethane with the same MRD-CI method (Figure 5), do not deviate appreciably from the value 1 during the twist of one C–C bond because the compound (**15**) is a topological biradical with $m^* \neq m^0$.

The analogous model with two π-electron subsystems can be used for the explanation of the paramagnetic properties of the Tschitschibabin hydrocarbon in which the rotation angle around the central double bond can be increased by appropriate bulky substituents.[31]

The high polarizability of some low-lying singlet zwitterionic excited states of biradicals which are created by a rotation around a double bond leads to the sudden polarization effect[40] (strong charge separation). It has been shown that the sudden polarization can be described and well understood employing the same full CI–PPP model as used in this contribution if the Coulomb integrals are modified so that the different chemical
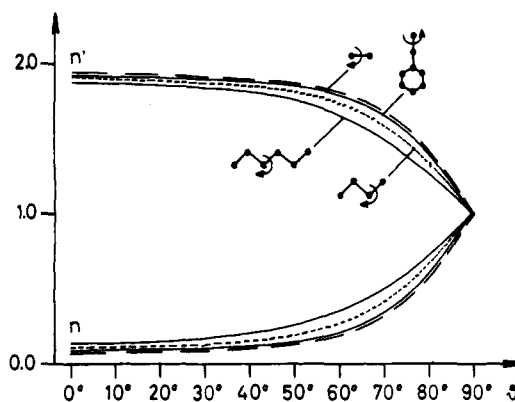
neighborhoods of different carbon atoms can be taken into account.[13] Systems like **17**, **25** (which in principle can be considered as composed from two allyls), and **27** are already biradicals in the planar conformation. Their low-lying zwitterionic states, which are not necessarily the lowest singlet excited states, exhibit a strong charge separation even before the overlap between two biradical sites is nearly interrupted as in the case of the centrally twisted *s-cis,s-trans*-diallyl.[13]

V. Conclusions

The values of the natural orbital occupation numbers n and

n' can be generally used as a quantitative measure of the biradicaloid character for a molecular system with a given geometrical conformation.

Various classes of conjugated hydrocarbon biradicals have been found with an exactly soluble PPP-model Hamiltonian employing the full CI technique. The general properties of alternancy and nonalternancy of conjugated systems figure in an especially transparent way in the PPP approach owing to the ZDO approximation. This has made possible extraction of the important properties for the classification of biradicals which, although in detail could be changed by a more sophisticated approach, explains the overall behavior of the system.

Class 1. *Alternant topological biradicals* with an unequal number of starred and unstarred atoms ($m^* \neq m^0$) have two NOONs exactly equal to one ($n = n' = 1$). The corresponding NOs cannot be chosen in such a way that each NO with NOONs $n = n' = 1$ can be confined to one of the two disjoint AO sets. This property of NOs is also related to the fact that in this class of biradicals the triplet is the lowest state.

Class 2. The *alternant topological biradicaloids* with $m^* = m^0$ and with no Kekulé structure exhibit n and n' only approximately equal to one ($n \simeq n' \simeq 1$) and each of the two corresponding NOs is localized at one of the disjoint sets of AOs and the ground state is therefore a singlet state.

Class 3. In the case of *symmetrical biradicals,* for which a Kekulé structure can be drawn, high symmetry can cause exact linear dependence of two rows or columns of the matrix **R**. The ground state of the symmetrical biradicals is a singlet state owing to the fact that NOs with NOONs $n = n' = 1$ have analogous localization properties to relevant NOs of the alternant topological biradicaloids with $m^* = m^0$. Lowering of the molecular symmetry can lead to deviation of the NOON values from one. If n and n' remain close to one, one can define such species as symmetrical biradicaloids.

Class 4. The transition from an alternant biradical to a *nonalternant biradicaloid* is accompanied by a decrease of biradicaloid character. For the investigated species we have found a sudden change from biradical to normal character due to the crossing of the two lowest lying singlet states.

The NOs of *n*-polyenic chains with a molecular geometry which is not in agreement with the prediction based on the Kekulé formulas show a striking analogy with the Shockley end states which can be taken as an indication of surface dangling bonds.

For systems twisted around a double bond the NOONs show the expected increase of biradicaloid character with increased "twist angle".

The sharp division of the obtained classes of biradicals is certainly dependent on the properties of the model used. On the other hand, the essential features of the different kinds of the biradicals should be independent of the specificities of the PPP approach and several comparisons made here with the ab initio results document this very clearly (cf., for example, Figures 4 and 5). In fact, the uncoupled electrons are preferentially described by the orbitals of π symmetry in all important configurations of the CI approach.[41]

References and Notes

(1) Salem, L.; Rowland, C. *Angew. Chem.* **1972**, *90*, 86–106. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92–111. Michl, J. *Mol. Photochem.* **1972**, *4*, 243–255, 257–286, 287–314. *Photochem. Photobiol.* **1977**, *25*, 141–154. Wentrup, C. "Reaktive Zwischenstufen", Vol. 1; Georg Thieme Verlag: Stuttgart. 1979.

(2) Dowd, P. *Acc. Chem. Res.* **1972**, *5*, 242–248.
(3) Levek, T. J.; Kiefer, E. F. *J. Am. Chem. Soc.* **1976**, *98*, 1875–1879. Gajewski, J. J. *Ibid.* **1975**, *97*, 3457–3461. Beetz, T.; Kellogg, R. M. *Ibid.* **1973**, *95*, 7925–7926. Jacobs, T. L.; Kammerer, R. C. *Ibid.* **1972**, *94*, 7190–7191. Baldwin, J. E.; Fleming, R. H. *Fortschr. Chem. Forsch.* **1970**, *15*, 281–310.
(4) Wilson, E. B.; Wang, P. S. C. *Chem. Phys. Lett.* **1972**, *15*, 400–403.
(5) Dewar, M. J. S. *Angew. Chem.* **1971**, *83*, 859–946. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 761–766.
(6) Zimmermann, H. E. *Acc. Chem. Res.* **1971**, *4*, 272–280.
(7) Flynn, C.; Michl, J. *J. Am. Chem. Soc.* **1974**, *96*, 3280–3288.
(8) Fukutome, H. *Prog. Theor. Phys.* **1972**, *47*, 1156–1180; **1973**, *49*, 22–36; **1973**, *50*, 1433–1451. Yamaguchi, K. *Chem. Phys. Lett.* **1975**, *35*, 230–235; **1975**, *33*, 330–335. Yamaguchi, K.; Ohta, K.; Yabushita, S.; Fueno, T. *Ibid.* **1977**, *49*, 555–559. Yamaguchi, K.; Fueno, T.; Fukutome, H. *Ibid.* **1973**, *22*, 461–465. Yamaguchi, K.; Fueno, T. *Ibid.* **1976**, *38*, 47–51.
(9) Paldus, J. *J. Chem. Phys.* **1974**, *61*, 5321–5330.
(10) The PPP Hamiltonian $\hat{H}$ has in the formalism of the second quantization the form

$$\hat{H} = \sum_{i \neq j}^{M} \beta_{ij} \hat{E}_{ij} + \frac{1}{2} \sum_{i,j}^{M} (\hat{E}_{ii} - 1)(\hat{E}_{jj} - 1)\gamma_{ij} + \sum_{i}^{M} \alpha_i \hat{E}_{ii}$$

where each atom in the conjugate skeleton contributes one electron only; α_i are the Coulomb integrals for center i, β_{ij} are the resonance integrals between centers i and j ($i \neq j$), the γ_{ij} are the electron–electron repulsion integrals, and $\hat{E}_{ij}$ are the transfer operators (see eq 3). The following parametrization has been used:

$$\beta_{ij}(r_{ij}) = -57.05 \exp(-2.206 r_{ij}) [\text{eV}]^{11}$$
$$\gamma_{ij} = [1.0 - 0.18 \exp(-3.2 r_{ij})]/(1.328 + r_{ij}) [\text{eV}]^{12}$$

If not explicitly stated the distances between nearest neighboring centers (r_{ij}) and the angles between the bonds ending in one center are taken equal to 1.4 Å and 120°, respectively.
(11) Pariser, R.; Parr, R. G. *J. Chem. Phys.* **1953**, *21*, 767–776.
(12) Thulstrup, E. W.; Michl, J. *J. Am. Chem. Soc.* **1976**, *98*, 4533–4540.
(13) Bonačić-Koutecký, V.; Čížek, J.; Döhnert, D.; Koutecký, J. *J. Chem. Phys.* **1978**, *69*, 1168–1176.
(14) McLachlan, A. D. *Mol. Phys.* **1959**, *2*, 271–284; **1961**, *4*, 49–56. Koutecký, J. *J. Chem. Phys.* **1966**, *44*, 3702–3706.
(15) Koutecký, J., *J. Chem. Phys.* **1966**, *45*, 3668–3675.
(16) The topology of an alternant π-electron system allows the division of the centers into two classes consisting of starred (*) and unstarred (0) atoms, in such a way that each of the centers from one class is bounded only to the centers of the other class. The number of centers in class (*), denoted by m^*, is not necessarily equal to the number of unstarred centers, m^0.
(17) Koutecký, J.; Laforque, A. *Int. J. Quantum Chem.* **1977**, *11*, 505–523.
(18) Longuet-Higgins, H. C. *J. Chem. Phys.* **1950**, *18*, 265–274.
(19) The proof of Longuet-Higgins can be formulated for our purposes in quite a simple way. The value of a determinant is equivalent to a linear combination of all products in the following manner. All centers of class (*) are used as row labels and all centers of class (0) in various sequences are used as column labels with the restriction that each label must be used only once. It follows that each product can be assigned to a Kekulé structure. If no Kekulé structure can be drawn, the value of the determinant of the adjacency matrix **A** is zero and at least two NBMOs exist.
(20) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587–4594.
(21) (a) Baumgartner, P.; Weltin, E.; Wagnière, G.; Heilbronner, E. *Helv. Chim. Acta* **1965**, *48*, 751–764. (b) Platt, J. R. In "Handbuch der Physik", Flügge, S., Ed.; Springer-Verlag: Heidelberg, 1961; Vol. 37/2, pp 173–281. (c) Ovchinnikov, A. O. *Theor. Chim. Acta* **1978**, *47*, 297–304.
(22) Dowd, P. *J. Am. Chem. Soc.* **1966**, *88*, 2587–2598; **1976**, *98*, 5726–5727.
(23) (a) Kothe, G.; Denkel, K.-H.; Sümmermann, W. *Angew. Chem.* **1970**, *82*, 935–937. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 906–907. Luckhurst, G. R.; Pedulli, G. F. *J. Chem. Soc. B* **1971**, 329–334. (b) Gisin, M.; Rommel, E.; Wirz, J.; Burnett, M. N.; Pagni, R. M. *J. Am. Chem. Soc.* **1979**, *101*, 2216–2218. (c) Platz, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 3398–3399.
(24) Schmidt, R.; Brauer, H.-D. *Angew. Chem.* **1971**, *83*, 498–499. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 506–507. Hinrichs, K.; Kurreck, H.; Niemeier, W. *Tetrahedron* **1974**, *30*, 315–320. Broser, W.; Kurreck, H.; Niemeier, W.; Plato, M. *Ibid.* **1975**, *31*, 1769–1799.
(25) Pagni, R. M.; Burnett, M. N.; Dodd, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 1972–1973. Watson, C. R.; Pagni, R. M.; Dodd, J. R.; Bloor, J. E. *Ibid.* **1976**, *98*, 2551–2562; **1974**, *96*, 5064–5066. Muller, J.-F.; Muller, D.; Dewey, H. J.; Michl, J. *Ibid.* **1978**, *100*, 1629–1630.
(26) In the case of biradical **29** the matrix **P** has an extremely simple form, namely

$$\begin{pmatrix} p_{11} & p_{12} \\ p_{12} & p_{11} \end{pmatrix}$$

See section II.
(27) Gerhartz, W.; Poshusta, R. D.; Michl, J. *J. Am. Chem. Soc.* **1977**, *99*, 4263–4271.
(28) Bigwood, M.; Boué, S. *J. Chem. Soc., Chem. Commun.* **1974**, 529–530.
(29) Beckmann, H.-O.; Koutecky, J.; Botschwina, P.; Meyer, W. *Chem. Phys. Lett.* **1979**, *67*, 119–126.
(30) Wassermann, E.; Hutton, R. S.; Kuck, V. J.; Chandros, E. A. *J. Am. Chem. Soc.* **1974**, *96*, 1965–1966.
(31) Sartorius, R.; Brauer, H.-D. *Angew. Chem.* **1972**, *84*, 546–547. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 531–532.
(32) Agranat, I.; Tapuhi, Y. *J. Am. Chem. Soc.* **1979**, *101*, 665–671. Nakazaki, M.; Yamamoto, K.; Yanagi, J. *Ibid.* **1979**, *101*, 147–151. Feringa, B.; Wynberg, H. *Ibid.* **1977**, *99*, 602–603.

(33) Bonačić, V.; Koutecký, J. *J. Chem. Phys.* **1972**, *56*, 4563–4573.
(34) Shockley, W. *Phys. Rev.* **1939**, *56*, 317–323. Koutecký, J. *Adv. Chem. Phys.* **1965**, *9*, 85–168.
(35) Odell, B. G.; Hoffmann, R.; Imamura, A. *J. Chem. Soc. B* **1970**, 1675–1678. See also ref 6.
(36) The parametrization for the full CI–PPP calculations is the same as given in ref 7. The resonance integrals for the bond which is twisted by the angle are approximated by $\beta_{ij}(\theta) = \beta_{ij}(0°) \cos \theta$ [eV]. The electron–electron repulsion integrals γ_{ij} are calculated according to the recipe of ref 7 because the estimated difference between the values of the relevant electron–electron repulsion integrals of the type $(\pi\pi|\overline{\pi\pi})$ and $(\pi\pi|\pi\pi)^{37}$ is only of the order of 10%.[38] This difference is of great importance for the relative stability of the twisted conformation but only of second-order importance for the qualitative nature of the states under consideration.
(37) Roothaan, C. C. J. *J. Chem. Phys.* **1951**, *19*, 1445–1458.
(38) Hoffmann, R.; Imamura, A.; Zeiss, G. D. *J. Am. Chem. Soc.* **1967**, *89*, 5215–5220. Gondo, Y. *J. Chem. Phys.* **1964**, *41*, 3928–3938.
(39) Buenker, R. J.; Peyerimhoff, S. *Theor. Chim. Acta* **1974**, *35*, 33–58. Buenker, R. J.; Peyerimhoff, S.; Butscher, W. *Mol. Phys.* **1978**, *35*, 771–791.
(40) Bonačić-Koutecký, V.; Bruckmann, P.; Hilberty, P.; Koutecký, J.; Leforestier, C.; Salem, L. *Angew. Chem.* **1975**, *87*, 599–601. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 575–576. Bruni, M. C.; Daudey, J. P.; Langlet, J.; Malrieu,

J. P.; Momicchioli, F. *J. Am. Chem. Soc.* **1977**, *99*, 3587–3596. Brooks, B. R.; Schaefer III, H. F. *Ibid.* **1979**, *101*, 307–311. Yamaguchi, K.; Yabushita, S.; Minokawa, O.; Fueno, T. *Chem. Phys. Lett.* **1978**, *59*, 303–307. Berthier, G.; Levy, B.; Praud, L. *Gazz. Chim. Ital.* **1978**, *108*, 377–381. Meerman-van Benthem, C. M.; Jacobs, H. J. C.; Mulder, J. J. C. *Nouveau J. Chim.* **1978**, *2*, 123–127. Koutecký, J.; Bonačić-Koutecký, V.; Čížek, J.; Döhnert, D. *Int. J. Quantum Chem., Suppl.* **1978**, *12*, 357–369. Bonačić-Koutecký, V.; Buenker, R. J.; Peyerimhoff, S. *J. Am. Chem. Soc.* **1979**, *101*, 5917–5922. See also ref 13.
(41) Our conjecture of the importance of the π electrons is based besides general considerations and results summarized in Figure 5 on the following facts: STO-3G calculations of Borden and Davidson[20] show the relative positions of singlet and triplet in complete agreement with our full CI-PPP approach. The nature of the sudden polarization effect can be well understood in the PPP full CI approach.
(42) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724–728. Pople, J. A., et al. *QCPE* **1978**, *11*, 368.
(43) Bonačić-Koutecký, V.; Buenker, R. J.; Pogliani, L., results from a work in progress.
(44) Bonačić-Koutecký, V.; Sevin, A.; Döhnert, D., results from a work in progress.
(45) Döhnert, D.; Koutecký, J.; Bonačić-Koutecký, V., results from a work in progress.

Torsional Modes in the Multiphoton Ionization Spectrum of Tetrachloroethylene

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Abstract: Hyperconjugation has been identified by Mulliken as the cause of nonplanarity in the (π, 3s) Rydberg state of ethylene. This nonplanarity is signaled by the highly abnormal contributions of the torsional mode to the one-photon vibronic spectrum. The two-photon resonance to the corresponding excited state in tetrachloroethylene is observed to be much sharper than its one-photon counterpart, and vibronic analysis of it shows a near absence of torsional activity, consonant with a planar upper state and no hyperconjugative interaction. The two-photon polarization ratio as measured in the multiphoton ionization spectrum is very close to zero (<0.05), as appropriate for a totally symmetric vibronic upper state. The major intensity-inducing vibrations in the two-photon spectrum (ν_{11}' and ν_{12}') have b_{3u} symmetry, and the electronic origin is at 50 429 cm^{-1}.

Though this paper is formally focused on the tetrachloroethylene (TCE) molecule, we were prompted in this direction by a consideration of the interesting spectroscopic and geometric problems presented by ethylene, the parent molecule. Consequently, we open with a brief discussion of the transition to the lowest Rydberg state of ethylene in order to present a proper frame of reference for an evaluation of the results on TCE. The key papers on the electronic excitations in ethylene are those of Wilkinson and Mulliken[1,2] and the more recent analyses by Merer and Schoonveld[3a] and Foo and Innes.[3b] Reviews on the spectra of olefins can be found in ref 4 and 5.

The optical or electron-impact excitation of an electron from the π MO of ethylene (b_{3u}) into the lowest Rydberg orbital, 3s, displays a vibronic envelope very much like that observed in the photoelectron spectrum corresponding to ionization from the π orbital.[5] Thus it is clear that the 3s Rydberg orbital is essentially nonbonding as regards the core, and that the geometric changes are induced by the extraction of the electron from the π orbital. Removal of an electron from the π MO has two direct consequences: (a) the C–C bond order decreases, and so a progression in the C–C stretch (ν_2) is excited. This vibrational frequency decreases from 1623.3 cm^{-1} in the ground state to 1368 cm^{-1} in the (π, 3s) excited state, and simultaneously the C–C distance expands from 1.338 to 1.41 Å. (b) The decrease in C–C π-bond order on excitation dramatically decreases the force constant for torsional motion (ν_4), such that its frequency drops from 1023 cm^{-1} in the ground

state of ethylene-h_4 to only 96 cm^{-1}, and from 726 cm^{-1} to only 41 cm^{-1} in ethylene-d_4.

In the (π, 3s) upper state of ethylene, the twisting potential is centered about the planar geometry (for $v_4 \geqslant 2$ in the torsional mode ν_4), and so in the electronically allowed excitation the ν_4 vibrations can appear only as changes of double quanta, i.e., $0 \to 2$, $0 \to 4$, $1 \to 3$, etc. Even though allowed by symmetry, such vibrations in general are not expected to be very intense, for, as explained by Herzberg,[6] in the usual case where a vibrational frequency ω'' of ca. 1000 cm^{-1} decreases by 20% or so upon excitation, but the potential curves are not displaced, 99.4% of the Franck–Condon intensity remains at the origin, according to the formula

$$\frac{I(0,0)}{\sum_v I(0,v)} = \frac{2\sqrt{\omega'\omega''}}{\omega' + \omega''}$$

In fact, in the extraordinary case of ethylene, the double-quantum excitation of ν_4' in the one-photon spectrum is quite prominent, and indeed the formula above predicts that, owing to the extreme reduction in vibrational frequency, only 56% of the intensity is found at the origin. Moreover, irregular intensities in these twisting doublets, as well as irregularities observed in their frequencies, also suggest a double minimum along the torsional coordinate in the upper state. Further experimental and theoretical analysis[7,8] confirms that in the upper level the ethylene molecule (and positive ion) is twisted by 25–30°, with a barrier height of 280 cm^{-1}.