The Photochemistry of 1,3-Butadiene Rationalized by Means of Theoretical Resonance Structures and Their Weights

Vinzenz Bachler* and Kurt Schaffner[a]

Dedicated to Prof. Dr. Frans de Schryver on the occasion of his 60th birthday

Abstract: A complete active-space self-consistent-field wave function for the π-electron part of s-*trans*-1,3-butadiene has been expanded into a set of localized bonding schemes and their weights. These bonding schemes are close to the resonance structures used in organic chemistry. The expansion technique has been applied to both the electronic ground state and the electronically first-excited singlet and triplet π,π* states. The manifolds of large-weight bonding schemes represent approximate resonance hybrids for the ground and the singlet and triplet π,π* states of s-*trans*-1,3-butadiene. These resonance hybrids, obtained by theory alone, permit a qualitative rationalization of a significant part of the known singlet and triplet photochemistry.

Keywords: ab initio calculations · butadiene · photochemistry · valence bond

Introduction

Resonance structures are the classic tool of organic chemists to describe the electron distribution of molecules qualitatively. The lines in resonance structures symbolize spin-coupled electron pairs localized in bonds or in lone pairs. When the electrons are delocalized in a molecule, several resonance structures are needed to describe the electron distribution. Such a manifold of resonance structures is called the resonance hybrid for a molecule.[1] In general, the resonance structures appear in the resonance hybrid with different weights. Those with large weights represent the classic qualitative notation of organic chemistry for electron distribution in molecules and their reactivity.[2] It is important, therefore, to know the resonance structures that enter the resonance hybrid with large weights. Those weights have been extensively calculated in the early days of quantum chemistry by means of valence-bond theory.[3] An appealing modern version is the spin-coupled valence-bond method of Cooper et al.,[4] which produces rather compact valence-bond functions. Qualitative valence-bond theory is also the basis of the successful modern curve-crossing model for chemical reactivity as advocated by Shaik et al.[5]

The organic chemist writes large-weight resonance structures as guided by qualitative rules[6] and by a wealth of accumulated chemical experience; this works well for molecules in the electronic ground state and for their thermal reactions. Photochemical reactions, however, start out from electronically excited states, and the photochemically relevant large-weight resonance structures are much harder to envisage. Nevertheless, resonance structures based on valence-bond theory are an important tool for the qualitative interpretation of photochemical reactivity. Michl and Bonancic-Koutecky[7], for example, explicitly describe the transformation between molecular orbital (MO) and valence-bond wave functions for important two-electron cases, and both MO and valence bond schemes are applied to discuss the electronic properties of two-electron σ and π bonds. This type of transformations has been frequently applied in the past to interpret computed MO wave functions in the framework of valence-bond theory.

Hiberty et al. were the first to devise[8] and apply[9] a general scheme for expanding a delocalized MO wave function into the set of valence-bond functions. In recent years Karafiloglou et al. developed a poly-elctron population analysis to interpret a delocalized MO wave function in terms of poly-electron distributions that are strictly local.[10] Central to this procedure is Moffitt's theorem,[11] which allows the expansion of a delocalized MO Slater determinant into AO (atomic orbital) Slater determinants that contain atomic orbitals localized at the atoms of the molecule. Many applications of Karafiloglou's procedure[12] show that complicated delocalized MO wave functions can be interpreted in terms of localized bonding schemes, which are close to organic resonance structures. Recently, a theoretical procedure has been introduced[13] that allows the expansion of an MO determinantal

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0947-6539/00/0606-0959 $ 17.50+.50/0

wave function into a set of determinantal wave functions composed of localized atomic orbitals (AOs). A concise expansion formula has been suggested which produces the *whole set* of AO determinants contained in the MO determinant.[13] This procedure affords localized bonding schemes and their weights from a delocalized MO determinantal wave function.

In the following we extend this procedure by expanding a multi-configurational MO wave function obtained by means of the complete active-space self-consistent-field (CASSCF) method.[14] We have applied the expansion technique to obtain the approximate resonance hybrid for the 1^1A_g ground state of s-*trans*-1,3-butadiene. Moreover, we derived for the first time, approximate resonance hybrids for the first excited 1^3B_u triplet and 1^1B_u singlet states of s-*trans*-1,3-butadiene by expanding a CASSCF wave function.[15] We show in this paper that the resonance structures obtained and their weights prove compatible with the well-known $^3\pi,\pi^*$ and $^1\pi,\pi^*$ photochemistry of butadiene. This supports the major issue of this paper, namely the notion that resonance hybrids, obtained from theory alone (i.e., from vertically excited-state MO wave functions), might represent a qualitative tool for rationalizing, and eventually predicting, photochemical reactions.

Computational Methods

The CASSCF computations were performed by means of the Gaussian92/DFT suite of ab initio programs.[17] A CASSCF wave function was obtained as a linear combination of MO Slater determinants, which are in general not eigenfunctions to S^2, rather than as a linear combination of configuration state functions.[18] Thus, the spin-adapted CASSCF wave function Ψ_i for an electronic state i is given by Equation (1).

$$\Psi_i = \sum_{j=1}^{m} c_{ij}^{\mathrm{MO}} \Phi_j^{m} \tag{1}$$

The MOs contained in the m MO Slater determinants, Φ_j^{MO}, were obtained by averaging the ground state and the five lowest excited states, which consist of triplet and singlet states.[19] Thus, the subsequent analysis was performed by using a set of MOs that was *identical* for the ground and the first-excited singlet and triplet π,π^* states. In order to obtain localized bonding schemes and their weights, all MO determinants Φ_j^{MO} were expanded into a set of N_D AO determinants Ψ_μ^{AO}.[13] Therefore, for any Φ_j^{MO} of Equation (1), Equation (2) holds.

$$\Phi_j^{\mathrm{MO}} = \sum_{\mu=1}^{N_D} c_\mu^j \Psi_\mu^{\mathrm{AO}} \tag{2}$$

The AO determinants Ψ_μ^{AO} contain AOs localized on the atoms of the molecule. The coefficients c_μ^j in Equation (2) are determinants formed from the linear combination atomic orbital (LCAO) coefficients of the MOs contained in Φ_j^{MO}. By substituting Equation (2) into Equation (1) we obtain[21] Equation (3), and the coefficients C_μ^i are given by Equation (4).

$$\Psi_i = \sum_{\mu=1}^{N_D} \sum_{j=1}^{m} c_\mu^j c_{ij}^{\mathrm{MO}} \Psi_\mu^{\mathrm{AO}} = \sum_{\mu=1}^{N_D} C_\mu^i \Psi_\mu^{\mathrm{AO}} \tag{3}$$

$$C_\mu^i = \sum_{j=1}^{m} c_\mu^j c_{ij}^{\mathrm{MO}} \tag{4}$$

Thus, the CASSCF wave function Ψ_i for a definite electronic state i is expanded into the set of N_D AO determinants Ψ_μ^{AO} [see Eq. (3)]. The linear combination coefficients C_μ^i reflect how strongly the AO determinant Ψ_μ^{AO} is contained in the CASSCF wave function Ψ_i. The various Ψ_μ^{AO}s consist of local atomic spin orbitals and they describe local spin occupations in a molecule.[13] By means of Equations (3) and (4), therefore, a correlated delocalized CASSCF wave function can be analyzed in terms of local spin occupations. We employed extended basis sets for the AOs. As a consequence, any Ψ_μ^{AO} in Equation (3) contains contracted groups of Gaussian functions rather than AOs. We calculated the weights for the various Ψ_μ^{AO} to obtain weights for local spin occupations by following the general sampling procedure outlined in ref. [13]. Bonding schemes which closely resemble resonance structures of organic chemistry, can be obtained in this way from a delocalized CASSCF wave function. A similar intention has been pursued by Thorsteinsson et al.,[22] who constructed a genuine valence-bond function by maximizing the overlap between a computed CASSCF wave function and a set of spin eigenfunctions or by minimizing an energy criterion. We, however, expand the CASSCF wave function directly [see Eq. (3)] into the set of crude Ψ_μ^{AO}s that are not spin eigenfunctions. Recently, a CASSCF wave function was used to partition the total energy of diatomic molecules into local covalent and ionic energy increments.[23] This decomposition was performed by calculating expectation values over local operators.[24] We computed for a definite Ψ_μ^{AO} the coefficients c_μ^j for all m Φ_j^{MO}s. All c_μ^js were multiplied by the corresponding coefficient c_{ij}^{MO} of Equation (1). By adding up these products, coefficient C_μ^i was obtained [see Eq. (4)] which reflects the content of AO determinant Ψ_μ^{AO} in the CASSCF wave function Ψ_i. Similar contents have been obtained in the past by computing the weight for Ψ_μ^{AO}s by means of a formula which accounts for the non-orthogonality of the AO determinants.[25] A rapid process for computing such weights has been suggested and applied.[26] We, however, determined the weight for Ψ_μ^{ao} by means of the simple weight formula [Eq. (5)] which neglects the non-orthogonality of the Ψ_μ^{ao}s.

$$w_\mu^i = \frac{C_\mu^{i2}}{\sum_{\nu=1}^{N_D} C_\nu^{i2}} \tag{5}$$

Karafiloglou et al. use orthogonal AOs in their expansion technique.[27] For those cases Equation (5) produces weights that are probabilities for finding electronic events in the MO wave function, which are indicated by the corresponding AO determinants. An electronic event, for example, would be the presence of two π electrons at one terminal carbon atom of butadiene and to find *simultaneously* two π electrons in the remaining terminal π bond. Inspite of the only assumed orthogonality in this work, Equation (5) should produce weights which are approximate probabilities for electronic events. Equation (5) has previously produced reasonable weights for AO determinants and bonding schemes.[13] This encouraged us to use it also in the following applications.

Results and Discussion

The computed vertical excitation spectrum of s-*trans*-1,3-butadiene: The electronic properties of butadiene, the parent compound of polyenes, have been investigated extensively by experimental[28] and theoretical methods.[29] Large basis sets, including diffuse Rydberg functions, and accurate methods for computing electronic correlation energies are needed to reproduce satisfactorily the electronic transition energies of

Abstract in German: *Eine CASSCF-Wellenfunktion für den π-Elektronenteil des s-trans-1,3-Butadiens wurde in einen Satz von lokalisierten Bindungsschemata und deren Gewichte entwickelt. Diese Bindungsschemata sind den Resonanzstrukturen der organischen Chemie sehr ähnlich. Das Entwicklungsverfahren wendeten wir auf den Grundzustand und die ersten angeregten Singulett- und Triplett-π,π*-Zustände an. Die Sätze von Bindungsschemata, die Schemata mit großen Gewichten enthalten, stellen ungefähre Resonanzhybride für den Grundzustand und die Singulett- und Triplett-π,π*-Zustände von s-trans-1,3-Butadien dar. Diese Resonanzhybride, erhalten allein durch Theorie, erlauben es einen großen Teil der bekannten Photochemie des s-trans-1,3-Butadiens qualitativ zu erklären.*

butadiene. The 1^1B_u π,π^* state is known to have an appreciable Rydberg character.[28a] Moreover, this electronic state is significantly ionic.[29i,n] This property implies that for a correct computation of the $1^1A_g - 1^1B_u$ transition energy it is mandatory to apply configuration interaction methods in which σ and π electrons are considered explicitly.[29] However, we are mainly interested in bonding schemes and their weights which are close to a valence-bond function for the π electrons. It should therefore suffice for our purpose to expand a CASSCF wave function where the active electrons are the π electrons only. Nevertheless, it is of interest to estimate the quality of this π electron restriction with respect to the various transition energies. We employed a complete active space for the four π electrons of butadiene distributed among the n π MOs designated as CAS(4,n).[17] In order to derive the energies with comparable quality, we state-averaged[20] the ground state and the five lowest excited states. The results are compiled in Table 1.

Table 1. Vertical electronic excitation energies [eV] of s-*trans*-1,3-butadiene computed by means of the complete active-space self-consistent field (CASSCF) procedure and various basis sets.[a]

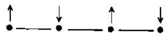
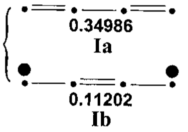
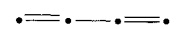
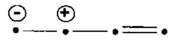
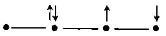
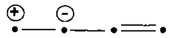
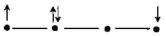
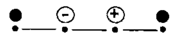
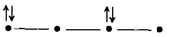
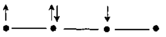
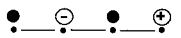
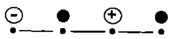
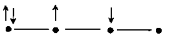
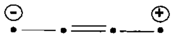
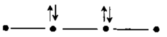
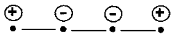
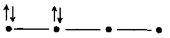
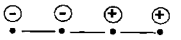
State	CAS(4,4)/ 6-311G[b]	CAS(4,4)/ 6-311++G[b]	CAS(4,6)/ 6-311++G**[b]	Theor	Exptl
1^1A_g	−154.941746	−154.941834	−155.006778	–	–
1^3B_u	3.36	3.33	3.39	3.39[c]	3.22[e]
1^3A_g	4.98	4.92	4.88	5.08[c]	4.91[e]
2^1A_g	6.78	6.71	6.56	6.64[c]	–[f]
2^3B_u	8.04	7.95	7.65	6.66[d]	–[g]
1^1B_u	9.01	8.83	7.24	8.54[c]	5.92[e]

[a] CAS, which contained only the four active π electrons, was adopted for the computation of the values in columns 2–5. The employment of polarization and diffuse functions improved slightly the transition energies of the values in columns 2–4. [b] This work. [c] See ref. [29v] for details of computation. [d] Value computed in ref. [32]. [e] Values cited in ref. [29v]. [f] Resonance Raman data place the 2^1A_g state below the 1^1B_u state; however, see ref. [28g] for the problems involved with values to this entry. [g] Not available.

Employing the 6-311G basis sets[30] and a CAS(4,4), we have achieved a satisfactory agreement with experiment for the excited states 1^3B_u and 1^3A_g (Table 1). Single-photon excitation to the doubly excited 2^1A_g state is dipole forbidden and therefore difficult to observe.[31] Our value, however, accords with the CASSCF energy given by Serrano-Andrés et al.[29v] (Table 1). For the excited 2^3B_u and 1^1B_u states the agreement with experiment and even simple all-valence configuration interaction calculations[32] is unsatisfactory. The failure for the 1^1B_u state may originate from the large ionicity of this state which is discussed below. This ionicity requires the inclusion of σ electrons in a correlation treatment of the 1^1B_u π,π^* state. By augmenting the basis sets with diffuse functions (6-311++G), a marginal lowering of all transition energies towards their experimental values has been achieved (Table 1). The increase of the active space by two further virtual π orbitals, CAS(4,6), supplemented by the addition of polarization functions, led to a significant lowering (~1.6 eV) of the transition energy for the 1^1B_u π,π^* state. Nevertheless, the experimental transition energy is still far from being reproduced. The approximate resonance hybrids for the 1^1B_u and 1^3B_u π,π^* states of butadiene were finally obtained by expanding the corresponding CASSCF wave functions (see below). The employment of these wave functions is based on our assumption that, contrary to the excitation energies, the π electron distributions in both states are described by the CASSCF wave functions with comparable quality.

The resonance hybrid for the 1^1A_g ground state of s-*trans*-1,3-butadiene: We performed CASSCF calculations at the CAS(4,4)/6-311G level of theory by state-averaging the six electronic states listed in Table 1. Thus, a common set of π orbitals was obtained for this state manifold. Moreover, we considered only the π electrons in the Φ_j^{MO}s which make up the function Ψ_i [Eq. (1)]. Therefore, only a correlated π electron wave function for 1^1A_g ground-state butadiene was expanded. The expansion coefficients c_{ij}^{MO} [Eq. (1)] for the 1^1A_g state make up the eigenvector of the lowest root of the CASSCF eigenvalue problem. The expansion results are summarized in Table 2.

Table 2. Localized spin occupations for the π AOs and the resulting bonding schemes for the 1^1A_g ground state of s-*trans*-1,3-butadiene.[a]

	Spin occupation	Degeneracy	Bonding scheme
I	 0.46188	1	 0.34986 Ia 0.11202 Ib
II	 0.32246	1	 0.32246
III	 0.01264	1	 0.01264
IV	 0.07968	2	 0.07968
V	 0.07706	2	 0.07706
VI	 0.01504	2	 0.01504
VII	 0.00590	2	 0.00590
VIII	 0.00553	2	 0.00553
IX	 0.00514	2	 0.00514
X	 0.00276	2	 0.00276
XI	 0.00143	1	 0.00143
XII	 0.00015	2	 0.00015

[a] Numbers below the figures are weights. Spin occupations were obtained by expanding the π part of a CAS(4,4)/6-311G wave function. The pure covalent spin occupations evolve from the expansions with large weights. This is an improvement compared to expansions where simple uncorrelated restricted MO determinants are employed.

The localized spin occupations **I – XII**/2[33] are listed in the sequence of decreasing weights. They also include weights for spin-inverted spin occupations and for degenerate spin occupations. The meaning of spin degeneracy is illustrated by spin occupation **IV**/2 in which two electrons are localized at one terminal carbon and two electrons in a terminal π bond. A second spin occupation of the same weight appears in the expansion in which four electrons occupy the alternative terminal carbon and π bond, respectively. Therefore, **IV**/2 represents a spin occupation of twofold degeneracy. Table 2 shows that the covalent spin occupations **I – III**/2 evolve from the expansion with by far the largest weight. They are dominated by **I**/2, which is characterized by a complete spin alternation.

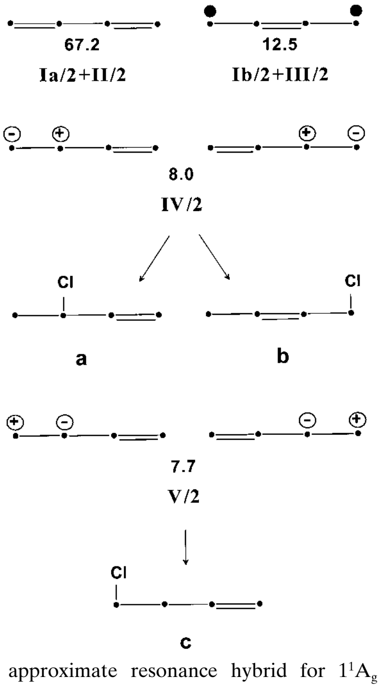
This dominance of covalent weights is a significant improvement with regard to expansion results derived from an uncorrelated restricted MO determinant. In this determinant covalent and ionic resonance structures appear with weights which are too small and too large, respectively. This fact is known as the overionicity of a restricted MO determinant.[34] Therefore, covalent resonance structures, known by the chemist to have large weights in delocalized π systems, cannot be derived with proper weights from a simple restricted MO determinant, but are obtained from the CASSCF wave function (Table 2). A similar reasonable weighting has been found previously by Hiberty and Ohanessian[35a] who expanded a complete configuration interaction wave function. Our results illustrate, furthermore, that the CASSCF wave function emphasizes the left – right π-electron correlation in the ground state of butadiene.

Spin occupations **IV**/2 and **V**/2 succeed to the covalent occupations in terms of decreasing weights. They are monoionic in character but still have a covalent alternating spin occupation in a terminal π bond. Structure **X**/2 is also monoionic, but the covalent alternating spin occupation makes up the long central bond. Such a spin occupation should be unfavourable, and accordingly **X**/2 has a much smaller weight than **IV**/2 and **V**/2. Finally, spin occupations **VII**/2, **XI**/2 and **XII**/2 are diionic in character. Adjacent charges of equal sign lead to very small weights for **XI**/2 and **XII**/2. The alternation of negative and positive charges, however, affords a larger weight for **VII**/2 than for **XI**/2 and **XII**/2. Thus, the sequence order of computed weights appears to be rational.

The localized spin occupations of Table 2 are translated into localized bonding schemes[13] which are close to the chemist's resonance structures. A covalent π bond in a bonding scheme is represented by a line between two adjacent atoms. Such a line symbolizes two electrons of opposite spin shared by two atoms, while it designates an electron pair when two such electrons occupy one and the same atom. This bond and lone pair definition differs from the one employed in Hiberty's expansion technique.[8] There, an MO wave function is expanded into the set of genuine valence-bond functions that are linear combinations of AO determinants and eigenfunctions of the S^2 spin operator. These valence bond functions represent the various spin coupling schemes of the electrons occupying localized AOs, and any singlet spin coupling scheme represents a definite way of drawing bonds. The bond definition adopted in this work, however, is based on the energy expectation values for the crude AO determinants which are not eigenfunctions of S^2. By considering next neighbour interactions only, one can show that a simple spin alternation between adjacent atoms lowers the energy for that AO determinant relative to the energy of the corresponding high-spin determinant.[36] This energy lowering is an energy increment characteristic for a bond represented by two electrons of opposite spins. Thus, a bonding scheme obtained from a crude AO determinant symbolizes the partitioning of the energy expectation value for that AO determinant into energy increments for bonds indicated by the bonding scheme.

The complete spin alternation in **I**/2 implies that its weight contributes to the weights of the two bonding schemes **Ia**/2 and **Ib**/2. Bonding scheme **Ia**/2 is made up of two terminal π bonds, and **Ib**/2 has a central π bond combined with a 1,4-diradicaloid character. The probability of finding a spin alternation between adjacent carbon atoms is known to correlate with the π bond lengths in polyenes.[36] The computed weights of the spin alternation for the terminal and the central carbon – carbon bonds were used to partition the weight of spin occupation **I**/2 into the weights for **Ia**/2 and **Ib**/2. Thus, the weight partitioning was implicitly guided by the bond strengths of the bonds in the bonding schemes. The classical resonance structure for butadiene was found to prevail and the 1,4-diradicaloid form to be of minor importance. Bonding schemes with a 1,3-diradical character appear with very small weights.

These results lead to an approximate resonance hybrid for 1^1A_g ground state butadiene. The corresponding bonding-scheme weights comprise about 95% of the total weight (Scheme 1).



Scheme 1. The approximate resonance hybrid for 1^1A_g ground state s-*trans*-1,3-butadiene. Resonance structures and their weights arise from the predominant localized spin occupations of the π AOs in Table 2.

While the prevalent covalent resonance structure **I a**/2+**II**/2 has a weight of 67 %, the 1,4-diradical **I b**/2+**III**/2 is significantly less important (12 %), as are the monoionic structures **IV**/2 and **V**/2 (overall contribution about 16 %).

In the spin-coupled valence-bond method of Cooper et al. non-orthogonal AOs are also employed, but they are optimized for the molecule.[4] This optimization produces AOs that extend slightly towards the neighbouring atoms[37] and they are not strictly local. A worthwhile consequence of this fact is that the ionic structures vanish[38] and their valence-bond functions comprise only few covalent structures.[38] Thus, rather compact valence-bond functions are obtained. In our scheme we expand a delocalized CASSCF wave function, which is optimized by means of the state-averaging procedure.[19] The appearance of the ionic structures in Scheme 1 is a direct consequence of the use of AOs that are strictly localized at the atoms. As in the classic valence-bond method, the ionic structures are essential for describing the delocalization of the π electrons.[39] Therefore, N_D in Equation (2) becomes very large for more electrons and basis functions[13] and the information is scattered in a large number of expansion terms.

On the basis of the monoionic structures **IV**/2 and **V**/2 the addition of HCl to butadiene, for example, can be rationalized. The similar weights for **IV**/2 and **V**/2 demand that protonation of the negatively charged carbons should occur at all positions, C1 to C4, with equal probability. The protonated species arising from **IV**/2 is stabilized by allylic delocalization of the positive charge, which is not possible in the protonation product of **V**/2. Of the three possible products upon subsequent Cl addition (**a**–**c**, Scheme 1), only those two (**a** and **b**) are formed[40] which are both predicted to be accessible from **IV**/2. Compound **c**, which would be expected as the product of **V**/2, has not been isolated. This is in accord with the lack of allylic stabilization after protonation. An alternative potential route subsequent to protonation of **V**/2, however, could be a 1,2-hydride shift leading to the precursor of **a** and **b**. This a priori possible role of **V**/2 as a contributor to reactivity has now been ruled out by Leitich[41] in appropriate isotope labelling experiments. The agreement between experimental and theoretical results confirms that we have generated an approximate classic resonance hybrid for ground state butadiene by expanding the π part of a CASSCF wave function. The results support the notion that we may apply the expansion technique also to cases for which chemical experience is less abundant.

The general idea of obtaining resonance structures and their weights from a computed MO wave function has also been adopted by Glendening and Weinhold[43] in their natural resonance theory. The procedure was applied to the ground state of s-*trans*-1,3-butadiene by considering σ and π electrons.[44] As a result, the covalent resonance structure **Ia**/2+**II**/2 dominates the resonance hybrid with 71 % and the ionic structure **X**/2, with a central double bond, contributes with a weight of 7.9 %. All other structures appear in the resonance hybrid with significantly smaller weights. This is at variance with our own resonance hybrid (Scheme 1) where the ionic structures **IV**/2 and **V**/2, both of which retain one terminal double bond, have significant weights, and where **X**/2, the central bond of which has a weak π nature only, can be neglected (Table 2). These theoretical results are borne out satisfactorily by experiment. Moreover, they are in line with the different π bond strenghts of the terminal and central π bonds.

The resonance hybrid for the 1^1B_u π,π* excited state of s-*trans*-1,3-butadiene: The molecule s-*trans*-1,3-butadiene is transformed into a variety of photoproducts.[45] In solution with light of 2537 Å, the photoreaction is initiated by vertical excitation into the singlet 1^1B_u π,π* state. Measured absolute resonance Raman excitation profiles suggest that after vertical excitation a fast transition to the doubly excited 2^1A_g electronic state should occur.[28g] Thus, the photochemistry seems to proceed primarily on the 2^1A_g potential energy surface. This conclusion has been substantiated by Robb and co-workers[29w] by CASSCF computation of the potential energy surfaces for selected photochemical pathways. It was shown that the excitation energy indeed flows from 1^1B_u to the doubly excited 2^1A_g state, which forms a conical intersection region with the 1^1A_g ground state. The excitation energy is thus funneled[7, 46] onto the 1^1A_g surface and thereby transformed into vibrational excitations of the ground-state reacting system.[29w] As a consequence, the unsensitized photochemistry of butadiene is characterized by complicated photophysics involving potential energy surfaces of several electronic states. Nevertheless, the various reaction pathways seem to be entered already at the very beginning of the photophysical overall process. The energy flow between several potential energy surfaces serves mainly to distribute early in the reaction the excitation energy between various electronic states. Therefore, we adopted the crucial notion that the wave function of the vertically excited 1^1B_u state already contains information that can be extracted in a suitable form to predict products. Thus, we attempt to gain information on products solely from the reactant wave function, which is the wave functions for the 1^1B_u electronic state of butadiene. The feasibility to gain information on products from a reactant wave function alone is one assumption in the static approach to chemical reactivity.[47] The other supposition is that a reaction pathway that is favourable at the beginning of the pathway remains favourable up to the products.[47] Both assumptions are the basis for the employment of classic reactivity indices[48] and of frontier orbital densities.[49]

In the following we derive information on products by obtaining an approximate resonance hybrid from the 1^1B_u reactant wave function of butadiene. Weights for valence-bond-like resonance structures for this electronic state have already been obtained by Michl and Bonancic-Koutecky[7] as a function of the twist angle for rotation about one terminal π bond. The authors state, however, that their procedure “does not permit an extrapolation to the planar geometry”.

We have now performed CASSCF computations for 1^1B_u butadiene at the CAS(4,4)/6-311G level of theory. Our intention was to generate localized bonding schemes that describe the distribution of the valence π electrons only. Therefore, Rydberg and polarization functions were not included in the Gaussian basis sets used. The π MOs in the

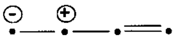
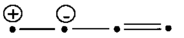
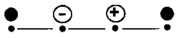
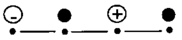
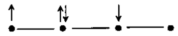
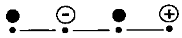
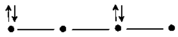
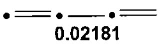
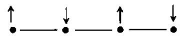
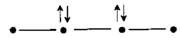
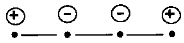
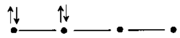
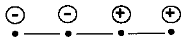
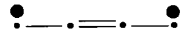
Φ_j^{MO} of Equation (1) are the MOs obtained from a state-averaging CASSCF computation of the six states recorded in Table 1. The coefficients c_{ij}^{MO} [see Eq. (1)] for the target 1^1B_u state, however, are the eigenvectors of the sixth root of the CASSCF eigenvalue problem. The resulting localized spin occupations and bonding schemes are recorded in Table 3 in the sequence of decreasing weights.

The monoionic bonding schemes **I**/3 and **II**/3 with one π bond each are dominant, followed by the monoionic 1,4-singlet diradical **III**/3. Bonding schemes **IV-VI**/3 are also monoionic, but have either a central π bond or a 1,3-singlet diradical. The diionic bonding schemes **VII**/3, **X**/3 and **XI**/3 are of smaller weights, and so are—in contrast to the ground state expansion—the covalent bonding schemes **VIII**/3, **IX**/3 and **XII**/3.

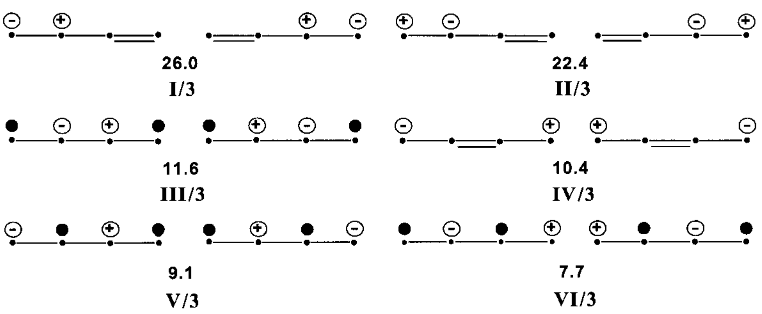
It is of interest to compare the 1^1B_u π,π^* state expansion with the previous expansion for the 1^1A_g ground state. On the one hand, the 1^1A_g expansion is dominated by the classic covalent bonding scheme possessing *two* π bonds (Table 2). The 1^1B_u expansion, on the other hand, is characterized by a manifold of different bonding schemes with similar weights (Table 3). Nevertheless, the weights for the monoionic schemes **I**/3 and **II**/3 with only one π bond dominate. These findings immediately afford a localized picture of the vertical excitation process. The electronic excitation energy serves to disrupt *one* of the two covalent π bonds of butadiene, tantamount to an intramolecular electron transfer between the adjacent carbon atoms of the π bond broken. This process is indicated by the dominant monoionic bonding schemes **I**/3 and **II**/3. Moreover, the 1^1B_u state should have a significant singlet diradical character as indicated by the weights for the bonding schemes **III**/3, **V**/3 and **VI**/3. The expansion leads to an approximate resonance hybrid for the 1^1B_u state given in Scheme 2.

The weights of the resonance structures recorded in Scheme 2 comprise 87.2 % of the total weight. The leading monoionic resonance structures **I**/3 and **II**/3, each with one π bond, appear with 48.4 %. A characteristic 1,3-diradical character is indicated by the monoionic resonance structures **V**/3 and **VI**/3 which total 16.8 %. An appreciable 1,4-diradical character (11.6 %) is attested by the monoionic structure **III**/3. Of comparable importance (10.4 %) are the monoionic structures **IV**/3 with a central double bond. The similarity of the weights shows that all resonance structures of Scheme 2 should be considered in a proper description of 1^1B_u butadiene. We illustrate in the following section that this resonance hybrid is in line with both the photochemistry of butadiene and with detailed computations.

Table 3. Localized spin occupations for the π AOs and resulting bonding schemes for 1^1B_u π,π^* s-*trans*-1,3-butadiene.[a]

	Spin occupation	Degeneracy	Bonding scheme
I	 0.26030	2	 0.26030
II	 0.22449	2	 0.22449
III	 0.11618	2	 0.11618
IV	 0.10392	2	 0.10392
V	 0.09084	2	 0.09084
VI	 0.07686	2	 0.07686
VII	 0.05651	2	 0.05651
VIII	 0.01337	1	 0.02181
IX	 0.00844	1	
X	 0.00673	1	 0.00637
XI	 0.00260	2	 0.00260
XII	 0.00157	1	 0.00157

[a] Spin occupations were obtained by expanding the π part of a CAS(4,4)/6-311G wave function. State-averaged MOs, but singlet configuration interaction coefficients, of the target state were employed. The monoionic spin occupations evolve from the expansions with large weights. The weights for the pure covalent spin occupations are negligible. The expansions illustrate the ionic character of the 1^1B_u π,π^* state.



Scheme 2. The approximate resonance hybrid for 1^1B_u π,π^* s-*trans*-1,3-butadiene. Spin occupations and their weights were derived from the π part of the CAS(4,4)/6-311G wave function. The resonance structures and their weights were obtained by sampling the weights of localized spin occupations for the π AOs. The resonance hybrid reveals the ionic character of the 1^1B_u state.

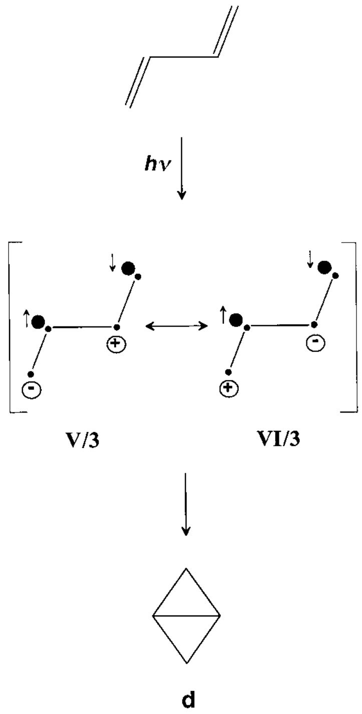
The photochemistry of s-*trans*-1,3-butadiene and the resonance hybrid for the 1^1B_u state: The monoionic structures **I**/3 (26.0 %) and **II**/3 (22.4 %) in Scheme 2 appear with similar and significant weights. The relevance of these two resonance structures for the characterization of the 1^1B_u π,π^* state has been debated in the past. Dauben and Ritscher[50] inferred from the photoreactivity of ethylidene cyclooctenes that an allyl-anion–methyl-cation electronic arrangement is relevant for the reactivity of the diene system. This conclusion is in agreement with the importance of structure **II**/3. Squillacote and Semple[51] interpreted the observation of a fast rotation about the terminal π bond in appropriately deuterium-labelled penta-1,3-dienes in terms of an allyl-cation–methyl-anion arrangement that dominates the 1^1B_u π,π* state. Such an electron distribution is exhibited by the significant structure **I**/3. The large and similar weights for **I**/3 and **II**/3 indicate that the allyl anion[50] and allyl cation[51] structures are both relevant for the 1^1B_u π,π* state.

Structures **I**/3 and **II**/3 (Scheme 2) contain *one* covalent and *one* ionic π bond. A rotation about an ionic π bond should have a small rotational barrier. Consequently, facile rotation about a *single* terminal bond should be the preferred geometry relaxation mode after vertical excitation. This conclusion is supported by computations of Bonancic-Koutecky et al.[29i] After vertical excitation, the high energy of s-*trans*-1,3-butadiene at the C_{2h} geometry is significantly lowered by a geometry relaxation comprising mainly a rotation about only *one* terminal bond. This rotation proceeds essentially without a rotational barrier which is in agreement with the presence of an ionic π bond in **I**/3 and **II**/3.

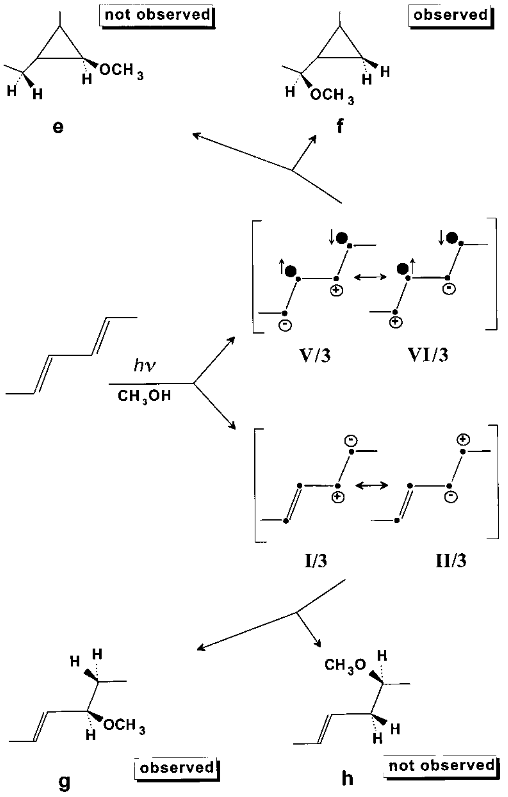
A superposition of the similarly weighted **I**/3 and **II**/3 indicates that π charges at the carbon atoms of the ionic bond are negligible. A slight geometry distortion, however, should destroy the weight balance between the two structures. This imbalance could be induced by a pyramidalization of one terminal carbon. It should result in a significant dipole moment in the 1^1B_u π,π* state and an energy lowering by stabilizing the negative π charge at the terminal carbon atom. Such an induced dipole moment is the essence of the sudden polarization effect in polyenes, and the further energy lowering was found by means of computations.[52] The sudden polarization is a consequence of the ionic character of the 1^1B_u state. This ionicity is hard to see when computations in a delocalized MO basis are performed in C_{2h} symmetry. It emerges naturally, however, from our analysis in which a delocalized MO wave function is interpreted in a localized picture.

The weight of the structures **IV**/3 (10.4 %) indicates that the central carbon–carbon bond should have a significant double bond character in the 1^1B_u π,π* state. The corresponding weight for the 1^1A_g ground state is slightly larger (Scheme 1: 12.5 %). Therefore, one may expect the rotational barriers around the central carbon–carbon bond to be similar in the two electronic states. Indeed, the computed barrier in the 1^1A_g ground state is 6 kcal mol^{-1},[53] and that in the 1^1B_u excited state is slightly larger (about 10 kcal mol^{-1}).[32]

Scheme 2 shows that the 1^1B_u state should have a significant zwitterionic singlet 1,3-diradical character, represented by the structures **V**/3 (9.1 %) and **VI**/3 (7.7 %). By comparison the 1,4-diradical character of **III**/3 (11.6 %) is smaller than the combined weight for **V**/3 and **VI**/3. The expected photochemical behaviour therefore is as summarized in Schemes 3 and 4.



Scheme 3. The photochemical formation of bicyclo[1.1.0]butane starting from 1^1B_u π,π* s-*trans*-1,3-butadiene. The reaction is expected to arise from the monoionic 1,3-diradicaloid bonding schemes **V**/3 and **VI**/3.



Scheme 4. The ^{1}π,π* photochemical products of all-*trans*-2,4-hexadiene in methanol, as expected on the basis of zwitterion scavenging indicated by **V**/3 and **VI**/3 (to form **e** and **f**) and of **I**/3 and **II**/3 (to form **g** and **h**).

In the zwitterionic singlet 1,3-diradicals **V**/3 and **VI**/3 the two unpaired electrons with opposite spins represent a long bond.[54] They are predestined to ring closure, as are the two carbons with opposite charges. As a result bicyclo[1.1.0]butane(**d**) should be formed (Scheme 3). Upon direct irradiation of s-*trans*-butadiene with light of 2537 Å, in nonpolar solvents and in the gas phase, **d** is indeed formed, albeit in minor yield.[45] Bicyclo[1.1.0]butane formation should be favoured by experimental conditions which stabilize the zwitterionic bonding schemes **V**/3 and **VI**/3. Such conditions are the use of a polar solvent and/or appropriate substituents. In point of fact, when 2-cyanobuta-1,3-diene in diethyl ether was irradiated with 2357 Å light, the corresponding product of type **d** was formed with a quantum yield of 0.029.[55] A much smaller quantum yield of 0.009 was determined for the cyclobutene formation. The predominance of bicyclo[1.1.0]butane formation may well be a consequence of both the polar solvent (stabilizing both zwitterionic bonding schemes) and the cyano group (stabilizing **VI**/3 by delocalizing the negative charge at C-2). This qualitative accord between experiment and theory supports the notion that **V**/3 and **VI**/3 are relevant for 1^1B_u state butadiene.

Bonding schemes **V**/3 and **VI**/3 suggest, furthermore, that zwitterion scavenging should occur when butadiene is irradiated in a protic solvent. Thus, irradiation of the homologous 2,4-hexadiene in the presence of methanol is expected to afford cyclopropanes **e** and **f** (Scheme 4).

Indeed, the product **f** has been isolated in 18% yield.[56] We have to keep in mind, however, that possibly **f** is not a photoproduct of butadiene, but rather has been formed by a thermal solvolytic cleavage of the bicyclobutane homologue of **d**. Among the photoproducts of 2,4-hexadiene in methanol also the allylic methyl ether **g** (5% yield) is present. It evidently results from protonation of the localized negative charge of the leading monoionic scheme **I**/3 in preference to protonation of the alternate **II**/3, which is less strongly stabilized (see above). These experimental findings are in accord with our expectations based on theory that monoionic structures (such as **I**/3) and zwitterionic singlet 1,3-diradicals (such as **V**/3 and **VI**/3) are significant for 1^1B_u butadiene. Nevertheless, the major photoreaction of butadiene is the formation of cyclobutene.[45] It is generally accepted that this product is formed from the $^1\pi,\pi^*$ state of s-*cis*-butadiene.[57] In the *cis* isomer equivalents to the structures **III**/3 and **IV**/3 should be important. Such structures evidently would be candidates to undergo 1,4-bond formation. Thus, a large part of the photochemistry of 1,3-dienes can be qualitatively rationalized by the resonance hybrid given in Scheme 2 which, as we recall, has solely been obtained by theory. The qualitative accord between theory and experiment supports the concept that expanding a CASSCF wave function into a set of AO determinants leads to approximate resonance hybrids that are photochemically meaningful.

The resonance hybrid of the 1^3B_u π,π^* state of s-*trans*-1,3-butadiene: An approximate resonance hybrid for triplet 1^3B_u butadiene was derived by expanding the wave function for the π electrons obtained from the CAS(4,4)/6-311G wave function for this electronic state. The CASSCF wave function was again computed by state-averaging the six electronic states recorded in Table 1. Thus, the MOs adopted in the Φ_j^{MO}s of Equation (1) are the same for all six states. The c_{ij}^{MO}s of Equation (1), however, represent the eigenvectors of the second-lowest root of the CASSCF eigenvalue problem. The resulting local spin occupations are listed in Table 4 in the sequence of decreasing weights.

Table 4. Localized spin occupations for the p AOs and the resulting bonding schemes for 1^3B_u π,π^* s-*trans*-1,3-butadiene.[a]

	Spin occupation	Degeneracy	Bonding scheme
I	↑—↑—↓—↑ 0.63109	2	●—•═•—● 0.38257 **Ia** ●—●—•═• 0.24852 **Ib**
II	↑—↑—↑—↓ 0.17948	2	●—●—•═• 0.17948
III	↑↓—•—↑—↑ 0.04015	2	⊖—⊕—●—● 0.04015
IV	•—↑↓—↑—↑ 0.03864	2	⊕—⊖—●—● 0.03864
V	↑—↑↓—•—↑ 0.02305	2	●—⊖—⊕—● 0.02305
VI	↑—↑↓—↑—• 0.01663	2	●—⊖—●—⊕ 0.01663
VII	↑↓—↑—•—↑ 0.01346	2	⊖—●—⊕—● 0.01346
VIII	↑↓—↑—↑—• 0.00740	2	⊖—●—●—⊕ 0.00740

[a] Spin occupations were obtained by expanding the π-part of a CAS(4,4)/6-311G wave function. State-averaged MOs, but triplet configuration interaction coefficients of the target state are used. The pure covalent spin occupations evolve from the expansions with large weights. The weights for the ionic spin occupations are much smaller. The expansion illustrates the covalent triplet diradical character of the 1^3B_u π,π^* state.

The pure covalent spin occupations **I**/4 and **II**/4 dominate the expansion. They are characterized by two and one spin alternation, respectively. The larger the number of spin alternations, the larger should be the weight of a covalent AO determinant.[36] This theoretical result is exemplified by **I**/4 and **II**/4, the former of which has the larger weight. All remaining monoionic spin occupations, **III – VIII**/4, evolve from the expansion with significantly smaller weights.

For the partitioning of the weight of **I**/4 between the bonding schemes **Ia**/4 and **Ib**/4, as shown Table 4, weights for the local spin occupations with alternating spins for the central and the terminal carbon–carbon bonds were computed. It is known that the probability of finding an alternating spin arrangement in the π bonds of polyenes correlates with their bond lengths.[36] The ratio of the weights for **Ia**/4 and **Ib**/4 thus reflects the bond alternation weight ratio for the central and the terminal carbon–carbon π bonds. The resulting bonding schemes constitute an approximate resonance hybrid for the 1^3B_u electronic state. The most important structures and their weight percentages are given in Scheme 5.

The resonance structures of the resonance hybrid, the weight percentages of which amount to 81% of the total, indicate that 1^3B_u butadiene is a triplet diradical. The similarly weighted 1,2- and the 1,4-diradical characters should be equally important for the photochemical behaviour of this $^3\pi,\pi^*$ state. In the following we demonstrate that in fact these diradical structures serve as a qualitative theoretical tool to

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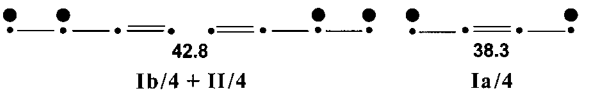
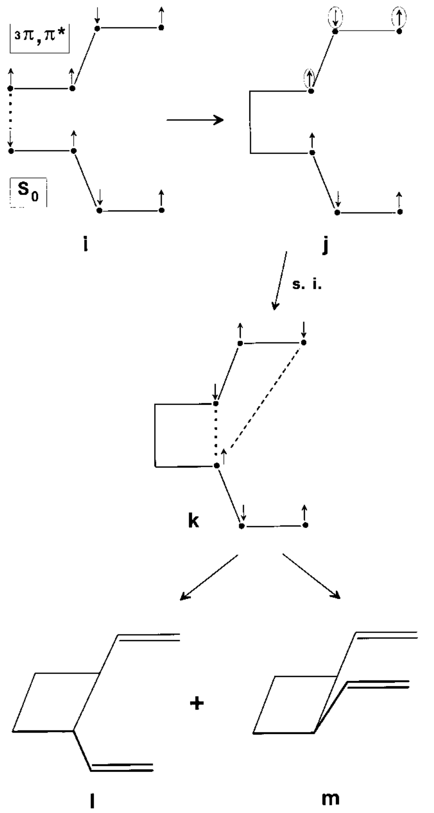


Scheme 5. The approximate resonance hybrid for 1^3B_u π,π^* s-*trans*-1,3-butadiene. Resonance structures and their weights were obtained by sampling the weights for localized spin occupations of the π AOs. Spin occupations and their weights were derived from the π part of the CAS(4,4)/6-311G wave function. The resonance hybrid illustrates the triplet diradical character of the 1^3B_u state.

rationalize the product distributions found in the triplet-sensitized photochemistry of butadiene and butadiene derivatives.[55]

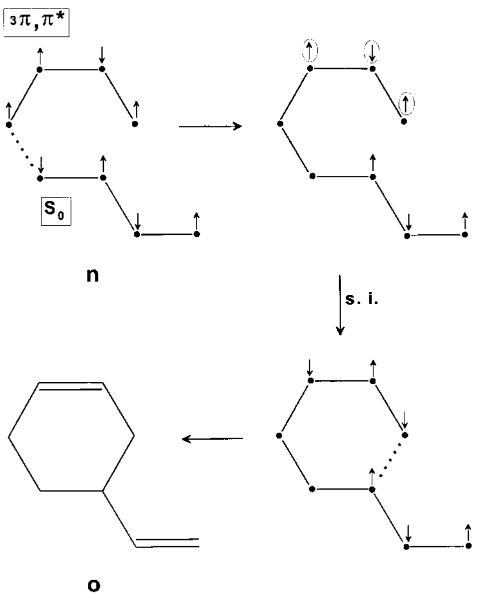
The photochemistry of s-*trans*-1,3-butadiene and the resonance hybrid for the 1^3B_u $^3\pi,\pi^*$ state: Upon population of the 1^3B_u state by triplet sensitized irradiation, fast electronic relaxation to the singlet ground state is spin forbidden. Therefore, the lifetime of the 1^3B_u state is in the range of microseconds.[59] Such rather long lifetimes permit the triplet-excited molecule to encounter their ground state counterparts. Hence, there is a preference for bimolecular reactions, which can be rationalized on the basis of the corresponding localized spin occupations obtained by theory alone.

The interaction of a 1^3B_u and a ground state 1^1A_g s-*trans*-butadiene is qualitatively described by the encounter complex **i** (Scheme 6). Both states are represented by the local spin occupations **I**/4 and **I**/2, respectively. Unfortunately, the corresponding AO determinants are not eigenfunctions of total spin operator S^2. They do not represent spin pure 1^3B_u and 1^1A_g electronic states. However, they are the largest single contributions in the expansions for the spin pure 1^3B_u and 1^1A_g CASSCF wave functions. Therefore, we assume that **I**/4 and **I**/2 are representatives for the 1^3B_u and the 1^1A_g state, respectively. Two terminal carbon atoms in **i** carry π electrons with opposite spins which can form the new σ bond of intermediate **j**. This intermediate possesses two allyl radicals with an overall triplet spin orientation. Formation of any second new bond between the allyl radical parts appears to be highly unfavourable. However, spin inversion of the encircled electrons in **j** affords the singlet species **k**, which is characterized by complete spin alternation. Malrieu[35b] has shown that such a spin pattern leads to the lowest energy and, in this particular case, it corresponds to a nuclear arrangement on the singlet 1^1A_g ground state potential energy surface. In **k** cyclization to the experimentally observed[57] diastereoisomeric divinylcyclobutanes **l** and **m** is readily feasible. An alternative way to spin couple two π electrons in **k** would be the formation of a six-membered ring with a *trans* double bond. However, the ring strain introduced would be prohibitive.



Scheme 6. The photochemical reaction of 1^3B_u π,π^* s-*trans*-1,3-butadiene with a ground state 1^1A_g s-*trans*-1,3-butadiene. Both molecules are shown in the encounter complex **i** with their predominant spin occupations. Upon intersystem crossing by spin inversion of the encircled spins in **j** the divinylcyclobutanes **l** and **m** can be formed. Note that the alternative cyclization would afford a *trans*-cyclohexene product which is very highly strained. s.i.: spin inversion.

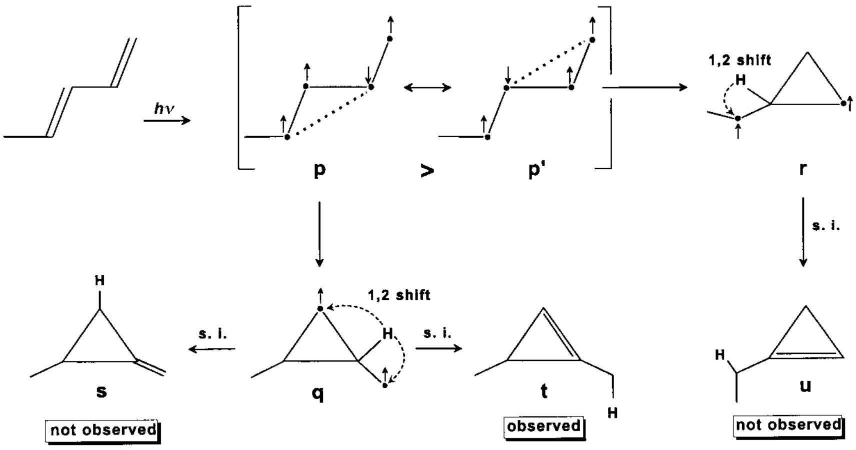
The more favorable pathway to a *cis*-cyclohexene (**o**) starts out from $^3\pi,\pi^*$ s-*cis*-butadiene in an encounter complex **n** with a ground state s-*trans*-butadiene (Scheme 7). We should note that the formation of **n** from s-*trans*-butadiene through s-*trans* – s-*cis* isomerization in the $^3\pi,\pi^*$ state has proven to be inefficient.[58] This is also suggested by the relatively large weight of 1,4-diradical structure **Ia**/4, which implies the presence of a significant rotational barrier about the central carbon – carbon bond. Indeed, divinylcyclobutanes **l** and **m** as



Scheme 7. The photochemical reaction of 1^3B_u π,π^* s-*cis*-1,3-butadiene with a ground state s-*trans*-1,3-butadiene. Both molecules are shown in the encounter complex **n** with their predominant spin occupations. Intersystem crossing by inversion of the encircled spins and subsequent bond formation affords the vinylcyclohexene **o**. s.i.: spin inversion.

well as vinyl cyclohexene **o** (Scheme 7) are the major reaction products in the sensitized $^3\pi,\pi^*$ photodimerization of s-*trans*-butadiene[57] and, moreover, the triplet excited s-*trans*- and s-*cis*-butadienes have been found to react as different species.[58]

The expansion results for 1^3B_u s-*trans*-butadiene serve also to rationalize *intra*molecular cyclizations originating from this state. As an example, the mercury-sensitized irradiation of all-*trans*-1,3-pentadiene in the gas phase[60] is given in Scheme 8, supplemented with a combination of the proposed mechanism[57] and our theoretical results derived for 1^3B_u butadiene.



Scheme 8. Intramolecular cyclodaddition of *trans*-1,3-pentadiene resulting from sensitized $^3\pi,\pi^*$ excitation. The bond formation to the three-membered ring is indicated by the predominant spin occupation **p** and **p′** which correspond to **I**/4 (Table 4). Subsequent 1,2 hydrogen atom shifts and spin inversion lead, inter alia, to the observed cyclopropene product **t**. s.i.: spin inversion.

The $^3\pi,\pi^*$ state of 1,3-pentadiene is described by the spin occupations **p** and **p′**, corresponding to **I**/4 which dominates the $^3\pi,\pi^*$ expansion for butadiene (Table 4). Both spin occupations are characterized by two adjacent localized electrons with equal spin. Such a spin localization is energetically unfavorable, and the two electrons have a strong tendency to avoid each other.[61] This can be achieved for spin occupation **p** where spin density can move to the adjacent methyl group; this cannot occur in spin occupation **p′**. Consequently, the weight of **p** should be larger than that of **p′**. Spin coupling in **p** should afford the triplet diradical **q** through 1,3-bond formation in the $^3\pi,\pi^*$ state. A subsequent 1,2-hydrogen shift and inversion of one spin yields either 1,3-dimethylcyclopropene (**t**) or 2-methylmethylenecyclopropane (**s**). Product **t** has in fact been observed.[60] The 2,4-bond formation, the reaction mode of the less important spin occupation **p′**, should lead via **r** to 1-ethylcyclopropene (**u**), which has not been reported.[60]

Conclusion

The thermal and photochemical reactions of butadiene have been extensively used in the past to test the predictive power of MO correlation diagram techniques. The Woodward–Hoffman rules adequately rationalize the observed stereochemistry of the thermal and photochemical cyclizations of s-*cis*-butadiene that yield cyclobutene.[62] This MO correlation diagram technique characterizes a given reaction pathway by retaining a definite symmetry element along the pathway. The pathway is called allowed provided the occupied reactant and product MOs correlate within the symmetry retained. In order to single out an allowed pathway from a variety of pathways, all of them must be evaluated separately. This situtation is different in Halevi's[63] orbital correspondence analysis in maximum symmetry (OCAMS) which uses effectively the formalism of group theory. If a high-symmetry reaction pathway is symmetry forbidden, a systematic group theoretical rule is employed to select an allowed pathway by lowering the pathway symmetry. Another successfull qualitative procedure is the two-state reactivity model,[64] in which valence-bond structures for reactants and products are used to determine reaction pathways with a low activation energy. In contrast, our procedure gains qualitative information on possible reaction pathways by analysing the computed reactant wave function only. A reaction pathway which is favorable at the beginning of the reaction is assumed to remain favourable all the way to product. This is also the basic assumption of the Bader–Pearson concept[65] in which the symmetry of reaction pathways is determined by the symmetry of transition densities. For ground-state reactions the symmetry of these transition densities is the direct product between the symmetries of the ground state and of the first excited state wave function.[65] Our approach is a population analysis of the reactant CASSCF wave function in terms of localized bonding schemes. Any bonding scheme corresponds to a manifold of AO determinants which are local many-electron functions. Therefore, a computed weight is a measure for the probability of finding a definite local many-electron distribution in the expanded CASSCF wave function. As an example, the weight of **IV**/2 is the probability of finding two π electrons at one terminal carbon atom of butadiene and *simultaneously* two π electrons in the other terminal carbon–carbon bond. Thus, our qualitative results are based on a many-electron analysis of an MO wave function. In contrast, qualitative MO methods are rooted within the one-electron framework. The expansion technique leads naturally to approximate resonance hybrids which are different for the $^1\pi,\pi^*$ and the $^3\pi,\pi^*$ states of s-*trans*-1,3-butadiene. This is different to MO correlation diagram techniques where it is hard to distinguish between singlet and triplet reactivities.[66] Another appealing feature of our approach is that the singlet and triplet diradical characters of an excited state appear in a strictly localized picture. A significant singlet diradical character is characterized by two electrons of opposite spins localized at atoms which are not bonded but can approach each other. This situation can lead to intramolecular bond formation in the excited state as outlined for 1^1B_u butadiene. Moreover, the zwitterionic character of an electronic state emerges naturally when the expansion technique is applied. Both a *local* singlet diradical and a zwitterionic character are difficult to treat by means of MO correlation diagrams.

All results obtained in this work are derived by expanding wave functions for the vertically excited electronic states. Thus, our analysis does not account for the complicated photophysics that occur on the 2^1A_g and 1^1A_g potential surfaces after the vertical excitation. The organic photochemist writes resonance structures to indicate the main features of the electron distributions in electronically excited states. This is usually done by employing the ground state molecular geometry. Thus, conclusions on photochemical reactivity are made based on simplified descriptions of vertically excited states. We adopted this successful qualitative notion in this work. Our intention was to obtain those resonance structures from CASSCF wave functions without a guidance of photochemical experience. The agreement achieved between the resonance structures derived and the observed photochemistry of the diene entity support the notion that local bonding schemes, as obtained from the π electron part of a CASSCF wave function, are qualitatively meaningful.

Acknowledgement

The authors are grateful to Dr. G. Olbrich for fruitful discussions and to Dr. J. Leitich for communicating unpublished results. We thank one referee for bringing ref. [47] to our attention.

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Received: May 3, 1999 [F1762]