

Pi-Electron Structure of Butadiene*

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The spectrum and structure of butadiene have been considered by application of several nonempirical methods to the problem of the energy levels of the π -electron system. Six spatial configurations of the nuclei have been treated, of which three correspond to the *trans*- form of the molecule and three, *cis*. The methods used include the use of antisymmetrized molecular orbitals with and without configuration interaction, electron-pair bonds, a model based on two neighboring vinyl radicals, and the method of atoms in molecules as applied to the preceding techniques. A comparison of the results given by the different theories permits an evaluation of the theories, at least in the case of unsaturation electrons.

I. INTRODUCTION

THE butadiene molecule has been the subject of many investigations concerned with the electronic structure of systems of π electrons.¹⁻¹⁰ A qualitative explanation of its structure and spectrum can be derived readily from a semiempirical molecular orbital treatment, with or without inclusion of what Moffitt has termed "first-order configuration interaction"¹¹ which is necessary to make such a treatment self-consistent. Nonempirical methods of dealing with this molecule have been rather unsuccessful, particularly in light of the fact that logically consistent refinements of the methods have led to results that are in greater divergence from experiments than the initial, cruder approximations. The long-wavelength transition, for example, which is observed at 6.0 eV,¹² can be correlated with the transition from the ground state to an excited 1B_u state (V_1 in Mulliken's notation) predicted by the antisymmetrized molecular orbital (ASMO) method, but considerable imagination is necessary to find in the theoretical results such a transition when configuration interaction is included. For reasons of this sort, it was deemed worthwhile to examine the structure and ultraviolet spectrum which several theories and models predict for the butadiene molecule. It was felt that perhaps the results derived from some nonempirical approach could be correlated unambiguously with the observed spectrum, and that an analysis of the results of all the various treatments would provide some insight into the peculiarities of the molecule and of the theories themselves.

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¹ C. A. Coulson and J. Jacobs, Proc. Roy. Soc. (London), **A206** 287 (1951).

² J. E. Lennard-Jones, Proc. Roy. Soc. (London) **A158**, 280 (1937).

³ Y. Mori, Bull. Chem. Soc. Japan **28**, 291 (1955).

⁴ R. S. Mulliken, J. Chem. Phys. **7**, 121 (1939).

⁵ R. K. Nesbet, Proc. Roy. Soc. (London) **A230**, 312 (1955).

⁶ R. G. Parr and R. S. Mulliken, J. Chem. Phys. **18**, 1338 (1950).

⁷ A. Pullman, J. chim. phys. **51**, 188 (1954).

⁸ A. Pullman and J. Baudet, Compt. rend. **238**, 241 (1954).

⁹ A. Pullman and H. Berthod, J. chim. phys. **52**, 771 (1955).

¹⁰ W. T. Simpson, J. Am. Chem. Soc. **73**, 5363 (1951).

¹¹ W. Moffitt, J. Chem. Phys. **22**, 1320 (1954).

¹² W. C. Price and A. D. Walsh, Proc. Roy. Soc. (London) **A174**, 270 (1940).

In addition to the spectrum, the structure of the molecule was investigated by carrying out all the calculations for six spatial configurations of the nuclei. Of these, three corresponded to the *trans*- form of the molecule and three to the *cis*; the three cases of each form were chosen to correspond to a completely conjugated structure with three equal carbon-carbon bond lengths of 1.40 Å, a structure with the bond distances 1.46 and 1.35 Å found by Schomaker and Pauling,¹³ and to an unconjugated structure with carbon-carbon bond of the lengths found for ethane¹⁴ and ethylene,¹⁵ 1.54 and 1.33 Å, respectively.

The methods used for computing the energy levels of the π -electron system are all of the LCAO type. They were, furthermore, carried out only to the approximation that the nuclei, core electrons, and σ -bond electrons could be treated as an effective potential field and all hydrogen atoms could be neglected. The methods themselves included antisymmetrized molecular orbitals without and then with configuration interaction (including all configurations derived from four $2p\pi$ atomic orbitals), electron pair bonds (including only the two covalent structures), a method based on two interacting vinyl radicals in molecular orbital representations, and the method of atoms in molecules as applied to all these methods.

II. DETAILS OF THE CALCULATIONS

The molecular orbitals were constructed from the atomic orbitals by means of the transformation

$$\psi = \pi \mu \nu d, \quad (1)$$

where ψ and π are four-dimensional vectors representing the four molecular orbitals and atomic orbitals, respectively. The matrix μ takes the atomic orbitals π into a set of symmetry orbitals

$$\psi''_1 = \pi_1 + \pi_2 + \pi_3 + \pi_4, \quad (2a)$$

$$\psi''_2 = \pi_1 + \pi_2 - \pi_3 - \pi_4, \quad (2b)$$

$$\psi''_3 = \pi_1 - \pi_2 - \pi_3 + \pi_4, \quad (2c)$$

¹³ V. Schomaker and L. Pauling, J. Am. Chem. Soc. **61**, 1769 (1939).

¹⁴ G. E. Hansen and D. M. Dennison, J. Chem. Phys. **20**, 313 (1952).

¹⁵ I. L. Karle, J. Chem. Phys. **20**, 65 (1952).

and

$$\psi''_4 = -\pi_1 + \pi_2 - \pi_3 + \pi_4. \quad (2d)$$

The ν matrix makes the four orbitals orthogonal; d is a diagonal normalizing matrix. The final orbitals, ψ_1 , ψ_2 , ψ_3 , and ψ_4 fall, into two symmetry types. In the *cis*-form of the molecule, ψ_1 and ψ_3 transform like the irreducible representation B_1 while ψ_2 and ψ_4 transform like A_2 ; in the *trans*-case, ψ_1 and ψ_3 behave like A_u , ψ_2 and ψ_4 like B_g .

The orbitals obtained by this method were transformed into self-consistent field or SCF orbitals by allowing the two orbitals of each symmetry to mix with each other until the total energy of the four-electron system was minimized. For a given SCF orbital, the ratio of the squares of the mixing coefficients of the orthonormal symmetry orbitals never exceeded 0.01. The present calculation, for the cases corresponding to *cis*- and *trans*-structures with observed bond angle and lengths, corresponds to that of Parr and Mulliken,⁶ and the energy levels and atomic orbital coefficients of the two calculations are in agreement.

The configuration interaction was carried out beginning with the Hamiltonian matrix in the ψ representation defined above. All configurations which could be constructed from the four orbitals were included, so that the largest matrix was twelve by twelve. Evaluation of integrals over atomic orbitals is discussed in the appendix.

Other configuration interaction treatments of butadiene have been carried out by Coulson and Jacobs,¹ who used much more drastic approximations than those of the present work, and also Nesbet⁶ and Pullman and Baudet.^{7,8} Nesbet treated the *cis*- and *trans*-forms, using the observed structure, and included all the configurations arising from four $2p\pi$ orbitals. Pullman and Baudet dealt only with the *trans*-structure, using the observed bond angle and lengths for their carbon skeleton. They included all eight ^1Bu configurations but only nine of the twelve ^1Ag possibilities to obtain the two lowest excitation energies. The results for case B of the present work are in good agreement with those of Nesbet and with the $^1\text{Ag} \rightarrow ^1\text{Bu}$ transition energy computed by Pullman and Baudet. The latter authors' value for the first $^1\text{Ag} \rightarrow ^1\text{Ag}$ excitation energy is somewhat higher than that computed by Nesbet or by this author. It seems that although the high-energy configurations hardly effect the lowest state, they do enter for excited states.

The so-called two-vinyl model^{3,10} is based on wave functions in the form of products of two ethylenic configurational functions. The ground state of the four-electron system, for example could be written as

$$\Theta_N = \mathcal{A} \Psi^{R_N} \Psi^{S_N}, \quad (3)$$

where Θ is the butadiene function, \mathcal{A} is an antisymmetrizing operator, and Ψ^{R_N} and Ψ^{S_N} are the lowest configurational functions for the vinyl groups labeled

R and S , respectively. This model differs from the ASMO method only insofar as the latter permits charge transfer from one double bond to the other; the two-vinyl model requires that each double bond remain electrically neutral. A structure like $\text{C}^+ - \text{C} = \text{C} - \text{C}^-$ can only occur in the ASMO treatment, for example, but $\text{C}^- - \text{C}^+ - \text{C} = \text{C}$ is found in both models.

The approach used by Simpson¹⁰ is exactly the semiempirical parallel of this treatment. Rather than perform a nonempirical evaluation of the matrix element of interaction between an excited double bond and an adjacent unexcited bond, he has fitted the value from the butadiene spectrum data. The present work does, however, neglect contributions to the lowest state arising from excitation of both ethylene groups to their V states, which Simpson's treatment includes. The treatment of Mori³ for the observed structure of *trans*-butadiene is a nonempirical one identical with the two-ethylene method (based on ASMO functions) of the present work and corresponds to structure B in Fig. 1.

A valence bond treatment was tried to determine whether purely covalent, electron-pairing effects contributed significantly to provide the observed structure and to determine the importance of such structures to the total energy of the system. Energy levels were determined, corresponding to the two (non-orthogonal) covalent structures and to the two functions obtained by mixing the structures so as to minimize the total energy. No ionic structures were included because solution of the configuration interaction problem would achieve exactly the same result.

The method of atoms in molecules has been described in detail by Moffitt.¹⁶⁻²¹

In essence, this method assumes that the formation of a molecule from its atoms is a small perturbation on the electrons which are being considered explicitly. Exact wave functions may then be used for computing all but the perturbed part of the Hamiltonian. The usual antisymmetrized molecular orbital functions provide the most convenient representation for an approximate evaluation of the perturbation.

Such a calculation was carried out recently for the two lowest excitation energies of butadiene by Pullman and Berthod.⁹ They used the same model and approximations as those used by Pullman and Baudet in the configuration interaction treatment described above. Their results are in substantial agreement with those of the present work. Again, however, the predicted value for the lowest $^1\text{Ag} \rightarrow ^1\text{Ag}$ excitation energy is higher if only nine configurations are used to determine both states than if all twelve possibilities are included.

¹⁶ W. Moffitt, Proc. Roy. Soc. (London) **A210**, 224 (1951).

¹⁷ W. Moffitt, Proc. Roy. Soc. (London) **A210**, 245 (1951).

¹⁸ W. Moffitt and J. Scanlan, Proc. Roy. Soc. (London) **A218**, 464 (1953).

¹⁹ W. Moffitt, Proc. Roy. Soc. (London) **A218**, 486 (1953).

²⁰ W. Moffitt and J. Scanlan, Proc. Roy. Soc. (London) **A220**, 530 (1953).

²¹ W. Moffitt, Repts. Progr. in Phys. **17**, 173 (1954).

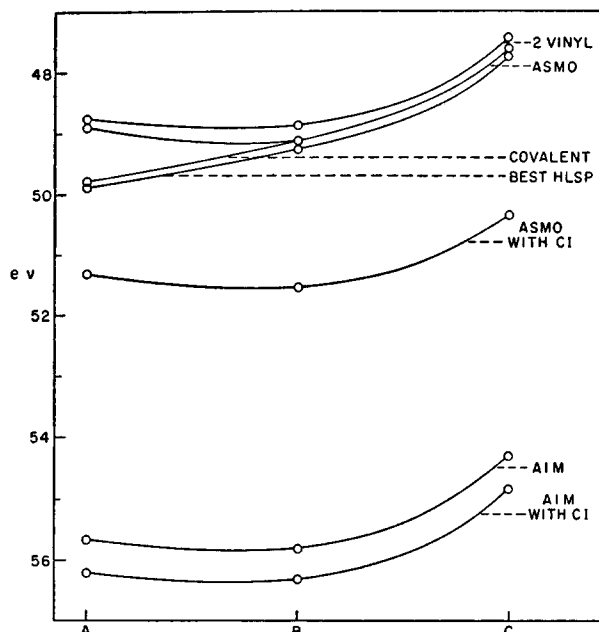


FIG. 1. Approximations to the lowest energy level of butadiene. The scale is drawn relative to W_{2p} , the energy of a π electron in an isolated sp^2 -hybridized carbon atom. A = unconjugated structure; B = observed structure; C = completely conjugated structure.

III. RESULTS

Insofar as all the methods considered herein are basically variational treatments, the first comparison that should be made of them would be among the predicted ground-state energies. These levels are shown in Fig. 1. The ASMO, valence bond, two-vinyl and ASMO configuration interaction treatments are all based on Slater-type approximate atomic orbitals; the atoms in molecules treatments utilize exact atomic functions except for the perturbing part of the Hamiltonian, which corresponds to formation of the double bonds in the molecule.

Of all the methods, only the valence bond treatment fails to predict π -electron interactions tending to shorten the center bond roughly to the length observed by Pauling and Schomaker. The lower level shown for the VB treatment is, of course, that derived by mixing the two covalent structures. This level, however, lies less than 0.1 eV below the structure represented by the conventional structural formula for butadiene.

The first figure, as well as those following, depict in detail only the *trans*-form. The *cis*-structures follow exactly the same pattern, but lie approximately 1 eV lower than the corresponding *trans*-structure according to all methods of calculation.

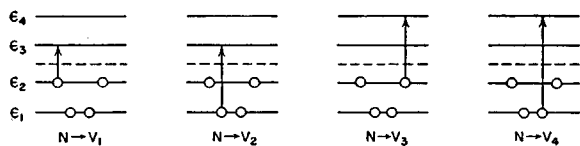


FIG. 2. Orbital excitations of butadiene.

A comparison of the excitation energies predicted by the various methods is given in Table I. In the table, two energies are given for each transition; the upper value corresponds to the *trans*-structure and the lower, *cis*. Both are taken for the observed internuclear distances. The nomenclature is that used by Parr and Mulliken⁶; the orbital excitations to which the transitions correspond in simple molecular orbital theory are indicated in Fig. 2. The configurations V_2 and V_3 mix to give the pair denoted by V_{23} and V_{23}^+ . The lowest triplet state, denoted as T , arises from the same one-electron orbital excitation as the V_1 state. This state is included in the table, but such a state has not yet been observed for butadiene.

The effects of configuration interaction on the ASMO and atoms in molecules levels are shown in Figs. 3(a) and 3(b). On the left of each diagram are the energies of

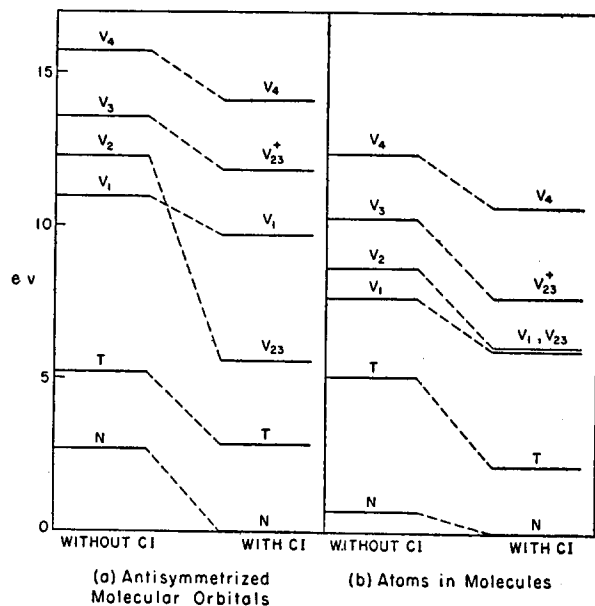


FIG. 3. The effects of configuration interaction on the energy levels.

pure configurations; on the right, the levels that result when the secular determinants are solved. The ground state after interaction was taken as the energy origin in both cases.

The agreement in the case of atoms in molecules with configuration interaction between calculated and observed values is, of course, quite fortuitous. The errors in round-off and, perhaps more important, in the electron affinity of an sp^2 -hybrid carbon atom, would place an uncertainty of about ± 0.5 eV. The error would surely be less than 1 eV.

On the basis of these calculations, therefore, the following identifications are made:

The observed 6.0 eV transition is attributed to the strongly allowed $N(^1A_g) \rightarrow V_1(^1B_u)$ excitation.

The weaker 7.2 eV transition is assigned as an $N \rightarrow A_g$ process; it is suggested that this is, in fact, due

TABLE I. Excitation energies of butadiene (ev).

	$N \rightarrow T$	$N \rightarrow V_1$	$N \rightarrow V_{23}$	$N \rightarrow V_{23}^+$	$N \rightarrow V_4$
Valence bond: Single structures		13.8 13.7			
resonating structures		19.9 19.6			
Two-vinyl: ASMO representation		9.7 9.3	12.2 12.7		
AIM representation		9.8 9.4	8.9 9.4		
ASMO: Without configuration interaction	2.5 2.5	8.3 7.8	9.6 9.8	10.9 11.1	13.0 12.9
With configuration interaction	2.8 2.8	9.7 9.4	5.6 5.6	11.9 11.7	14.0 14.0
AIM: Without configuration interaction	4.4 4.4	7.0 6.5	8.0 8.2	9.6 9.8	11.7 11.6
With configuration interaction	2.1 2.2	6.0 5.8	6.1 6.1	7.7 7.7	10.7 10.7
Observed ^a			6.0	7.2	9.5

^a W. C. Price and A. D. Walsh, Proc. Roy. Soc. (London) **A174**, 220 (1940).

to the $N \rightarrow V_{23}^+$ excitation, and that the $N \rightarrow V_{23}$ transition is masked by the intense $N \rightarrow V_1$ absorption.

Thirdly, if the 9.5-ev absorption is primarily a π -electron transition, then it is due in large part to the $N(^1A_g) \rightarrow V_4(^1B_u)$ excitation.

IV. DISCUSSION

An examination of Fig. 1 shows immediately that the electron-pairing effects described as double bond behavior at the central carbon-carbon bond are not the important factors in shortening the central link. The energy of the corresponding excited Heitler-London structure is too far above that of the ground state for such a structure to mix significantly. The curves for the other models, on the other hand, all show minima in the region of the observed structure. It may be concluded, then, that polarization of the π -electron cloud can account qualitatively for the observed structure.

The energy necessary to compress the central carbon-carbon σ bond and stretch the double bonds must come from the π -electron interaction energy. The energy required by the carbon skeleton in going from the unconjugated structure *A* to the observed structure *B* may be estimated by use of the force constants for carbon-carbon bond-stretching motions in ethane and ethylene. If these are taken as 5 and 10×10^9 dynes/cm, respectively, the energy which the π electrons must provide is approximately 0.1 ev. All the methods of calculation except the Heitler-London give this order of magnitude as the energy difference between the *A* and *B* structures; atoms in molecule with configuration interaction give 0.1 ev as the energy drops.

Furthermore, electron transfer from one double bond to the other is not necessary for an explanation of the

shortened bond. This is demonstrated by the satisfactory way in which the two vinyl model accounts for the structure by allowing polarization of double bonds but no charge transfer. The ASMO treatment leads to almost exactly the same stabilization energy for the observed structure, about 0.5 ev.

The excited states, on the other hand, do seem to require some electron transfer from one end of the molecule to the other. This may be inferred from the way the energy gap between the V_1 or V_{23} and N levels drops as the upper state takes on more and more ionic character. The valence bond model of a covalent excited state is far beyond the range of the observed excitations; the two vinyl picture, in which an ethylene-like $N \rightarrow V$ excitation is delocalized and permitted to travel across the molecule is more satisfactory; but only when charges are permitted to travel from one double bond to the other do the corresponding wave functions show quantitative accuracy. It might be noted that charge transfer is slightly more important in lowering the energy of the V_1 level than it is for V_{23} . This may be seen by comparing the AIM energies before configuration interaction with the corresponding two vinyl model. High configurations, on the other hand, are seen to influence these two levels in the reverse order.

The differences between the ASMO and atoms in molecules methods are just what would be expected from the fact that the former overestimates the energy necessary to form a C^+ , C^- ion pair from two neutral sp^2 -hybridized carbon atoms. All the lower AIM levels are below their ASMO counterparts. Before configuration interaction, each excited AIM level is higher or lower, relative to the lowest configuration, than its ASMO counterpart, depending on whether it is pri-

marily covalent or ionic in nature. The estimates for the T and V_1 states illustrate this very clearly; the configuration representing the T state is highly covalent, and that corresponding to V_1 is primarily ionic. As a result, the $T-V_1$ splitting is much larger with an ASMO treatment than with the AIM approach.

The effects of configuration interaction in the two schemes display perhaps the most significant comparisons of the methods and, in addition, allow some insight into the orbital approximation upon which they are both based. From Fig. 3, it is apparent how the levels are drastically changed in the ASMO treatment and simply shifted in the AIM treatment. The lowest level, for example, moves almost 3 eV in the former method but only about 0.7 eV in the latter. The highly ionic V_2 configuration interacts very strongly in ASMO to become much more covalent, while in atoms in molecules, it may retain most of its ionic character and still have a relatively low energy. By the same token, the T level, the lowest triplet, is more affected by configuration interaction in atoms in molecules than in ASMO just because in AIM it may take on more ionic character than in ASMO.

Finally, the atoms in molecules method in a way vindicates the semiempirical molecular orbital treatment, whose worth seemed questionable in light of the results derived from its logical consequents like the ASMO method with configuration interaction. Clearly the orbital approximation is a reasonably good one for the lowest level, as is shown by Fig. 3, at least when accurate atomic energies are used. The excited states according to atoms in molecules also support the use of molecular orbitals for a first approximation; this cannot necessarily be said of the states derived by an ASMO method. Not only does the former approach show a simpler picture of configuration interaction than the latter, but also the final wave functions are much more like the initial configurations. For example, after configuration interaction the V_{23} state according to the ASMO method is composed of a large number of configurations, no one of which is particularly dominant; the same state as represented by an AIM treatment is predominantly composed of the configuration from which it arises on an energy diagram like Fig. 3. In the final AIM function, the coefficient of the parent configuration V_2 is 0.8; the rest of the configurations are obviously entering as correction terms.

It seems that for a system in which the electrons under consideration are not entirely unlike atomic electrons, the orbital approach is a reasonable one, providing accurate atomic functions form the basis of the atomic Hamiltonian. The error introduced by the

use of approximate functions in the atomic Hamiltonian more than overcomes the correction arising from configuration interaction. When accurate functions are used, however, it seems that quantitatively useful predictions may be made about the energy levels and structure of systems of weakly interacting electrons.

V. APPENDIX

The integrals over atomic orbitals which were necessary for calculation of the Hamiltonian matrix elements were calculated in the following way. The basic functions have been taken to be Slater orbitals of the form

$$\frac{1}{2(2\pi)^{\frac{1}{2}}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\rho_i \exp(-\rho_i) \sin\theta \cos\varphi,$$

where $Z=3.18$, a_0 is the Bohr radius, and $\rho=Zr/2a_0$. The overlap integrals and the one-center integral were calculated exactly. The two-center Coulomb integrals were broken into an algebraic part and an exponential part; the former was computed exactly and the latter, interpolated from logarithmic plots made of the exponential contribution to the integrals evaluated by Parr and Mulliken⁶ and Kopineck.²²⁻²⁴ The exchange, hybrid and one-electron integrals were interpolated from logarithmic plots of the values of the corresponding integrals in the tables of Parr and Mulliken⁶ and Kopineck.²²⁻²⁴ The three- and four-center integrals were computed using the approximation of Parr and Mulliken⁶; i.e.,

$$\int \pi_k(1)\pi_l(2)\frac{1}{r_{12}}\pi_m(1)\pi_n(2)d\tau_1d\tau_2 \\ = S_{km}S_{ln} \int \pi_r(1)\pi_s(2)\frac{1}{r_{12}}\pi_r(1)\pi_s(2)d\tau_1d\tau_2,$$

where S_{km} is the overlap integral between π_k and π_m , and π_r is a $2p\pi$ orbital located midway between k and m ,

VI. ACKNOWLEDGMENTS

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²² H. J. Kopineck, Z. Naturforsch. 5, 420 (1950).

²³ H. J. Kopineck, Z. Naturforsch. 6, 177 (1951).

²⁴ H. J. Kopineck, Z. Naturforsch. 7, 785 (1952).