

the lower its orbital energy, and the greater its interaction with the nitrogen lone pair. In the initial stages, where the reaction coordinate is not controlled by orbital overlap considerations, the main interaction would appear to be between the local electric dipoles of the nucleophilic and the carbonyl groups. These conclusions are somewhat analogous to the interplay of charge polarization and orbital overlap occurring in the course of SN-type reactions, according to recent SCF-MO calculations.¹³

(13) J. P. Lowe, *J. Amer. Chem. Soc.*, **93**, 301 (1971).

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Low-Lying π -Electron States of *trans*-Butadiene

Sir:

A series of extensive configuration interaction calculations on the π -electron states of *trans*-butadiene has been carried out and will be described in detail elsewhere.¹ They were based on a self-consistent field representation of the σ core, obtained from an all-electron SCF calculation on the ground state using a double- ζ contracted Gaussian basis set² (the SCF energy was -154.87712 hartree). In line with recent calculations on ethylene³⁻⁵ in which the singlet ($\pi\pi^*$) state was found to have a diffuse charge distribution,⁶ the π basis was augmented with two diffuse $2p\pi$ functions (Gaussian exponents 0.03477 and 0.01075) on each carbon atom. All the configurations which could be constructed by distributing the four π electrons in all possible ways between the 16 SCF occupied and virtual π orbitals (2752 configurations for 1A_g , 3556 for 3A_g , 924 for 5A_g , 2688 for 1B_u , and 3584 for 3B_u) were included in the configuration interaction treatment, which can thus be characterized as full π -electron CI with a frozen SCF σ core.

The main results are summarized in Table I in terms of the vertical excitation energies from the ground state (the computed ground state CI energy was -154.94015 hartree). The electronic states are characterized as either valence-like or diffuse (Rydberg-like), in terms of the spatial extent of the wave function; no intermediate cases have been found.¹

(1) R. P. Hosteny, T. H. Dunning, Jr., R. R. Gilman, A. Pipano, and I. Shavitt, to be submitted for publication. A preliminary report was given at the 26th Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, June 1971.

(2) T. H. Dunning, Jr., *J. Chem. Phys.*, **53**, 2823 (1970).

(3) T. H. Dunning, Jr., W. J. Hunt, and W. A. Goddard III, *Chem. Phys. Lett.*, **4**, 147 (1969).

(4) C. F. Bender, T. H. Dunning, Jr., H. F. Schaefer III, W. A. Goddard III, and W. J. Hunt, *Chem. Phys. Lett.*, **15**, 171 (1972).

(5) R. J. Buenker, S. D. Peyerimhoff, and W. E. Kammer, *J. Chem. Phys.*, **55**, 814 (1971); R. J. Buenker, S. D. Peyerimhoff, and H. L. Hsu, *Chem. Phys. Lett.*, **11**, 65 (1971).

(6) It should be noted that the diffuse nature of the ($\pi\pi^*$) singlet state of planar ethylene has been questioned by a number of workers, notably H. Basch and V. McKoy, *J. Chem. Phys.*, **53**, 1628 (1970), and J. A. Ryan and J. L. Whitten, *Chem. Phys. Lett.*, **15**, 119 (1972), but the results of the recent CI calculations of Bender, *et al.*,⁴ and of H. Basch, *Chem. Phys. Lett.*, **19**, 323 (1973), while indicating that electron correlation has a significant effect on the charge distribution in this state, do not support the objections of these authors.

Table I. Calculated and Experimental Vertical Excitation Energies for Selected π -Electron States of *trans*-Butadiene (in eV)

State	Excitation energies		
	Calcd	Optical	Electron impact ^a
Valence Single-Excitation States			
1^3B_u	3.45	3.22 ^b	3.20
1^3A_g	5.04	(3.90 ^b)	4.91
Valence Double-Excitation States			
2^1A_g	6.77		
$3^3B_u^c$	8.08		
1^5A_g	9.61		
Diffuse (Single-Excitation) States ^d			
1^1B_u	7.05	6.05 ^e	5.92
2^1B_u	8.06	$\geq 7.06^e$	7.28
3^1A_g	7.82		
4^1A_g	7.87		

^a Reference 7. ^b D. F. Evans, *J. Chem. Soc.*, 1735 (1960); the 3.9 eV state has not been confirmed by other data and is considered spurious. ^c The 2^3B_u state is a Rydberg state and has a calculated excitation energy of 7.14 eV. ^d The calculated excitation energies for the diffuse states are believed too high by about 1 eV, see text. ^e W. C. Price and A. D. Walsh, *Proc. Roy. Soc., Ser. A*, **174**, 220 (1940). The 7.05 eV state was assigned by R. S. Mulliken, *J. Chem. Phys.*, **7**, 121, 373 (1939), as 1^1A_g .

The two lowest triplet states, 1^3B_u and 1^3A_g , are found to be valence states with calculated vertical excitation energies of 3.45 and 5.04 eV, respectively, in good agreement with recent electron impact^{7,8} and ion impact⁹ spectra. Agreement is less good for the corresponding singlet states. In contrast to the assumptions of π -electron theory and in line with the *ab initio* results for planar ethylene,³⁻⁵ the $1,2^1B_u$ and $3,4^1A_g$ states of butadiene are found to be Rydberg-like in character (the 2^1A_g state is of a different type and is discussed further below). While the σ core obtained from the ground-state SCF calculation appears to be adequate for the treatment of the low-lying valence states,³ such as 1^3B_u and 1^3A_g , it is less appropriate for the diffuse Rydberg-like states; thus, in ethylene,³ relaxation of the σ core for the singlet ($\pi\pi^*$) state (upon carrying out an SCF calculation for the excited state) lowered the computed excitation energy by 0.6 eV (but this effect was smaller in recent CI calculations on butadiene with a smaller basis set by Shih, Buenker, and Peyerimhoff¹⁰). Furthermore, σ orbital correlation (neglected here and by Shih, *et al.*) appears to affect the $\pi\pi^*$ singlet states more than the ground state.^{4,11} The calculated vertical excitation energies are therefore expected to be too high, as indeed appears to be the case. The assignments used for these states¹ in Table I were suggested independently by Shih, *et al.*¹⁰

In addition to the states discussed above, three states with valence-like charge distributions were found with vertical excitation energies of 6.67 (2^1A_g), 8.08 (3^3B_u), and 9.61 eV (1^5A_g). They could not be correlated with any spectroscopic states and were found to be predominantly double-excitations relative to the ground-state Hartree-

(7) O. A. Mosher, W. M. Flicker, and A. Kuppermann, *Chem. Phys. Lett.*, **19**, 332 (1973).

(8) H. H. Brongersma, J. A. van der Hart, and L. J. Oosterhoff in "Fast Reactions and Primary Processes in Chemical Kinetics," S. Claesson, Ed., Interscience, New York, N. Y., 1967, p 211.

(9) J. H. Moore, Jr., *J. Phys. Chem.*, **76**, 1130 (1972).

(10) S. Shih, R. J. Buenker, and S. D. Peyerimhoff, *Chem. Phys. Lett.*, **16**, 244 (1972); a comparison of the results of these authors with those of ref 1 is given in their paper.

(11) K. Tanaka, *Int. J. Quantum Chem.*, **6**, 1087 (1972).

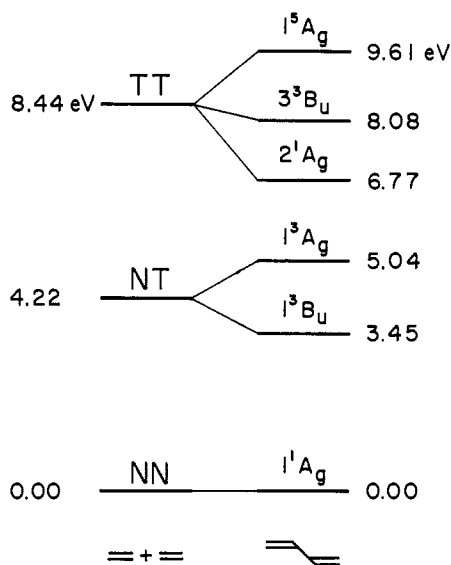


Figure 1. Correlation of computed valence states of butadiene (right) with those of two ethylene molecules (left).

Fock configuration.¹² The errors in their computed vertical excitation energies are probably quite small, as are the errors for the other valence states 1^3B_u and 1^3A_g . Being essentially doubly excited states, they are not expected to make significant contributions to either the optical or the electron impact spectra of butadiene, though the 2^1A_g state may be accessible in two-photon laser spectroscopy. These states, and particularly the 2^1A_g state, may play a role in the photochemistry of butadiene. For example, the semiempirical calculations of van der Lugt and Oosterhoff¹³ indicate that an excited 1^1A_g state is responsible for the cyclization of butadiene to cyclobutene; this state may be identified with the 2^1A_g state.¹

All the valence states of butadiene can easily be accounted for by a straightforward generalization of valence bond theory.¹ Using a "molecules-in-molecules" or exciton approach,¹⁴ the ground and excited states of butadiene are described in terms of the electronic states of the two localized ethylenic subunits (Figure 1). From the two π -electron valence states of ethylene, the ground $N(\pi^2)$ and excited triplet $T(\pi\pi^*)$ states, a total of six states of butadiene can be constructed. With the two ethylenic units in the N state, the ground state of butadiene, denoted as $NN(X^1A_g)$, is obtained. Two triplet states, $NT(^3B_u)$ and $NT(^3A_g)$, are obtained if one unit is in T and the other in N. In the absence of significant stabilization effects, their average excitation energy (4.24 eV for 1^3A_g and 1^3B_u in this calculation) is just the $N \rightarrow T$ excitation energy of ethylene (calculated as 4.22 eV). With both ethylenic units in the T state, three states can be formed, $TT(^1A_g)$, $TT(^3B_u)$, and $TT(^5A_g)$. Their average excitation energy

(12) Several workers have noted the large effect of doubly excited configurations on the location of the 2^1A_g state but did not realize that the resulting 2^1A_g state is not related to the 2^1A_g state obtained in a single-excitations-only CI calculation (the latter becoming the 3^1A_g state in double-excitation CI); see, e.g., J. Koutecky, *J. Chem. Phys.*, **47**, 1501 (1967), and references therein. Koutecky has pointed out that this state should be reachable by double-photon excitation from the ground state.

(13) W. Th. A. M. van der Lugt and J. Oosterhoff, *J. Amer. Chem. Soc.*, **91**, 6042 (1969).

(14) W. Moffitt, *J. Chem. Phys.*, **22**, 320 (1954); Y. Mori, *Bull. Chem. Soc. Jap.*, **28**, 291 (1955); R. S. Berry, *J. Chem. Phys.*, **26**, 1660 (1957).

should be approximately twice the $N \rightarrow T$ energy of ethylene, i.e., 8.44 eV. Correlating them with the calculated 2^1A_g , 3^3B_u , and 1^5A_g valence states of butadiene, we get $\Delta E_{av} = 8.15$ eV. The occurrence of such doubly excited states in conjugated systems is expected to be quite general.^{15,16}

The diffuse π -electron states of butadiene can be constructed in a similar manner. With one ethylenic unit in the singlet $V(\pi\pi^*)$ state we obtain the $NV(^1B_u)$ and $NV(^1A_g)$ states of butadiene. In contrast to the valence states, however, the diffuse states are well represented by a single SCF configuration; delocalization is thus significant, and the simple generalized valence bond description is less appropriate for these states.

(15) K. Schulten and M. Karplus, *Chem. Phys. Lett.*, **14**, 305 (1972), and J. Michl and J. Downing, Proceedings of the Summer Research Conference on Theoretical Chemistry, Boulder, Colo., June 1972 (to appear) have reported low-lying doubly excited states obtained in semiempirical calculations on large conjugated systems. See also J. Downing, V. Dvořák, J. Kolc, A. Manzara, and J. Michl, *Chem. Phys. Lett.*, **17**, 70 (1972), and references therein.

(16) The occurrence of related states in benzene has recently been demonstrated, see P. J. Hay and I. Shavitt, to be submitted for publication.

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Molecular Structure of (1,7-Cyclododecadiyne)hexacarbonyliron. Implications on the Alkyne Disproportionation Reaction

Sir:

Addition of cyclic alkadiynes to transition metal complexes has produced some interesting intramolecular cyclization reactions in which complexed cyclobutadiene and cyclopentadiene derivatives are formed.^{1,2} In particular, the reaction of 1,7-cyclododecadiyne (I) with $Fe(CO)_5$ has produced two complexes, $C_{12}H_{16}Fe_2(CO)_6$ (major product) and $C_{12}H_{16}Fe(CO)_3$ (trace). These compounds were originally formulated as II and III, respectively.^{1b} We have determined the structure of the major product, (1,7-cyclododecadiyne) $Fe_2(CO)_6$, via X-ray diffraction techniques and have found its geometry to be not II but IV.

Crystal data for $C_{12}H_{16}Fe_2(CO)_6$: space group $P3_1$ (trigonal, no. 144);³ $a = 9.186$ (3), $c = 18.604$ (6) Å; $V = 1359$ Å³; ρ_{calcd} (based on $Z = 3$) = 1.61 g cm⁻³,

(1) (a) R. B. King and C. W. Eavenson, *J. Organometal. Chem.*, **16**, P75 (1969); (b) R. B. King and I. Haiduc, *J. Amer. Chem. Soc.*, **94**, 4044 (1972); (c) R. B. King, I. Haiduc, and C. W. Eavenson, *ibid.*, **95**, 2508 (1973).

(2) R. B. King and A. Efraty, *J. Amer. Chem. Soc.*, **92**, 6071 (1970); **94**, 3021 (1972).

(3) No attempt was made to distinguish between the two enantiomorphic space groups $P3_1$ and $P3_2$. The validity of the crystallographic results described here is in no way affected by the arbitrary selection of $P3_1$ over $P3_2$.