1-1-1987

A Theoretical Investigation of Some Low-lying Singlet States of 1,3-butadiene

Robert J. Cave
Harvey Mudd College

Ernest R. Davidson
Indiana University - Bloomington

Recommended Citation

Cave, R.J.; Davidson, E.R. "A theoretical investigation of some low-lying singlet states of 1,3-butadiene," J. Phys. Chem. 1987, 91, 4481-4490. doi: 10.1021/j100301a013

reactions such as $M + O_2$, $M + H_2O$, and $MO + O_2$ (where M = Ba or Sr) were also studied. The $M + O_2$ reactions were found to give chemielectron spectra which were totally different from those seen in the $MO + H_2O$ reactions whereas the $MO + O_2$ and $M + H_2O$ reactions did not produce any chemielectrons. Although these reactions will be discussed in detail elsewhere,[23] a preliminary account of the $BaO + H_2O$ and $SrO + H_2O$ chemielectron spectra is presented here, as in the early stages of the BaO(s) and SrO(s) evaporation experiments these chemielectron spectra were found to make significant contributions to the photoelectron spectra recorded.

Spectra obtained from the $BaO + H_2O$ and $SrO + H_2O$ reactions are shown in parts a and b of Figure 4, respectively. In both cases, part of the spectrum was recorded with the photon source on and nitrogen was added to calibrate the energy scale. In the $BaO + H_2O$ case at a furnace temperature of 1900 ± 50 K, a structured band was observed with a peak maximum of 1.56 ± 0.05 eV (Figure 4a). The observed structure was regular with an average spacing of 1050 ± 100 cm^{-1}. As the furnace temperature was increased to 2000 ± 50 K, the chemielectron band broadened and its peak maximum moved to 1.86 ± 0.10 eV electron kinetic energy. In the $SrO + H_2O$ case, at a furnace temperature of 2050 ± 50 K a structured chemielectron band was also seen with a band maximum of 1.76 ± 0.15 eV (Figure 4b). Again regularly spaced structure was observed with an average separation of 850 ± 100 cm^{-1}. This band showed no noticeable temperature dependence up to a furnace temperature of 2150 ± 50 K. At this stage, a detailed mechanism for these chemielectron reactions cannot be presented as further experiments to measure more accurately the temperature dependence and structure of the observed bands are required and mass spectrometric measurements are needed to identify the ions produced. However, a possible mechanism would be electron transfer from a $M(OH)_2$ electronically and vibrationally excited state to the ground electronic state of the ion, $M(OH)_2^+$, with vibrational structure corresponding to transitions to different vibrational levels of the ion, as discussed earlier for the $O + CH$ and $Ce + O_2$ chemiionization reactions.[47]

In this work the UV photoelectron spectra of barium and strontium monoxides have been recorded for the first time. Although only one band has been observed for each molecule, the experimental band onsets have led to a determination of upper limits for the dissociation energies in the ionic ground states. The $X^2\Sigma^+$ and $A^2\Pi$ states of both BaO^+ and SrO^+ are very close in energy and higher resolution studies will obviously be required to establish their energy separation and probe the spectroscopic properties of these states.

Acknowledgment. We thank the S.E.R.C. for financial assistance. This work was also supported by the Air Force Office of Scientific Research (Grant No. AFOSR-83-0283) through the European Office of Aerospace Research (EOARD), United States Air Force.

Registry No. SrO, 1314-11-0; BaO, 1304-28-5; H_2O, 7732-18-5; SrO^+, 83018-04-6; BaO^+, 51403-88-4.

---

[47] Dyke, J. M. *J. Chem. Soc., Faraday Trans. 2* **1987**, *83*, 69.

A Theoretical Investigation of Some Low-Lying Singlet States of 1,3-Butadiene

Robert J. Cave and Ernest R. Davidson*

Department of Chemistry, Indiana University, Bloomington, Indiana 47405 *(Received: February 23, 1987)*

Results are presented from extensive ab initio calculations on several low-lying singlet states of *cis-* and *trans-*1,3-butadiene. The results indicate a qualitative difference between the cis and trans isomers for the lowest $\pi \rightarrow \pi^*$ transition. For the cis isomer, the first excited singlet state of the same symmetry as the ground state is found to lie above the lowest $\pi \rightarrow \pi^*$ transition, and we estimate that this is also the case for the trans isomer.

I. Introduction

The understanding of the electronic spectra of polyenes continues to be a challenging problem for experimentalists and theoreticians.[1] In particular, the long-chain polyenes have been of special interest due to their importance in the chemistry of vision. It has been generally assumed that the photophysics of the longer chain species should bear some resemblance to that of the shorter members of this class, and as a result molecules like butadiene, hexatriene, and octatetraene have received special attention.[2] Unfortunately, these short-chain species have proven to be complicated problems themselves. For example, for 1,3-butadiene, while there has been good agreement between experiment and ab initio theory for the two lowest triplet states and a number of the low-lying Rydberg states,[3-8] there is nearly total disagreement as to the nature and position of the excited state involved in the lowest optically allowed transition. The aim of the present article is to reexamine some of the low-lying singlet states of *trans-*1,3-butadiene, as well as to present results for analogous states of the cis isomer of 1,3-butadiene.

The low-lying singlet states which have been assigned to $\pi \rightarrow \pi^*$ excitations have the symmetry designations ^1A_g and ^1B_u. The ground state is of symmetry ^1A_g. The dominant feature in the optical[9-13] and electron impact spectra[14-20] (at low scattering angles) is a broad intense band stretching from 5.7 to 6.3 eV,

---

* Author to whom correspondence should be addressed.

[1] (a) Robin, M. B. *Higher Excited States of Polyatomic Molecules*, Vol. II; Academic Press: New York, 1975. (b) Robin, M. B. *Higher Excited States of Polyatomic Molecules*, Vol. III; Academic Press: New York, 1985.

[2] Hudson, B. S.; Kohler, B. E.; Schulten, K. In *Excited States*, Vol. VI, Lim, E. C., Ed.; Academic Press: New York, 1982; p 1.

[3] Buenker, R. J.; Whitten, J. L. *J. Chem. Phys.* **1968**, *49*, 5381.

[4] Hosteny, R. P.; Dunning, Jr., T. H.; Gilman, R. R.; Pipano, A.; Shavitt, I. *J. Chem. Phys.* **1975**, *62*, 4764.

[5] Shih, S.; Buenker, R. J.; Peyerimhoff, S. D. *Chem. Phys. Lett.* **1972**, *16*, 244.

[6] Buenker, R. J.; Shih, S.; Peyerimhoff, S. D. *Chem. Phys. Lett.* **1976**, *44*, 385.

[7] Nascimento, M. A. C.; Goddard, W. A. III *Chem. Phys.* **1979**, *36*, 147.

[8] Nascimento, M. A. C.; Goddard, W. A. III *Chem. Phys.* **1980**, *53*, 251.

[9] McDiarmid, R. *J. Chem. Phys.* **1976**, *64*, 514.

[10] McDiarmid, R. *Chem. Phys. Lett.* **1975**, *34*, 130.

[11] Wiberg, K. B.; Peters, K. S.; Ellison, G. B.; Dehmer, J. L. *J. Chem. Phys.* **1977**, *66*, 2224.

[12] Vaida, V.; McClelland, G. M. *Chem. Phys. Lett.* **1980**, *71*, 436.

[13] Hemley, R. J.; Dawson, J. I.; Vaida, V. *J. Chem. Phys.* **1983**, *78*, 2915.

[14] Mosher, O. A.; Flicker, W. M.; Kuppermann, A. *J. Chem. Phys.* **1973**, *59*, 6502.

[15] Doering, J. P. *J. Chem. Phys.* **1979**, *70*, 3902.

[16] McDiarmid, R. *J. Chem. Phys.* **1983**, *79*, 9.

[17] Doering, J. P.; McDiarmid, R. *J. Chem. Phys.* **1980**, *73*, 3617.

having three peaks separated by approximately 0.16 eV,[18] the intensity maximum occurring at 5.92 eV.[14] This feature has been assigned as the lowest $\pi \rightarrow \pi^*$ excitation to a state of ^1B_u symmetry. In C_{2h} symmetry this transition is formally allowed. On the basis of the band's intensity and its persistence in solution the state is believed to be predominantly valencelike.[1a]

A variety of assignments have been made for the $1^1A_g \rightarrow {}^1A_u$, ^1B_u (np) Rydberg series. Doering and McDiarmid[17,18] assigned the peaks at 6.67 and 7.07 eV to the 3p origins of two Rydberg series but did not differentiate between them as to whether the np series were in-plane or out-of-plane. Johnson[14] has suggested that for $n > 3$ the in-plane and out-of plane Rydberg series are nearly isoenergetic but did not assign the peaks at 6.67 and 7.07 eV. More recently, Reddish et al.[20] have assigned the 7.07-eV transition to a single $^1A_g \rightarrow {}^1A_u$ (3p) transition (i.e., an in-plane Rydberg state), although they leave open the possibility of a lower intensity $^1A_g \rightarrow {}^1B_u$ ($3p_x$) transition underlying the transition to the ^1A_u state.

Another low-lying singlet state of interest is the 2^1A_g state. The original assignment of this state was to a broad, weak, structureless feature around 7.3 eV.[14,18] However, motivated by the finding that for long-chain polyenes the lowest singlet state is a one-photon forbidden state of the same symmetry as the ground state,[2] a number of searches for a lower state of ^1A_g symmetry have been made. Electron impact[14,20] and two- and three-photon ionization spectroscopy[21,22] have failed to reveal any hint of a low-lying (i.e. below 6 eV) state of ^1A_g symmetry. An ion-impact study of substituted dienes by Staley et al. found a feature in the region of 6.1–6.7 eV which they suggested may be due to the 2^1A_g state.[23] A recent resonance Raman study[24] has found evidence suggestive of a ^1A_g-type state at energies between 5.4 and 5.8 eV, that is, below the energy of the first ^1B_u transition.

Theretical studies have also been attempted on butadiene and longer polyenes. This work can be broadly divided on the basis of whether semiempirical[25–27] or ab initio[3–8,28] methods were employed. One recent semiempirical treatment of polyene spectra used a Pariser–Parr–Pople Hamiltonian and allowed extensive CI within the π space[25] (the σ framework was chosen as a frozen core). Rydberg functions were not included in the basis set used, thus only valencelike states could be properly addressed. This treatment yielded excitation energies[25] of 5.8 and 5.5 eV to the 1^1B_u and 2^1A_g states, respectively, in reasonable agreement with CNDO/S + double excitation CI calculations on the same system.[25]

A number of groups have performed ab initio calculations on the low-lying states of butadiene.[3–8] The results of Hosteny et al.,[4] those of Buenker et al.,[6] and those of Nascimento and Goddard[7,8] are of particular interest. Hosteny et al.[4] used a DZ + π Rydberg basis, treated the σ framework as frozen, and performed up to and including full CI's in the π space (1^1B_u: Rydberg, 7.01 eV; 2^1A_g: valence, 6.73 eV; 2^1B_u: Rydberg, 8.02 eV). Buenker et al.[6] used a DZ basis + Rydberg functions on the C atoms and performed perturbation-theory-selected MRSDCI calculations (1^1B_u: Rydberg, 6.67 eV; 2^1A_g: valence, 7.02 eV; 2^1B_u: valence, 7.67 eV). Nascimento and Goddard[7,8] used a DZ basis + Rydberg functions on the C atoms and performed GVB plus limited CI calculations (1^1B_u: Rydberg, 6.67 eV; 2^1A_g: valence, 7.02 eV; 2^1B_u: Rydberg, 7.7 eV). All three studies were in excellent agreement with experiment on the lowest triplet states. Buenker et al. and Nascimento and Goddard were in excellent agreement with experiment on the lowest ^1B_g (3s Rydberg) state at 6.2 eV, assigned the allowed, relatively weak feature at 6.6 eV to the first ^1B_u Rydberg state, agreed with early experimental estimates on the position of the 2^1A_g state (i.e. near 7.1 eV), and suggested that the valencelike feature at 6.0 eV was probably due to a nonvertical transition.

Two previous studies concerning the excited states of the cis isomer have also been presented. Shih et al.[5] used a near DZ basis augmented with s and p Rydberg functions and performed π electron CI's which yielded excitation energies of 6.35 and 6.67 eV to the 1^1B_2 and 2^1A_1 states, respectively. Grimbert et al.[28] studied the disrotatory ring closing of *cis*-1,3-butadiene to yield cyclobutene and obtained excitation energies of 7.00 and 7.40 eV to the 1^1B_2 and 2^1A_1 states, respectively. In their work they used an STO-3G basis, augmented with diffuse p functions and performed limited π CI's.

In the present article we present results from a reinvestigation of some of the low-lying singlet states of *trans*-1,3-butadiene using SCF, MCSCF, and CI methods. We also present results for a number of the low-lying excited states of the cis isomer. The comparison of the excitation energies and spatial extents of the lowest singlet excited states in these two isomers is especially intriguing and suggests a subtle interplay between the geometry of the molecule and the qualitative description of the states. Further, our results indicate that care must be used in the CI treatments employed so as not to bias the state descriptions. The remainder of the article is organized as follows. In section II, the geometries and basis sets which were used are discussed, along with the various wave functions employed. In section III we present our results, and in section IV the results are discussed and compared with experimental and past theoretical results. Section V contains concluding remarks.

II. Calculational Methods

The geometry used for all states of *trans*-1,3-butadiene was that obtained experimentally by Haugen and Traetteberg[29] for the C_{2h} ground state. The geometry used for *cis*-1,3-butadiene was the theoretical estimate of the planar C_{2v} ground-state geometry of Feller and Davidson.[30] The geometry of the cis is more uncertain than that of the trans, as there is considerable experimental[31,32] and theoretical[33] debate over whether the cislike geometry has its most stable form for planar conformations or for twisted carbon skeletons with C–C–C–C dihedral angles of up to 39°.[33]

For convenience, for the remainder of the article, we will refer to basis functions and orbitals which are symmetric with respect to reflection in the plane of the molecule as σ, and those which are antisymmetric upon reflection as π. Both molecules are oriented so as to lie in the yz plane. In C_{2h} the σ orbitals have symmetries a_g and b_u while the π orbitals have symmetries a_u and b_g. In C_{2v} these correspond to a_1 and b_2 for σ, and b_1 and a_2 for π. Note that the C_2 axis is chosen to be along x in C_{2h} but is along z in C_{2v}.

The carbon basis set was a [5s,3p] contraction[34] of the Huzinaga et al. (14s,9p) basis.[35] The hydrogen basis was a [3s] contraction[34] of the van Duijneveldt (7s) basis.[36] For all calculations additional diffuse pπ functions (exponent = 0.021) centered on each carbon were included, along with a set of dπ functions on each carbon (exponent = 0.55). This basis gave virtually identical results for

---

(18) Doering, J. P.; McDiarmid, R. *J. Chem. Phys.* **1981**, *75*, 2477.
(19) McDiarmid, R.; Doering, J. P. *Chem. Phys. Lett.* **1982**, *88*, 602.
(20) Reddish, T.; Wallbank, B.; Comer, J. *Chem. Phys.* **1986**, *108*, 159.
(21) Johnson, P. M. *J. Chem. Phys.* **1976**, *64*, 4638.
(22) Rothberg, L. J.; Gerrity, D. P.; Vaida, V. *J. Chem. Phys.* **1980**, *73*, 5508.
(23) Staley, S. W.; Moore, Jr., J. H.; Sato, Y., private communication.
(24) Chadwick, R. R.; Gerrity, D. P.; Hudson, B. S. *Chem. Phys. Lett.* **1985**, *115*, 24.
(25) Dinur, U.; Hemley, R. J.; Karplus, M. *J. Phys. Chem.* **1983**, *87*, 924.
(26) Tavan, P.; Schulten, K. *J. Chem. Phys.* **1979**, *70*, 5407.
(27) Schulten, K.; Ohmine, I.; Karplus, M. *J. Chem. Phys.* **1976**, *64*, 4422.
(28) Grimbert, D.; Segal, G.; Devaquet, A. *J. Am. Chem. Soc.* **1975**, *97*, 6629.
(29) Haugen, W.; Traetteberg, M. In *Selected Topics in Structure Chemistry*, Anderson, P.; Bastiansen, O.; Furberg, S., Eds.; Universitetsforlaget: Oslo, 1967; p 113.
(30) Feller, D.; Davidson, E. R. *Theor. Chim. Acta* **1985**, *68*, 57.
(31) (a) Lipnick, R. L.; Garbisch, Jr., E. W. *J. Am. Chem. Soc.* **1973**, *95*, 6370. (b) Durig, J. R.; Bucy, W. E.; Cole, A. R. H. *Can. J. Phys.* **1975**, *53*, 1832.
(32) (a) Squillacote, M. E.; Sheridan, R. S.; Chapman, O. L.; Anet, F. A. L. *J. Am. Chem. Soc.* **1979**, *101*, 3657. (b) Squillacote, M. E.; Semple, T. C.; Mui, P. W. *J. Am. Chem. Soc.* **1985**, *107*, 6842.
(33) Breulet, J.; Lee, T. J.; Schaefer, H. F. III *J. Am. Chem. Soc.* **1984**, *106*, 6250.
(34) Cave, R. J.; Davidson, E. R., unpublished results.
(35) Huzinaga, S.; Klobukowski, M.; Tatewaki, H. *Can. J. Chem.* **1985**, *63*, 1812.
(36) van Duijneveldt, F. B. *IBM Res. Rep.* **1971**, RJ 945.

the excitation energies to the low-lying states of ethylene as that used by McMurchie and Davidson.[37] For results E and F of Table VII an augmented basis containing all of the above functions plus an additional diffuse pπ function on each carbon (exponent = 0.009) was employed.

All SCF energies reported below were from restricted Hartree–Fock (RHF) calculations performed using the MELD series of codes from this laboratory.[38] For states of the same symmetry as the ground state, a nonorthogonal SCF technique[39] was used to obtain variationally stable SCF wave functions. The CI results were also obtained by using the MELD series of electronic structure codes. In all nonnatural orbital calculations the virtual orbitals were transformed to the K orbitals (KO) of Feller and Davidson.[40]

MCSCF wave functions were obtained by using the QUEST series of electronic structure codes.[41] MCSCF wave functions which allowed all configurations having 4 π electrons in 6 or 8 π orbitals were performed, with the remaining electrons allowed to readjust self-consistently. While energy differences will be quoted below from the results of these calculations, the main intent in performing them was to obtain improved points of departure for the CI treatments. In all CI calculations involving the MCSCF wave functions the virtual orbitals outside the active space were transformed to K orbitals.

Natural orbitals (NO's),[42] obtained from relatively small CI's on a given state, were also used to improve the orbital basis as a starting point for CI. For the ^1B_u states of the trans isomer or the $^1B_2$ states of the cis isomer, where two roots of a given symmetry were sought, use of average-natural orbitals[43] (ANO's) was found to be a particularly effective means of minimizing bias toward one of the roots in the CI. That is, use of SCF or natural orbitals appropriate to one of the two roots leads to an inherent bias toward that root in a selected CI. Use of average-natural orbitals, which are the eigenfunctions of the average of the one-particle density matrices of the states of interest, was found to eliminate this bias to a large degree. For example, in calculations on ethylene similar to those of McMurchie and Davidson,[37] it was found that their CI2 excitation energies to the lowest two $^1B_{2u}$ states could be estimated in a single CI via the use of ANO's (one CI, ANO's: 1^1B_{2u} = 7.92 eV, 2^1B_{2u} = 9.48 eV; ref 37 two CI's: 1^1B_{2u} = 7.96 eV, 2^1B_{2u} = 9.23 eV). By contrast, their calculated excitation energies were from separate calculations for each state (with a different molecular orbital basis for each state), and the second state in each CI was poorly described.

Two different CI treatments were used in the present study; they are defined below. In all cases no excitations were allowed out of the two lowest orbitals in the a_g and b_u (i.e. σ) symmetries. These orbitals were composed essentially of the carbon 1s cores.

Since our aim was primarily to obtain energy differences relative to the ground states, exactly analogous calculations were performed on the 1^1A_g and 1^1A_1 states to those on the given excited state.

Molecular properties for the complete CI wave functions were evaluated by using the MELD series of programs. Transition moments between the ground and excited states were evaluated by using CI wave functions for the ground state expanded in the orbitals of the excited state of interest. The energy estimate for the ground state obtained by using the excited-state orbitals was generally in good agreement with that obtained by using orbitals appropriate to the ground state, and it is expected that no serious error in calculating the transition moment is introduced by this approximation.

The first type of CI treatment employed was the perturbation-theory selected multireference singles and doubles CI. In general, a small set of configurations was chosen (frequently the largest contributors to the wave function from a small CI) as a zeroth-order space. The electronic Hamiltonian was diagonalized over this small set of configurations and, for a calculation seeking *m* CI roots, the first *m* zeroth-order roots were chosen. The second-order Rayleigh–Schroedinger energy contribution of all configurations outside the zeroth-order space to each zeroth-order root was then calculated (only singly and doubly excited configurations can contribute) and a subset of all the configurations having the largest second-order energy contribution was selected and treated variationally in the CI. Inclusion of the effects of the remaining configurations was made via an extrapolation procedure,[44] and estimation of the effects of unlinked clusters was performed using a perturbative expression presented previously.[44,45] These unlinked cluster effects arise from the use of a truncated CI expansion (e.g. only allowing up to double excitations from the reference configurations) and give rise to so-called "size-inconsistency".[45] Such effects can also have a differential effect on excitation energies and it was found important to consider them in the present study. It should be noted that the perturbative expression only attempts to correct the energy of the given state and does not alter the coefficients of the configurations in the CI expansion. Thus, any effects of unlinked clusters on the spatial extents of the wave functions or the calculated transition moments are neglected in this approximation. Concerning the extrapolation procedure, we believe it is generally good to within 10% of the extrapolated energy increment, so that the uncertainties in the energies presented here are usually around 0.5 eV. While energy differences of the actual extrapolated energies are presented in the text, it is well to remember that their accuracy is dependent on a cancellation of any errors in the energy extrapolations for the two states. In the event that the reference space consists of a single configuration, that of the Hartree–Fock wave function, the CI is termed a Hartree–Fock singles and doubles CI (HFSDCI). When the reference space contains more than a single configuration the CI is termed a multireference singles and doubles CI (MRSDCI).

The second type of CI treatment used involved a priori selection of the configuration set. In these CI's, rather than attempting to correlate all σ and π electrons, attention was focused on the correlation of the π electrons, and those σ double excitations which might be expected to differentially affect the excitation energy of interest. In particular, we used two types of CI's, labeled CI1 and CI4, which can be viewed as extensions of the CI1 and CI2 treatments of ref 37. These CI's were of special use in calculations regarding the ^1B_u states, and we define them below with reference to these states.

In CI1, all single excitations from the Hartree–Fock reference function were included, along with all double excitations involving the electron in the $2a_u$ π^* orbital. In addition, all σ double excitations of the type termed "differential" (see below) were included with the π^* electron in the $2a_u$ and $3a_u$ orbitals. This CI was primarily used for the purpose of generating average natural orbitals for the CI4 calculations described below, since a comparable calculation on the ground state cannot be performed.[37]

Using the ANO's from CI1 for the two lowest ^1B_u roots, we performed CI's which we have termed CI4 calculations. The dominant configurations in the two lowest roots were the configurations having the $2a_u$ and $3a_u$ orbitals singly occupied, the remaining occupations being those of the ground state. All single excitations (σ and π) and all double excitations involving at least one of the π electrons from either dominant configuration were included in the CI. In addition, approximate inclusion of dif-

---

[37] McMurchie, L. E.; Davidson, E. R. *J. Chem. Phys.* **1977**, *66*, 2959.

[38] The MELD series of electronic structure codes was developed by L. E. McMurchie, S. T. Elbert, S. R. Langhoff, and E. R. Davidson, and was extensively modified by D. Feller and D. C. Rawlings.

[39] Davidson, E. R.; Stenkamp, L. Z. *Int. J. Quantum Chem. Symp.* **1976**, *10*, 21.

[40] Feller, D.; Davidson, E. R. *J. Chem. Phys.* **1981**, *74*, 3977.

[41] The MCSCF wave functions were obtained by using the QUEST-164 series of electronic structure codes, developed at Argonne National Laboratories under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy, under contract W-31-109-ENG-38.

[42] Davidson, E. R. *Rev. Mod. Phys.* **1972**, *44*, 451.

[43] Bender, C. F.; Schaefer, H. F. III *J. Chem. Phys.* **1971**, *55*, 4798.

[44] Rawlings, D. C.; Davidson, E. R.; Gouterman, M. *Int. J. Quantum Chem.* **1984**, *26*, 251.

[45] Davidson, E. R.; Silver, D. W. *Chem. Phys. Lett.* **1977**, *53*, 403.

TABLE I: CI4 Comparisons for the 1^1A_g State of *trans*-1,3-Butadiene

CI4 type[a]	MO	energy, hartree
complete	1^1A_g SCF/KO	−155.124 99
complete	^1B_u CI1 ANO	−155.121 59
1	1^1A_g SCF/KO	−155.121 64
2	1^1A_g SCF/KO	−155.120 55
3	1^1A_g SCF/KO	−155.117 95
3	^1B_u CI1 ANO	−155.113 04
4	1^1A_g SCF/KO	−155.098 29

[a] See description in text for definitions of CI4 types.

TABLE II: SCF and MCSCF Results for *cis*-1,3-Butadiene

	state	energy, hartree	ΔE, eV
SCF	1^1A_1	−154.9036	
	1^1B_2	−154.6990	5.57
MCSCF[a]	1^1A_1	−154.9705	
	2^1A_1	−154.7461	6.11

[a] Energies reported are from four-electron/–eight-π orbital MCSCF wave functions.

ferential $\sigma\sigma'$ correlation was made by using the following scheme. In the terminology of Sinanoglu,[46] valence-Rydberg mixing can be affected by "internal" or "semiinternal" correlation effects. These effects can arise because σ electrons can make use of valencelike π orbitals for correlation, and the availability of these π orbitals will change depending on whether the state is of valence or Rydberg character. Thus, in addition to those configurations discussed above, all configurations having up to double excitations from the σ space of the two dominant configurations (i.e. $2a_u$ or $3a_u$ singly occupied) into the $2a_u$, $3a_u$, and $1b_g$ π orbitals were included. This entire set of configurations was treated variationally and is termed a "complete" CI4 calculation.

Even for butadiene such CI's can rapidly become quite large, and as a result we tested a variety of smaller versions of the above scheme which involved restrictions on the orbital space in the following ways:

(1) Removal of the four highest K orbitals (or 4 NO's with the lowest occupation numbers) in the a_g and b_u (i.e. σ) symmetries, leaving a total of 27 orbitals in each σ symmetry.

(2) A calculation with the same orbital space as (1), but not allowing any $\pi\pi' \rightarrow \sigma^*\sigma'^*$ excitations.

(3) A calculation similar to (2), but further restricting the σ orbital space to 21 a_g and 18 b_u orbitals.

(4) A calculation similar to (2) but restricting the σ orbital space to 14 a_g and 12 b_u orbitals.

The relative accuracies of these truncation schemes for the estimation of excitation energies will be examined, and all will be shown to give similar results for the state splittings and spatial extents of the various states. In Table I these truncation schemes are compared for calculations on the ground state of *trans*-1,3-butadiene, using both the 1^1A_g SCF/KO and the ^1B_u ANO bases. The results indicate that for CI's of this type the truncation schemes 1–3 are in nearly quantitative agreement with the "complete" CI4 calculations, the energy difference between a "complete" calculation and one using truncation scheme 3 being approximately 0.2 eV.

Estimation of the effects of unlinked clusters on the CI4 results was made for the ^1B_u and $^1B_2$ states (and also the 1^1A_g and 1^1A_1 used in the calculation of the ^1B_u and $^1B_2$ excitation energies) using the perturbative expression mentioned above.[45] These results are designated CI4+Q in the text, since the largest unlinked terms generally come about due to the neglect of quadruple excitations in the CI treatment. Where both CI4 and CI4+Q results are being referred to the symbol CI4(+Q) will be used.

In the cases of the 2^1A_g state of the trans isomer (and the 2^1A_1 state of the cis isomer), MCSCF wave functions reveal true multiconfigurational zeroth-order wave functions, having variable occupancies of the two lowest a_u and b_g π-like orbitals. Choice of any one or two configurations on which to base a CI4 configuration would clearly lead to biased results, but a complete CI4 calculation, based on a reference space containing all ways of placing four electrons in four π orbitals is too large for us to perform. Thus, to perform a modified CI4 in these cases, we allowed a reference set consisting of the full four-electron/four-π orbital set, but restricted the σ orbital space to 14 a_g and 12 b_u orbitals. The differential σ excitations allowed were all $\sigma\sigma'$ single and double excitations into the two lowest orbitals of a_u and b_g symmetries for each reference configuration, and no $\pi\pi' \rightarrow \sigma^*\sigma'^*$ excitations were allowed. An unlinked cluster correction was not made for the CI4 results on the 2^1A_g and 2^1A_1 states (nor for the associated 1^1A_g 1^1A_1 calculations) since many of the important quadrupole excitations were already included in the reference space.

III. Results

We present the results for the cis and trans isomers separately.

(*a*) *cis-1,3-Butadiene.* (*1*) *SCF and MCSCF.* Results from SCF and MCSCF calculations on some low-lying states of the cis isomer are shown in Table II. The SCF orbital occupation for the 1^1A_1 state was: in a_1 symmetry, seven doubly occupied orbitals; in b_2 symmetry, six doubly occupied orbitals; and in symmetries a_2 and b_1, one doubly occupied orbital each. For the SCF calculation on the $^1B_2$ state, one electron was moved from the $1a_2$ orbital to the $2b_1$ orbital, relative to the ground-state occupation. No meaningful SCF calculations can be performed for the 2^1A_1 state. Instead, results from four-electron/eight-π orbital CASSCF calculations for the 1^1A_1 and the 2^1A_1 states are given in Table I. The excitation energies based on the corresponding calculations on the ground state are 5.57 eV to the 1^1B_2 state and 6.11 eV to the 2^1A_1 state.

(*2*) *Perturbation-Theory-Selected MRSDCI.* In Table III, results are shown for a variety of perturbation-theory-selected CI's on the cis isomer. Along with the extrapolated CI energies are shown the type of molecular orbitals used as an orbital basis, the number of spin-adapted configurations treated variationally, the number of reference configurations in the zeroth-order space, the percentage of the second-order perturbation-theory energy retained by keeping the given subset of configurations, and the value of $\langle x^2 \rangle$ for the CI wave function. This last value is the quantity most indicative of the Rydberg or valence character of the wave functions.

The Hartree–Fock SDCI results for the 1^1A_1 and 1^1B_2 states yield an excitation energy of 5.62 eV, in good agreement with the experimental estimate of this value, which is around 5.5 eV.[32] It should be noted that the spatial extent of the 1^1B_2 state is considerably larger than that of the ground state, but nevertheless is significantly less diffuse than a pure Rydberg state, as will be shown below.

To determine an estimate of the excitation energy to the 2^1B_2 state, average NO's were obtained for the two lowest $^1B_2$ roots from a modest CI. The ANO's of Table III were obtained from a MRSDCI consisting of an 11 reference-configuration zeroth-order space (all configurations of the form (σ core) $1b^2_1$ $1a^1_2$ nb^1_1, $n = 2$–12); perturbation-theory configuration-selection was performed using the two lowest zeroth-order roots and approximately 37 000 spin-adapted configurations were treated variationally. The agreement between the lowest root of the two-root calculation and that from the one-root HFSDCI is excellent. The second root is significantly larger in spatial extent and is a true Rydberg state. We know of no experimental estimates of the energy of this Rydberg state.

For the MRSDCI calculations on the 2^1A_1 state the orbital basis was that from the four-electron/eight-orbital MCSCF. The spatial extent of the 2^1A_1 state is essentially identical with that of the ground state, indicating that this state is a pure valencelike state. It is also a true multiconfigurational state, as is shown in Table IV, where the contributions of the first six configurations in the MRSDCI are shown and compared to those of the ground state.

---

(46) Sinanoglu, O. In *Chemical Spectroscopy and Photochemistry in the Vacuum Ultraviolet*, Sandorfy, C., Ausloos, P. J., Robin, H. B., Eds.; Reidel: Boston, 1974; p 337.

TABLE III: Perturbation Theory Selected CI Results for *cis*-1,3-Butadiene

state	MO[a]	no. of ref	% PTK[b]	no. of confs[c]	energy, hartree	ΔE, eV	$\langle x^2 \rangle$
1^1A_1	HF/KO	1	98.1	20106	−155.3915		22.59
2^1A_1	MCSCF/KO	8	86.6	79371	−155.1806	5.74	22.38
1^1B_2	HF/KO	1	97.8	50604	−155.1851	5.62	32.28
1^1B_2	ANO	5	92.6	50284	−155.1876	5.55	30.20
1^1B_2	ANO	5	92.8	50284	−155.1336	7.02	61.65

[a] Molecular orbital basis set used in the given CI. [b] Percentage of the second-order RS perturbation theory estimate retained for the given number of configurations. [c] Number of spin-adapted configurations treated variationally.

TABLE IV: CI Contributions[a,b] for the 1^1A_1 and 2^1A_1 States of *cis*-1,3-Butadiene

1^1A_1		2^1A_1	
configuration	contribution	configuration	contribution
$1b^2_1 1a^2_2$	0.8662	$1b^2_1 2b^2_1$	0.3473
$1b^1_1 2b^1_1 1a^1_2 2a^1_2$	0.0078	$1b^2_1 1a^2_2$	0.1847
$1b^2_1 2b^2_1$	0.0052	$1b^1_1 2b^1_1 1a^1_2 2a^1_2$	0.1761
$2b^2_1 1a^2_2$	0.0022	$1b^1_1 2b^1_1 1a^2_2$	0.1224
$1b^2_1 2a^2_2$	0.0018	$1b^2_1 1a^1_2 2a^1_2$	0.0347
$1a^2_2 2a^2_2$	0.0014	$2b^2_1 1a^2_2$	0.0098

[a] The orbitals used for the 2^1A_1 state are the MCSCF/KO MO's. The MCSCF orbitals are the NO's from the MCSCF calculation. For the 1^1A_1 state the orbitals used are the HF/KO MO's. For comparison, the overlaps of the various orbitals are $\langle 1^1A_1, 1b_1|2^1A_1 1b_1\rangle = 0.8290$, $\langle 1^1A_1, 1b_1|2^1A_1 2b_1\rangle = 0.5573$, $\langle 1^1A_1, 2b_1|2^1A_1 1b_1\rangle = 0.5054$, $\langle 1^1A_1, 2b_1|2^1A_1 2b_1\rangle = -0.7572$, $\langle 1^1A_1, 1a_2|2^1A_1 1a_2\rangle = 0.9488$, $\langle 1^1A_1, 1a_2|2^1A_1 2a_2\rangle = 0.3081$, $\langle 1^1A_1, 2a_2|2^1A_1 1a_2\rangle = -0.2966$, $\langle 1^1A_1, 2a_2|2^1A_1 2a_2\rangle = 0.8856$. [b] Contributions are the squares of the CI coefficients for the given configurations. For space-orbital products having more than a single spin coupling the contribution is the sum of the squares of the coefficients for each spin coupling.

Note that the orbital basis used in each case is the one appropriate to the given state. The only nonzero transition moment connecting the ground state and the 2^1A_1 state is $\langle z \rangle$ and is 0.1325 au, giving an oscillator strength of 0.00247.

(*3*) *CI's Having a Priori Selection of Configurations.* A CI1 calculation on the two lowest $^1B_2$ roots gave an energy separation between the roots of 2.09 eV, $\langle x^2 \rangle = 25.68$ au for the 1^1B_2, and $\langle x^2 \rangle = 56.72$ au for the 2^1B_2 state. Using the ANO's from this calculation for the $^1B_2$ states, and the SCF orbitals for the 1^1A_1 state, we performed two different CI4(+Q) calculations. The results are summarized in Table V. The insensitivity of the calculated excitation energies to the truncation scheme used should be noted. The CI4+Q results yield excitation energies approximately 0.15 eV lower than the CI4 results. For both the CI4 and CI4+Q results the excitation energies are in excellent agreement with those from the MRSDCI calculations. The calculated values of $\langle x^2 \rangle$ are somewhat smaller than the MRSDCI values but still present the same basic description of the two lowest $^1B_2$ states.

Finally, a CI4 calculation was performed on the 1^1A_1 and 2^1A_1 states as described above, using the MCSCF/KO basis of the 2^1A_1 state. The errors induced by not using the MCSCF/KO basis for the ground state will be shown below to be on the order of 0.16 eV for an analogous calculation for the trans isomer. The excitation energy obtained, 6.13 eV is in reasonable agreement with the MRSDCI value, and in excellent agreement with that from the MCSCF.

(*b*) *trans-1,3-Butadiene.* (*1*) *SCF and MCSCF Results.* Hartree–Fock energies for the 1^1A_g, 2^1A_g, and 1^1B_u states are shown in Table VI. The orbital occupation for the 1^1A_g state was: in the a_g symmetry, seven doubly occupied orbitals; in the b_u symmetry, six doubly occupied orbitals; and one doubly occupied orbital in each of the a_u and b_g symmetries. For the 1^1B_u state, the a_g and b_u symmetry occupations were those of the ground state, and the π occupation was $1a^2_u\ 1b^1_g\ 2a^1_u$. For the 2^1A_g state a nonorthogonal SCF was used; the a_g and b_u occupations were those of the ground state and the π occupation was $1a^2_u\ 1b^1_g\ 2b^1_g$. The overlap of the nonorthogonal orbitals for the 2^1A_g state was 0.01733. At the SCF level, both excited states are completely Rydberg-like, having excitation energies of 6.14 and 6.73 eV for the 1^1B_u and 2^1A_g states, respectively.

Results from four-electron/six-π orbital MCSCF's are also shown in Table VI. Of particular interest is the 2^1A_g state, which, while its excitation energy is virtually unchanged from that of the SCF value, has completely changed in character from a Rydberg-like state to a multiconfigurational valencelike state. The 1^1B_u state remains Rydberg-like and the MCSCF expansion is dominated by a single term. Increasing to a four-electron/eight-π orbital MCSCF wave function does not change the description of the 1^1B_u state.

(*2*) *Perturbation-Theory-Selected MRSDCI.* In Table VII, a variety of CI's are shown concerning the four states of interest. The orbital basis set used for the 2^1A_g state was from the MCSCF calculation described above. The fraction of the perturbation-theory energy kept, 77.0%, is somewhat lower than would be desired. In this regard, the uncertainty in the energy estimate for this state is larger than for the other calculations presented. We comment further on this in the discussion. The value of $\langle x^2 \rangle$ indicates a valencelike state.

For the ^1B_u states, a number of different orbital basis sets were used. In Table VII, the results labeled A used the orbitals from the four-electron/eight-π orbital MCSCF. For calculation B, the natural orbitals from the second root of a calculation similar to A were used. These NO's were valencelike. In calculation B two zeroth-order roots were used for perturbation-theory selection and two CI roots were sought. In C, the average NO's used were obtained from an eleven-reference-configuration MRSDCI (the eleven reference configurations being all those of the type (σ core) $1a^2_u\ 1b^1_g\ na^1_u$, with n from 2 to 12) and in D–F, the average NO's from a CI1 calculation were used.

Comparison of calculations A and B shows that, while the spatial extent of the wave function is altered dramatically by the

TABLE V: CI4(+Q) Results for *cis*-1,3-Butadiene

CI4 type[a]	state	MO	CI4 energy, hartree	CI4 ΔE, eV	CI4+Q energy, hartree	CI4+Q ΔE, eV	$\langle x^2 \rangle$
2	1^1A_1	HF/KO	−155.1103		−155.1384		22.24
2	1^1B_2	CI1/ANO	−154.9035	5.63	−154.9365	5.49	25.97
2	2^1B_2	CI1 ANO	−154.8510	7.06	−154.8805	7.02	56.93
3	1^1A_1	HF/KO	−155.1079		−155.1351		22.20
3	1^1B_2	CI1 ANO	−154.9003	5.65	−154.9331	5.50	26.00
3	2^1B_2	CI1 ANO	−154.8478	7.08	−154.8770	7.02	56.95
	1^1A_1	2^1A_1 MCSCF/KO	−155.1045				21.95
	2^1A_1	2^1A_1 MCSCF/KO	−154.8794	6.13			22.34

[a] See Calculational Methods section for a description of the CI4 types.

TABLE VI: SCF and MCSCF[a] Results for *trans*-1,3-Butadiene

	state	energy, hartree	ΔE, eV
SCF	1^1A_g	−154.91667	
SCF	1^1B_u	−154.69089	6.14
SCF	2^1A_g	−154.66949	6.73
MCSCF	1^1A_g	−154.97693	
MCSCF	1^1B_u	−154.73023	6.71
MCSCF	2^1A_g	−154.73152	6.68

[a] The energies reported for the MCSCF wave functions are obtained from a four-electron/six-π orbital CASSCF.

change in orbital basis, the excitation energy is only marginally affected. The value of 6.42 eV for the excitation energy from calculation A is lower than any previous ab initio estimate for the 1^1B_u state obtained to date. It is, however, approximately 0.5 eV higher than the experimental value[9–20] and is significantly more Rydberg-like than the 1^1B_u state is believed to be on the basis of experiment. In calculation B, the lowest root of the CI is most similar to the second root of the zeroth-order space (which was obtained by diagonalizing the Hamiltonian over the zeroth-order space), while the second CI root is most like the lowest zeroth-order root. This "root flip" is brought about due to a bias toward the valencelike root by use of the valencelike NO's. The extrapolated energy of the second root of the CI for calculation B (not shown) gives an excitation energy of 4.89 eV. This is clearly in error and is caused by a combination of use of an inappropriate orbital basis (for this root) and a somewhat low fraction of the second-order perturbation-theory energy kept (75.6%).

In calculation C, a somewhat more even-handed description of the two states is obtained through the use of ANO's. For both roots essentially the same fraction of the second-order energy is recovered. It is seen that both states are essentially Rydberg-like, the lower of the two is still 0.5 eV higher than the experimental estimate of the vertical transition energy.

In calculation D the two lowest roots are again found to have similar (large) spatial extents, but the excitation energies to the two lowest ^1B_u states have dropped considerably, in part due to the use of the CI1 ANO's. In this case, when the eigenvalues of the Hamiltonian over the zeroth-order space were used for the perturbation-theory selection, there were significant changes in the relative values of the coefficients of the reference space in proceeding from the zeroth-order wave functions to the actual CI expansion. Both the perturbation-theory energy estimate and the extrapolation are most accurate when this change is small, so an iterative scheme for defining the zeroth-order wave function was used in calculation D (as well as calculations E and F). Initially, the zeroth-order wave functions used were those obtained from diagonalizing the Hamiltonian over the reference space and from these roots a modest MRSDCI was performed. In the next step, the coefficients of the zeroth-order wave functions were taken as their (renormalized) values obtained from the CI expansion, the zeroth-order energies being the expectation values of the Hamiltonian with each zeroth-order function. This procedure was iterated until convergence was reached. With these zeroth-order wave functions a large CI was performed on the lowest two roots. The results from this procedure are those labeled D in Table VII. The character of each ^1B_u state obtained by using this basis was found to be intermediate between pure valence and pure Rydberg states. The calculated oscillator strengths to the 1^1B_u and 2^1B_u states were 0.457 and 0.487, respectively.

Results E and F of Table VII are the only calculations in the present work to use the augmented basis set mentioned in section II. The aim of calculations E and F was to examine the sensitivity of the state descriptions to increased flexibility in the diffuse portion of the basis. The excitation energies reported in Table VII for results E and F are relative to a calculation on the ground state in the augmented basis, which yielded an energy of −155.4027 au. The ANO's for these two calculations were obtained from a CI1 calculation on the three lowest roots of ^1B_u symmetry for the trans isomer. The results labeled E are from a calculation similar to result D. The oscillator strengths for transitions from the 1^1A_g to the 1^1B_u state and the 2^1B_u state are 0.508 and 0.413, respectively. The results labeled F are from a calculation analogous to D and E, but seeking three roots of ^1B_u symmetry rather than two. It should be noted that complete convergence in the coefficients of the zeroth-order wave functions for roots two and three was not obtained for calculation F. Therefore, the excitation energies presented are subject to somewhat greater uncertainties in the energy extrapolation than results D or E. The oscillator strengths for transitions from the 1^1A_g to the 1^1B_u, 2^1B_u, and 3^1B_u states are 0.348, 0.573, and 0.0166, respectively.

(3) CI's Using a Priori Selection of Configurations. A CI1 calculation on the two lowest roots of ^1B_u symmetry, beginning from the SCF wave function, gave an energy separation of 1.36 eV between the 1^1B_u and 2^1B_u states, and values of $\langle x^2 \rangle$ of 26.66 and 54.55 au, respectively. This result differs radically from the MRSDCI results on the ^1B_u states, in that it clearly obtains a valence-like state as the lowest CI root of ^1B_u symmetry.

To further examine the ^1B_u states, truncated CI4(+Q) calculations were performed. The results of CI4(+Q) calculations 2–4 (see the Calculational Methods section for definitions of these truncation schemes) are shown in Table VIII. All CI4 calculations yield essentially the same prediction: that the lowest state of ^1B_u symmetry is best described as somewhere between a valence and a Rydberg state, that it is 6.4–6.5 eV above the ground state, that the second state of ^1B_u symmetry is 0.8–0.9 eV above the 1^1B_u, and is a Rydberg state. However, inclusion of the correction for unlinked terms (CI4+Q results) significantly lowers the excitation energies for both ^1B_u states. Comparing these results with the CI4(+Q) results for the cis isomer shows that the 1^1B_u state is somewhat more diffuse than the 1^1B_2 state.

The results in Table VIII for the 2^1A_g state yield a valencelike state at 6.77 eV above the ground state. Use of the 2^1A_g MCSCF/KO to describe the ground state leads to an excitation

TABLE VII: Perturbation Theory Selected CI Results for *trans*-1,3-Butadiene

CI type[a]	state	MO[b]	no. of ref	% PTK[c]	no. of confs[d]	energy, hartree	ΔE, eV	$\langle x^2 \rangle$
	1^1A_g	HF/KO	6	92.4	15472	−155.4025		
	2^1A_g	MCSCF/KO	13	77.0	62706	−155.1732	6.24	23.28
A	1^1B_u	MCSCF/KO	6	90.9	39387	−155.1665	6.42	52.46
B	1^1B_u	VAL NO	8	88.6	54181	−155.1583	6.65	28.65
C	1^1B_u	ANO	5	92.9	55858	−155.1640	6.49	49.25
	2^1B_u	ANO	5	92.4	55858	−155.1271	7.50	46.93
D	1^1B_u	ANO	9	86.7	58171	−155.1744	6.21	41.34
	2^1B_u	ANO	9	87.5	58171	−155.1449	7.01	40.52
E[e]	1^1B_u	ANO	9	88.6	70374	−155.1761	6.17	40.76
	2^1B_u	ANO	9	88.6	70374	−155.1452	7.01	51.26
F[e]	1^1B_u	ANO	10	84.9	83265	−155.1793	6.08	55.95
	2^1B_u	ANO	10	85.6	83265	−155.1542	6.76	56.27
	3^1B_u	ANO	10	86.0	83265	−155.1220	7.64	90.73

[a] See Calculational Methods section for a description of the type of CI4 calculation performed. [b] Molecular orbital basis set used in the given CI. [c] Percentage of the second-order RS perturbation theory estimate retained for the given number of configurations. [d] Number of spin-adapted configurations treated variationally. [e] See the Results section for a description of these calculations.

TABLE VIII: CI4(+Q) Results for *trans*-1,3-Butadiene

CI4 type[a]	state	MO	CI4 energy, hartree	CI4 ΔE, eV	CI4+Q energy, hartree	CI4+Q ΔE, eV	$\langle x^2 \rangle$
2	1^1A_g	HF/KO	−155.1205		−155.1468		22.12
2	1^1B_u	CI1 ANO	−154.8842	6.43	−154.9179	6.23	32.67
2	2^1B_u	CI1 ANO	−154.8519	7.31	−154.8836	7.16	48.87
3	1^1A_g	HF/KO	−155.1179		−155.1432		22.08
3	1^1B_u	CI1 ANO	−154.8801	6.47	−154.9137	6.25	32.69
3	2^1B_u	CI1 ANO	−154.8478	7.35	−154.8792	7.18	48.91
4	1^1A_g	HF/KO	−155.0983				21.98
4	1^1B_u	CI1 ANO	−154.8592	6.51			33.37
4	2^1B_u	CI1 ANO	−154.8294	7.32			48.58
	1^1A_g	1^1A_g HF/KO	−155.1154				21.93
	1^1A_g	2^1A_g MCSCF/KO	−155.1097				21.82
	2^1A_g	2^1A_g MCSCF/KO	−154.8667	6.77[b]			23.50

[a] See the Calculational Methods section for descriptions of the CI4(+Q) types. [b] Relative to the 1^1A_g result obtained by using the 1^1A_g HF/KO molecular orbitals.

TABLE IX: Modified CI4 Results[a] for *trans*-1,3-Butadiene

state	MO	energy, hartree	ΔE, eV	$\langle x^2 \rangle$
1^1A_g	HF/KO	−155.2328		22.09
1^1A_g	CI1 ANO	−155.1762		
1^1B_u	CI1 ANO	−154.9376	6.49[b]	37.11
2^1B_u	CI1 ANO	−154.9052	7.37[b]	44.82

[a] See the Results section for a description of the CI performed. [b] ΔE relative to the 1^1A_g calculation using the ^1B_u ANO's, see text.

energy of 6.61 eV, or an error of 0.16 eV.

The results presented in Table IX are from calculations which attempt to explore the effects of $\sigma\sigma'$ excitations on the description of the ^1B_u states. In these CI's, all configurations contained in CI4 number 4 from Table VIII are included (i.e. no $\pi\pi' \rightarrow \sigma^*\sigma'^*$ excitations, 14 a_g and 12 b_u σ orbitals), along with all $\sigma\sigma' \rightarrow \sigma^*\sigma'^*$ excitations within the 14 a_g, 12 b_u orbital σ space. The excitation energies obtained were similar to the CI4 results of Table IX, but the character of the lowest ^1B_u state changed markedly, becoming significantly more diffuse. The results in Table IX are complicated, however, by the fact that the average NO's were calculated from a CI1 calculation, where no $\sigma\sigma'$ excitations into the σ virtuals were allowed. Thus, there is no reason to expect that when the σ virtual space is truncated the orbitals kept will necessarily be effective in correlating the σ electrons. This is the main cause of the disparity between the two 1^1A_g results in Table IX, where the HF/KO MO's are significantly more effective for σ correlation. In other calculations (see Table I) where both ^1B_u average NO's and the ^1A_g SCF orbitals are used for the same state the disparity is not nearly so great. Nevertheless, even if one restricts attention to the ^1B_u states, these calculations indicate that neglect of $\sigma\sigma'$ correlation can alter the description of the ^1B_u states.

IV. Discussion

The results presented above for the low-lying states of the cis isomer illustrate an important point regarding the calculational methods used. For the cis isomer, the MRSDCI results and the a priori selected CI results are in virtually exact agreement for the calculated excitation energies, with or without inclusion of the unlinked cluster correction in the CI4(+Q) results. Each technique neglects a portion of the CI scheme included in the other; the MRSDCI selects configurations based on their second-order perturbation-theory energy lowering, and therefore neglects some of the $\pi\pi'$ and $\pi\sigma$ correlation explicitly included in the CI4(+Q) calculations, whereas the CI4(+Q) calculation completely neglects any $\sigma\sigma'$ correlation, other than that termed differential (see above). Two possibilities exist. Either that which is neglected by each technique is not important to the calculation of the excitation energy (nor can it be of qualitative importance to the spatial description of the state), or the portions neglected by each method lead to the same gross error in state descriptions and excitation energies. While the second alternative is possible, it seems highly unlikely, and it is more likely that the two descriptions agree because they both contain the essential physics of the states examined.

Comparing the spatial extents of the MRSDCI and CI4(+Q) wave functions for the 1^1B_2 states it is seen that the MRSDCI results tend to yield somewhat larger values of $\langle x^2 \rangle$. The difference is on the order of 4 au^2. Possible reasons for this are discussed below in conjunction with similar results for the trans isomer.

The agreement between the experimental estimate of the 1^1B_2 state excitation energy and that obtained here also lends support to the accuracy of the methods. Again, this agreement could be fortuitous, but the agreement of the two quite different CI methods suggests that the results are most likely not artifacts.

Thus, regarding the description of the 1^1B_2 state, the present calculations suggest that it is of the "classical" $\pi \rightarrow \pi^*$ type, with the exception that the π^* orbital is somewhat more diffuse than, for instance, the 1^3B_2 π^* orbital. However, it is nowhere near as large as a true Rydberg orbital. The results indicate that the transition to the 1^1B_2 state should be strongly allowed and much more intense than the transition to the 2^1B_2 state, based on the spatial extents of the wave functions obtained here. The results also locate the 2^1A_1 state above the 1^1B_2 state, by anywhere from 0.2 to 0.6 eV, probably 0.4 eV above (i.e. a transition energy of 6.0 eV) is a reasonable compromise. The transition is expected to be quite weak, due to the predominantly doubly excited nature of this state, and will be virtually impossible to observe in the presence of the trans isomer. We believe the accuracy of the methods is sufficient to be able to discern the energy difference between the 1^1B_2 and 2^1A_1 states and therefore feel reasonably certain that the lowest excited singlet state of the cis isomer is, in fact, the 1^1B_2. Differences between our results and previous theoretical studies[5,28] can be attributed to our larger basis set and inclusion of important σ correlation effects.

Turning to the trans isomer, we first consider the CI results for the ^1B_u states. The MRSDCI results of Table VII indicate the sensitivity of the CI wave function to the MO basis set used. Results A and B give similar estimates of the excitation energy to the 1^1B_u state but yield vastly different values of $\langle x^2 \rangle$, indicating a qualitative difference between the two results. This sensitivity arises from a number of factors, among which are the nearness of the two lowest ^1B_u roots and the inherent bias of the CI result toward the root which is better described by the chosen MO basis.

A less biased description can be obtained by use of ANO's, as is demonstrated by results C-F in Table VII. It is seen that the percentage of the second-order perturbation-theory energy-lowering is nearly identical for the two roots in these cases, as is the coefficient of the zeroth-order root in the final CI (not shown). The main difference between result C and results D-F is in the character of the states obtained from the modest CI's used to calculate the ANO's. In C, the two zeroth-order roots in the small CI were both Rydberg-like and as a result the two lowest CI roots tended to be Rydberg-like as well. In D-F the CI1 calculations used to obtain the ANO's produced a lowest valence-like root and the ANO's had greater flexibility in the description of the wave function when a limited CI was performed. Result D places the energy of the 1^1B_u states at 6.2 eV above the ground state, or 0.3 eV above the experimental intensity maximum. However, the feature assigned to the 1^1B_u state experimentally is composed of three broad peaks, one at approximately 6.1 eV, quite close to the result of calculation D. The oscillator strength for the transition to the lowest ^1B_u state from calculation D is in reasonable agreement with the experimental estimate,[1a] although the value for the 2^1B_u state is far too large, independent of whether the 6.67- or 7.07-eV transition (or any other transition in this region) is assigned to the 2^1B_u transition.

Result E of Table VII, obtained by using an augmented basis set, addresses the question of whether the description of the 2^1B_u state obtained in D is an artifact by adding extra flexibility to the Rydberg portion of the basis. It is seen that, while the results for the 1^1B_u state are quite similar to those of calculation D, the 2^1B_u state is far more diffuse and the oscillator strength has dropped somewhat. The effect of extra diffuse functions on the character of a Rydberg state when a low-lying mixed valence-Rydberg state exists has been discussed previously in the case of ethylene.[47] However, the oscillator strength for the 2^1B_u is still larger than expected based on a comparison of the experimental intensities for the 1^1B_u state and the Rydberg transitions at 6.67 or 7.07 eV. While additional Rydberg functions might alter the results further, neither the qualitative descriptions of the two lowest ^1B_u states nor the excitation energies are expected to change significantly from result E for a calculation of this type.

Comparison of results E and F of Table VII indicates some of the dangers which can occur when (by necessity) a truncated configuration set with an essentially fixed number of configurations is used in the performance of a CI. In proceeding from E to F it is seen that by seeking a third root, the qualitative nature of the lowest root is changed. It is possible that this is an error in result F arising from the selection of more configurations appropriate to the correlation of Rydberg-like states in the MRSDCI treatment (since configurations are selected on the basis of their energy contribution to any root and, at least at the CI1 level, two of the roots are Rydberg-like). Alternatively, it may be that result E is in error, precisely because an insufficient number of configurations which correlate the Rydberg-like states was included. At present this must be considered an open question, one for which further work is mandated. Given that result E yields better agreement with the supposed qualitative state descriptions, we feel it is the most accurate MRSDCI result. Thus, our best MRSDCI results predict the 1^1B_u state to have an excitation energy of approximately 6.2 eV, to be of mixed valence-Rydberg character, with $\langle x^2\rangle = 40.76$ and the oscillator strength to be 0.508. The 2^1B_u is predicted to occur at 7.01 eV, being more Rydberg-like than the 1^1B_u state, ($\langle x^2\rangle = 51.26$) and having oscillator strength in a transition from the ground state of 0.413. The calculated value of the oscillator strength is too high for a true Rydberg state and is significantly higher than any observed transitions in this region of the spectrum. This is most likely an error in the present results, wherein too much valence-like character is being incorporated into the 2^1B_u state. However, given the insensitivity of the calculated excitation energies for results A–C in Table VII to the spatial extent of the ^1B_u state obtained, we still feel that the present excitation energy is reasonably accurate. Thus, as an assignment of the 2^1B_u state, our results indicate that at least a portion of the intensity observed at 7.07 eV in the experimental spectrum is due to the 2^1B_u state, which has significant $1^1A_g \rightarrow {}^1B_u\ (3p_x)$ character.

Considering the CI4(+Q) calculations on the ^1B_u states, the results in Table VIII are unique in that for the first time ab initio calculations have produced a lowest state of ^1B_u symmetry which is basically valencelike in character. While this result may be viewed as a triumph, it remains ambiguous in relation to the experimental results on the lowest ^1B_u state. In comparison with experiment it is seen that the calculated CI4+Q excitation energy (~6.25 eV) is still 0.3 eV higher than the experimental intensity maximum for this state. (The CI4 results, due to the inclusion of unlinked terms in the CI expansion, are even farther from the experimental values, the difference from experiment being 0.55 eV.) The agreement between the CI4+Q excitation energies to the two lowest ^1B_u states and the MRSDCI results labeled D in Table VII (which use the same basis as the CI4+Q results) is quite encouraging and lends support to the present estimates. However, the lowest ^1B_u state in the CI4(+Q) results is significantly less diffuse than any of the MRSDCI calculations which treat the two lowest states on an equal basis (CI's C, D, E, and F in Table VII). This last fact need not negate the CI4+Q result, but in the event that two methods yield results in disagreement it is not obvious which is the more accurate, especially when neither is in exact agreement with the experimental value for the transition energy.

Thus, while the two CI methods yield similar results for the excitation energies to the two lowest ^1B_u states, the spatial extents obtained are somewhat different. This difference in spatial extents between the two methods is similar to (but somewhat larger than) what was encountered in the case of the two lowest $^1B_2$ states of the cis isomer when comparing the MRSDCI and CI4(+Q) $\langle x^2\rangle$ values. Two possibilities present themselves as reasons for the difference in the calculated $\langle x^2\rangle$ values between the two CI methods: (1) lack of $\sigma\sigma'$ double excitations in the CI4 calculations and (2) size-consistency effects.

Concerning possible $\sigma\sigma'$ double excitation effects, the results of Table IX are of interest in comparing the CI4(+Q) results with the MRSDCI results for the ^1B_u states. It is seen that augmenting the CI4 wave functions with a specific subset of all $\sigma\sigma'$ double excitations actually increases the spatial extent of the 1^1B_u state, without seriously altering the excitation energy. While it may be argued that only a subset of the σ virtual space has been included and that those orbitals included are not optimal for $\sigma\sigma'$ correlation, the result is nevertheless suggestive of a more diffuse description of the 1^1B_u state when the σ electrons are correlated.

The theoretical results for the "V" state of ethylene also yield a mixed valence-Rydberg type of state,[37,47–49] and given the qualitative similarity between the ethylene "V" state and the 1^1B_u state it is not unreasonable to expect a somewhat diffuse 1^1B_u state for butadiene. It is interesting to note that even for ethylene the CI2 type of calculation[37] yields a less diffuse "V" state than any of the CI treatments which attempt to correlate all electrons,[47–49] a similar result to that obtained here for butadiene. Whether this increase in $\langle x^2\rangle$ upon correlating the σ space is physical or is an artifact due to the deterioration of CI treatments as the number of electrons correlated increases[49] ("size-inconsistency" arising from unlinked cluster effects on the CI coefficients) cannot be assessed at the present time and must await the refinement of size-consistent techniques for the treatment of excited states.

Regarding the 2^1A_g state of the trans isomer, we found that the qualitative description of the state is entirely analogous to that of the 2^1A_1 state of the cis isomer. The multiconfigurational zeroth-order description is again found to contain significant contributions from nominally doubly-excited configurations, as has been discussed previously.[4,7] The calculated excitation energy of 6.2 eV at the MRSDCI level (or 6.7 eV at the MCSCF level) is significantly lower than the more recent ab initio estimates[6,7] and is more in line with earlier estimates.[4,5] While it would be desirable to assign a single cause to our present lower estimate, differences in CI methodology make such comparisons difficult. However, two possible choices may be: (1) the inclusion of dπ polarization functions (which might be expected to improve the description of a highly correlated π state), and (2) the use of zeroth-order descriptions obtained from MCSCF wave functions for the states of interest. One qualitative difference between our results and those of ref 7 is our finding that inclusion of $\sigma \rightarrow \sigma'$ excitations at the CI4 level changes the $1^1A_g \rightarrow 2^1A_g$ excitation

---

(47) (a) Buenker, R. J.; Peyerimhoff, S. D. *Chem. Phys.* **1976**, *9*, 75. (b) Buenker, R. J.; Shih, S.-K.; Peyerimhoff, S. D. *Chem. Phys.* **1979**, *36*, 97.

(48) Brooks, B. R.; Schaefer, H. F. III *J. Chem. Phys.* **1978**, *68*, 4839.

(49) Sunil, K. K.; Jordan, K. D.; Shepard, R. *Chem. Phys.* **1984**, *88*, 55.

energy little relative to the MCSCF value (+0.09 eV), while similar calculations in ref 7 showed a 0.23 eV increase in the excitation energy on inclusion of $\sigma \rightarrow \sigma'$ excitations. In addition, inclusion of further σ correlation effects (via the MRSDCI's) resulted in a lowering of the excitation energy. However, we stress that the energy extrapolation used to obtain the 2^1A_g state in the MRSDCI is by far the largest in the present study, and errors in the extrapolation generally tend to artificially lower a given state's energy. While we believe the extrapolation is reasonably accurate, it may not be sufficiently so to distinguish between the MRSDCI value of 6.2 eV and the MCSCF value of 6.7 eV. Thus, the fairest estimate of the excitation energy based on the present series of calculations is that the 2^1A_g state is located in the region from 6.2 to 6.8 eV above the ground state.

In comparing the cis results for the lowest $^1B_2$ state to those for the 1^1B_u state of the trans isomer, a number of differences should be noted. First, the SCF description of the 1^1B_u state is significantly more diffuse than that of the 1^1B_2 state (results not shown). CI's based on the respective SCF MO's (e.g. result A of Table VII for the 1^1B_u state and the HF/KO result of Table III for the 1^1B_2 state) yield vastly different values of $\langle x^2 \rangle$. This description of the 1^1B_u state as more diffuse than the 1^1B_2 state persists for the CI4(+Q) results as well as the ANO-based MRSDCI's. In addition, while the 1^1B_2 state's MRSDCI energy estimate is in apparent agreement with the experimental value, the 1^1B_u MRSDCI energy estimate is above that of experiment by approximately 0.3 eV. Also, while the CI4, CI4+Q, and MRSDCI calculations yield essentially exact agreement for the excitation energies of the 1^1B_2 state, only the CI4+Q and MRSDCI results are in agreement for the 1^1B_u state. Thus, if our results are correct, they indicate a qualitative difference between the 1^1B_2 state of the cis isomer and the 1^1B_u state of the trans isomer, which might not be expected to occur from merely rotating about a single carbon–carbon bond. It is interesting to examine what effects might be responsible for these differences.

One possibility is a strong 1–4 π interaction in the cis isomer, resulting in a stabilization of the valence component of the 1^1B_2 state which is not obtained for the trans isomer. Calculations of the SCF overlap population between carbons 1 and 4 (the terminal carbons) for the 1^1B_2 state give a value of 0.842, almost entirely from π contributions, as compared with a value of –0.080 for the 1^1A_1 state. Recalculation of the overlap population removing the contribution of the most diffuse π functions on each carbon yields an overlap population of 0.309 between the end carbons in the 1^1B_2 state, which still suggests a reasonable bonding interaction. For the trans isomer, the overlap population between the terminal carbons in the 1^1B_u state (for the augmented Rydberg basis at the SCF level) is 0.202, whereas upon removal of the two most diffuse basis functions the overlap population between the terminal carbons drops to 0.084. In part, this decrease is due to the increased Rydberg content of the SCF 1^1B_u wave function relative to the 1^1B_2 state, but the reason for the increased Rydberg character may lie in the lack of favorable 1–4 interaction in the trans isomer.

Another possible difference between the cis and trans isomers, based on a valence-bond analysis, may be a change in the stability of certain ionic configurations when proceeding from the cis to the trans isomer. As has been discussed previously,[4,7] the valence bond description of the 1^1B_u state (and also the 1^1B_2 state of the cis isomer) contains large contributions from configurations which are ionic in nature, while the ground state, the lowest triplets, and the 2^1A_g (or 2^1A_1) state are predominantly composed of covalent configurations. Thus, it is possible that the geometry of the cis may preferentially stabilize one (or more) of the ionic types of configurations, relative to the Rydberg configurations near their energies. For example, consider the valence-bond structures of the form $C{=}C{-}C^-{-}C^+$ ± res and $C^-{-}C{=}C{-}C^+$ ± res, which we denote A and B, respectively, where res indicates the corresponding symmetry related resonance structure. Of these valence-bond structures, A will, to lowest order, have similar stability in the cis and trans cases, as the electrostatic interactions can be assumed similar. However, structure B may be preferentially stabilized in the cis isomer where the distance between the charged ends is greatly reduced.

Considering the calculated excitation energy for the 1^1B_u state of the trans isomer, we note that our best estimates for the excitation are above the experimental intensity maximum by 0.3 eV. Although the possibility of inherent limitations in the CI's still exists for the 1^1B_u state, the results for the cis isomer are in close enough agreement with present experimental results that other reasons for the disagreement with experiment in the trans case are worth considering. Several possibilities suggest themselves as reasons for this discrepancy.

One possibility is that the transition is nonvertical, as has been suggested previously.[5,8] Experimental evidence[13] suggests that the 1^1B_u state has lengthened C–C terminal bonds and a shortened C–C central bond, a geometry which should significantly lower the 1^1B_u state's energy. If the transition moment were a strong function of position, and if the energy of the 1^1B_u state dropped steeply enough with displacement along the distortion to the estimated experimental geometry it is possible that an effect of this type might account for the difference between experiment and theory for the ^1B_u intensity maximum. SCF results on the 1^1B_u state using an experimental estimate of the excited-state geometry[13] still yield a Rydberg-like state. Further work is underway to address this question using correlated wave functions.

A second possibility is that, as mentioned above, the 1^1B_u state may have a large component of "ionic" configurations, which are biased against by the use of symmetry restricted MO's. Hosteny et al.[4] have performed full CI calculations in the π space and still found the lowest $\pi \rightarrow \pi^*$ state to be Rydberg-like and still significantly higher in energy than the experimental value. However, these calculations used the σ space of the ground state for all excited states and, furthermore, allowed no excitations from the σ space in their CI treatments. Our calculations strongly suggest that a proper description of the ^1B_u states requires explicit inclusion of σ–π correlation effects and that, without these, the valencelike component is strongly biased against (cf. the CI4(+Q) results). When a limited CI was performed with the possibility of incorporating greater flexibility in the π space along with some $\sigma\pi$ correlation (a four-electron/eight-π orbital CI from the average NO's of the CI1 calculation, which, in addition, allowed all $\sigma \rightarrow \sigma'$ excitations from all configurations, within the 14 a_g 12 b_u σ space), the two lowest states of ^1B_u symmetry had $\langle x^2 \rangle$ values of 39.60 and 42.76 au, with excitation energies of 6.68 and 7.47 eV, respectively. Clearly, if such a calculation were to provide a resolution to the current controversy, it would need to be more extensive than the one considered here. In particular, π ionic configurations will strongly polarize the σ space, and these effects are almost completely neglected in the above CI.

A third possibility is that the excited state is of lower symmetry than C_{2h}, and that the 1^1B_u and the 2^1A_g states mix and thereby stabilize the lower of the two. It is likely that, were this the case, the interaction of the 2^1A_g with the valencelike ^1B_u state would be largest and would thus preferentially stabilize the valencelike component. This argument also necessitates a nonvertical transition and would suggest strong mode-mixing in resonance Raman spectra in the region of the 1^1B_u state. Initial studies of this kind have found minimal evidence for such mode mixing.[24] The idea of a broken symmetry excited state is consistent with the short lifetime of the 1^1B_u state,[6] which in lower symmetry could nonradiatively decay to the ground state.

It should be stressed that, while there are further avenues for investigation, any arguments concerning errors in the calculations on the trans isomer could also be levied against the calculations on the cis isomer. The calculations on the cis isomer convincingly show that the methods are capable of describing the singlet $\pi \rightarrow \pi^*$ state in question. We believe that the discrepancies encountered in this work concerning the trans isomer are indicative of a more novel description of the 1^1B_u state, and not an inherent weakness in the description of $\pi \rightarrow \pi^*$ states.

We would also comment on the predicted ordering of the 1^1B_u and 2^1A_g states for the trans isomer. The present best results, taken at face value, place the 2^1A_g state 0.2 eV above the 1^1B_u

state. One might be tempted to additively correct both states by the error in the calculated 1^1B_u excitation energy, arguing that both states are $\pi \rightarrow \pi^*$ excitations, and that similar errors should be engendered in calculations on each. This could be an incorrect procedure, since the evidence on the cis isomer suggests that errors in calculated excitation energies are not uniform for all $\pi \rightarrow \pi^*$ excitations, as do results on the low-lying triplet and other Rydberg states.[4,6-8] In comparison with the experimental estimate for the 1^1B_u, our best results place the 2^1A_g above this value by from 0.3 to 0.9 eV. The correct interpretation may not be so simple, however, if the picture of the 1^1B_u is altered by some of the factors discussed above. We believe past estimates of the 2^1A_g state at approximately 7.0 eV[6,7] are in error. It is apparent that observation of the 2^1A_g state in the region in which we predict it to lie will be extremely difficult.

V. Conclusions

Results from ab initio calculations on the low-lying valencelike states for *cis*- and *trans*-1,3-butadiene have been presented. A variety of CI methods were employed which reveal a qualitative difference between the cis and trans isomers. Our results show the cis to have a lowest-lying $^1B_2$ state at approximately 5.5–5.6 eV, in good agreement with experimental estimates for this state. The second valencelike singlet state contains significant doubly excited character relative to the ground state and is analogous to the 2^1A_g state of the trans isomer, as well as similar states found in longer polyenes. The 2^1B_2 state is predicted to lie approximately 1.4 eV higher in energy than the 1^1B_2 and is found to be a completely Rydberg-like state.

In contrast, the 1^1B_u state for the trans isomer was found to lie 0.3 eV above the experimental intensity maximum for this state, and to have significantly more Rydberg character than the corresponding state in the cis isomer. The oscillator strength for this transition is, nevertheless, in reasonable agreement with the experimental value. On the basis of our results, we estimate that the 2^1A_g state lies above the experimental intensity maximum for the 1^1B_u state by from 0.3 to 0.9 eV (i.e. from 6.2 to 6.8 eV). The results suggest that the qualitative nature of the lowest $\pi \rightarrow \pi^*$ state of 1,3-butadiene is highly sensitive to the geometry of the molecule. Further work is in progress to assess the sensitivity of the states to other geometric variations.

Finally, the results presented here indicate that ab initio CI treatments on the $\pi \rightarrow \pi^*$ excited states of such polyenes which only treat $\pi\pi'$ correlation effects will be inadequate for the description of either excitation energies or of the spatial extents of the states. We conclude from this that the relative success of semiempirical treatments in the past must result from the approximate inclusion of $\sigma\pi$ correlation via the effective Hamiltonian employed.

Acknowledgment. The authors gratefully acknowledge financial support of this research by the National Institute of Health, Grant No. 2 R01 GM34081-03. The calculations were performed at the Indiana University Chemistry Computer Facility, the establishment of which was in part made possible by grants from the National Science Foundation, Grant No. CHE-83-09446 and CHE-84-05851.

Registry No. 1,3-Butadiene, 106-99-0.

Picosecond Laser Spectroscopy of 4-(9-Anthryl)-*N*,*N*-dimethylaniline and Related Compounds

Tadashi Okada,* Noboru Mataga,*

Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan

Wolfram Baumann,

Institute of Physical Chemistry, University of Mainz, D 6500 Mainz, West Germany

and Aleksander Siemiarczuk

The Photochemistry Unit, Department of Chemistry, The University of Western Ontario, London, Ontario, N6A 5B7, Canada *(Received: December 2, 1986; In Final Form: March 2, 1987)*

Picosecond time-resolved absorption spectra of 4-(9-anthryl)-*N*,*N*-dimethylaniline (ADMA) and related methyl derivatives in the excited singlet state have been measured in various solvents. Analysis of the solvent dependence of the transient absorption spectra indicates the existence of "multiple excited states" of ADMA with different degrees of charge transfer. Picosecond time-resolved transient absorption spectra in a viscous polar solvent, butanol, show a gradual change of the electronic structure of excited ADMA in the course of the reorientational relaxation of solvent molecules. The mechanisms of the solvent-induced change of the electronic structure of excited ADMA are discussed in relation to the TICT (twisted intramolecular charge transfer) model.

Introduction

Mechanisms of intramolecular charge transfer (CT) in the excited state of compounds with electron donor and acceptor groups separated by a single bond have been studied extensively mainly by means of stationary as well as time-resolved fluorescence measurements. Especially, the photoinduced intramolecular CT of 4-(*N*,*N*-dimethylamino)benzonitrile (DMABN), which is a typical compound showing the dual fluorescence phenomena in polar solvents, has been investigated intensively.[1-10]

To explain the origin of the dual fluorescence spectra of DMABN, level inversion between ^1L_b and ^1L_a states induced by

---

(1) Lippert, E.; Lüder, W.; Boos, H. In *Advances in Molecular Spectroscopy*; Mangini, A., Ed.; Pergamon: New York, 1962; Vol. 1, p 443.

(2) (a) Nakashima, N.; Inoue, H.; Mataga, N.; Yamanaka, C. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2288. (b) Nakashima, N.; Mataga, N. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3016.

(3) (a) Rotkiewicz, K.; Grellmann, K. H.; Grabowski, Z. R. *Chem. Phys. Lett.* **1973**, *19*, 315. (b) Rotkiewicz, K.; Grabowski, Z. R.; Jasny, J. *Chem. Phys. Lett.* **1975**, *34*, 55. (c) Rotkiewicz, K.; Grabowski, Z. R.; Krowczynski, A.; Kuhnle, W. *J. Lumin.* **1976**, *12/13*, 877. (d) Grabowski, Z. R.; Rotkiewicz, K.; Siemiarczuk, A.; Cowley, D. J.; Baumann, W. *Nouv. J. Chim.* **1979**, *3*, 443.

(4) Chandross, E. A. In *The Exciplex*; Gordon, M., Ware, W. R., Eds; Academic: New York, 1975; p 187.

0022-3654/87/2091-4490$01.50/0 © 1987 American Chemical Society