

Substituent Effects in Buta-1,3-diene Photochemistry: A CAS-SCF Study of 2,3-Dimethylbutadiene and 2-Cyanobutadiene Excited-State Reaction Paths

Massimo Olivucci,^{*,†} Fernando Bernardi,[†] Stefano Ottani,[‡] and Michael A. Robb^{*,§}

Contribution from the Dipartimento di Chimica "G. Ciamician" dell'Università di Bologna, Via Selmi 2, 40126 Bologna, Italy, Centro di Studio per la Fisica delle Macromolecole del C.N.R., Via Selmi 2 40126 Bologna, Italy, and the Department of Chemistry, King's College, London, Strand, London WC2R 2LS, U.K.

Received May 10, 1993[®]

Abstract: The low-energy reaction paths on the first excited state of buta-1,3-diene (butadiene), 2,3-dimethylbutadiene (2,3-DMB), and 2-cyanobutadiene (2-CNB) have been studied at the CAS-SCF level with 4-31G and DZ+d basis sets. Intrinsic reaction coordinate calculations indicate that each excited state pathway connects both the *s-cis* and *s-trans* excited state equilibrium structures of 2,3-DMB and 2-CNB to a conical intersection of the ground and excited state. The geometry of the lowest energy conical intersection points have been fully optimized. The conical intersections provide ultrafast radiationless decay channels and thus are a central feature in the mechanism of butadiene photolysis. The excited state reaction paths of the model (butadiene) and substituted systems involve a similar reaction coordinate corresponding to the deformation of the butadiene moiety by out-of-plane motion of the carbon framework coupled with asynchronous rotation of the terminal methylenes. The comparison of the excited state pathways for parent and substituted butadienes provides a basis for the rationalization of the dramatic substituent effects observed in the photoproduct quantum yield ratio of 2,3-DMB and 2-CNB. The result supports the idea that substituents mainly affect the nature of the ground-state relaxation occurring just after the decay. However, this effect is intimately related to the particular structure and dynamics that the photoexcited reactant acquires during its excited-state lifetime.

1. Introduction

Direct irradiation of buta-1,3-dienes yields a mixture of photoproducts which includes *s-cis*/*s-trans* isomers, double-bond *cis*/*trans* isomers, cyclobutenes, bicyclobutanes, and 1-methylcyclopropenes. The relative quantum yield of the different photoproducts is sensitive to the type of substituents or carbon structure connected to the butadiene moiety.¹ Thus, while the different products are all observed during the photoreaction, their rate of formation is affected by substituent effects. In this article we will focus on two rather dramatic examples of substituent effect on the quantum yields of butadiene photoproducts. Firstly, Squillacote and Sample² in a study of the matrix-isolated photolysis of *s-cis*- and *s-trans*-2,3-dimethylbutadiene (2,3-DMB) found that the photochemical electrocyclic ring-closure is about 50 times faster than *s-cis*/*s-trans* isomerization in *s-cis*-2,3-DMB. This is in contrast with the fact that photochemical electrocyclic ring-closure is less efficient than *s-cis*/*s-trans* isomerization in *s-cis*-butadiene, isoprene, 2-isopropylbutadiene, and 1,3-pentadiene. This is particularly surprising when one considers that the ground-state barriers for ring-closure are 10 times larger than for *s-cis*/*s-trans* isomerization in both butadiene³ and 2,3-DMB.² Thus the effect of the 2,3-dimethyl-substitution on the excited-state reaction is counterintuitive since the two eclipsed methyl groups appear to hinder the rotation about the C₂–C₃ bond in butadiene. A second example of substituent effect was reported

for the first time by Gale⁴ who measured the quantum yields of the photochemical production of 1-cyanocyclobutene (1-CNCB) and 1-cyanobicyclobutane (1-CNBCB) in a dilute solution of 2-cyanobutadiene (2-CNB) in ether. The quantum yield ratio of the two cyclic products was found to favor the production of the bicyclic product 1-cyanobicyclobutane (i.e. $\Phi_{\text{CNBCB}}:\Phi_{\text{CNCB}}$ is 1.5:1). In contrast, in unsubstituted butadienes the production of cyclobutene⁵ is favored (the corresponding quantum yield ratio of bicyclic to cyclic product is 1:16 in isoctane^{1b,6}). In this second example, the favored photochemical production of the 1-CNBCB product with a highly strained bicyclobutane moiety is again counterintuitive.

Recently, we have documented a novel mechanism for the photochemistry of butadiene.⁷ We have demonstrated the existence of two very efficient radiationless decay paths on the lowest energy (2¹Ag) excited state of this system. These reaction paths connect the *s-cis* and *s-trans* excited-state reactant wells, via low-energy transition states, to two distinct decay regions centered on conical intersection points of the excited- and ground-state potential energy surfaces. Such accessible conical intersections correspond to ultrafast radiationless decay channels (typically the decay occurs within one vibrational period⁸). The existence of these fast-decay channels has been demonstrated to provide the route to the many butadiene photoproducts listed above. Starting from the conical intersection point, the molecule relaxes on the ground-state potential energy surface until one of the accessible product wells is reached. Since the final photoproducts are the result of different relaxation paths on the ground-state surface originating from a common conical intersection point, the nature of the products and the final quantum yield are dictated primarily by the molecular structure at the conical intersection

[†] Università di Bologna.

[‡] Centro di Studio per la Fisica delle Macromolecole del C.N.R.

[§] King's College.

[®] Abstract published in *Advance ACS Abstracts*, January 15, 1994.

(1) (a) Gilbert, A.; Baggott, J. *Essentials of Molecular Photochemistry*; Blackwell Scientific Publications: Oxford, 1991. (b) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin Publishing: Reading, MA, 1978. (c) Ninomiya, I.; Naito, T. *Photochemical Synthesis*; Academic Press: New York, 1989. (d) Srinivasan, R. *Adv. Photochem.* 1966, 4, 113. (e) Leigh, W. J. *Chem. Commun.*; in press.

(2) Squillacote, M.; Semple, T. C. *J. Am. Chem. Soc.* 1990, 112, 5546.

(3) (a) Squillacote, M. E.; Semple, T. C.; Mui, P. W. *J. Am. Chem. Soc.* 1985, 107, 6842. (b) Squillacote, M. E.; Sheridan, R. S.; Champman, O. L.; Anet, F. A. L. *J. Am. Chem. Soc.* 1979, 101, 3657.

(4) Gale, D. M. *J. Org. Chem.* 1970, 35, 970.

(5) (a) Srinivasan, R. *J. Am. Chem. Soc.* 1963, 85, 4045. (b) Srinivasan, R. *J. Am. Chem. Soc.* 1968, 90, 4498.

(6) Sonntag, F. J.; Srinivasan, R. *Org. Photochem. Synth.* 1971, 1, 39.

(7) Olivucci, M.; Bernardi, F.; Ragazos, I. N.; Robb, M. A. *J. Am. Chem. Soc.* 1993, 115, 3710.

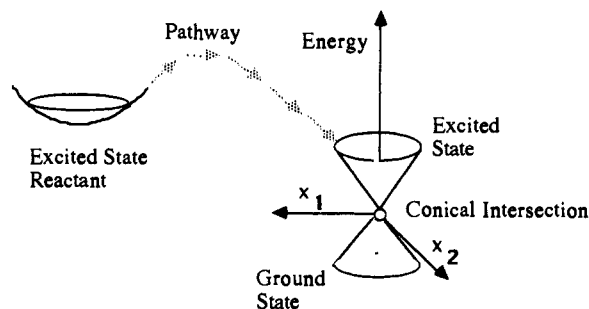
(8) Manthe, U.; Koppel, H. *J. Chem. Phys.* 1990, 93, 1658.

and motion of the excited state molecule at the moment of the decay. In fact, the momentum in this direction will be, in part, preserved on the ground-state surface.

In this paper we present a CAS-SCF study of the first (2^1A_g) excited-state potential energy surface of 2,3-DMB and 2-CNB. The *s*-cis and *s*-trans excited state pathways to two low-lying (one cisoid and one transoid) conical intersection points will be compared to the corresponding pathways found for the unsubstituted butadiene system.⁷ The investigation of substituent effects can be routinely applied to thermal reactions and involves a comparison of transition structures and barriers of the parent and substituted systems. The substituent effects in a thermal reaction are often related to the competition between two different pathways which start in the same reactant well and end up, via different transition structures, in two different product wells. In this case the substituents can favor one particular pathway respect to others causing a change in the product yield ratio. However, in this paper we will show that the origin of substituent effects in a photochemical reaction is subtly different. We will show that for a photochemical reaction different photoproducts originate from a *single* decay channel as the photoexcited reactant enters the conical intersection located at the end of an excited-state pathway. Remarkably, the presence of 2,3-dimethyl or 2-cyano substituents on the butadiene moiety do not alter the nature of the relevant excited pathways. Thus, these substituents, must induce a change in the ground-state motion occurring just after the decay.

The study of substituent effects in thermal (i.e. ground state) reactivity involves the computation of differences in the barriers of the rate-determining step for the transformation of unsubstituted and substituted reactants. This is possible because a thermal reaction starts and ends on the same (ground state) potential energy surface and the only bottleneck to product formation is the transition-state region. In contrast, in a photochemical reaction, the photoexcited reactant evolves on one or more excited-state surfaces before decaying back to the ground state via a radiative event (i.e. fluorescence) or a nonradiative process.^{1a,b} As a consequence, the characterization of a photochemical reaction mechanism involves the study of ground- and excited-state potential energy surfaces and a study of the region where the system decays to the ground state. One may encounter transition states before or after the decay to the ground state. Alternatively, the excited-state reaction path may be barrierless and the course of the reaction may be determined by the nature of excited-state reaction paths that simply continue on the ground state after decay. Our previous work⁷ supports a mechanism for the photolysis of butadienes that involves radiationless decay via a conical intersection. (For a general survey on conical intersections see ref 9.) The importance of conical intersections in chemistry has been pointed out in ref 10. While it is often assumed that conical intersections between the electronic states with same spin symmetry^{10a} were very rare, recent investigations have indicated that low-lying conical intersections can be a common

Scheme 1



feature in various organic¹¹ and inorganic systems.¹² We have demonstrated in other works that conical intersections are central features of the photochemical reaction mechanisms for butadiene and other organic systems.^{11a-f} In particular the detailed course of a photochemical reaction has been shown to depend on (1) the "molecular" structure at the conical intersection, (2) the nature of the excited-state reaction paths leading to the conical intersection and (3) the ground-state relaxation pathways which originate in this decay region. We will now briefly review these ideas.

In Scheme 1 we show a conical intersection of two potential energy surfaces as a point where the upper (excited) state and the lower (ground) state are degenerate. At a conical intersection point the degeneracy is lifted when the geometry of the system is distorted along the two linearly independent nuclear coordinates x_1 and x_2 that define the *branching space*.¹³ Thus, when the energy of the two states is plotted in the branching space (as shown in Scheme 1) the corresponding potential energy surfaces appear in the form of a double cone. The two vectors x_1 and x_2 and the excited-state pathways have a dynamic significance which can be discussed qualitatively in the framework of simple semiclassical methods like the trajectory surface-hopping (TSH) treatment.¹⁴ The photoexcited system (i.e. the excited-state reactant in Scheme 1) moves initially along classical trajectories concentrated near the pathways or valleys located on the excited-state sheet. When such a pathway terminates in the vicinity of a conical intersection point, the system undergoes a "surface hop" (i.e. a radiationless decay) from the excited state to the ground state. After the hop, the direction of the original excited-state motion (i.e. the momentum on the excited state) will not be conserved. In fact, in order to conserve total energy after the "hop", one must adjust a component of the momentum in the direction of the x_2 or x_1 vector.^{14c} Thus, in the trajectory that continues on the ground state, the original direction of motion on the excited state will be partly diverted along one of the directions contained in the plane formed by the vectors x_1 and x_2 .

From a mechanistic point of view a conical intersection funnel plays, in a photochemical reaction, the same role of a transition

(9) (a) Michl, J.; Bonacic-Koutecky, V. *Electronic Aspects of Organic Photochemistry*; Wiley: New York, 1990. (b) Bonacic-Koutecky, V.; Koutecky, J.; Michl, J. *Agnew. Chem. Ed. Engl.* **1987**, *26*, 170. (c) Von Neumann, J.; Wigner, E. *Physik. Z.* **1929**, *30*, 467. (d) Teller, E. *J. Phys. Chem.* **1937**, *41*, 109. (e) Herzberg, G.; Longuet-Higgins, H. C. *Trans. Faraday Soc.* **1963**, *35*, 77. (f) Herzberg, G. *The Electronic Spectra of Polyatomic Molecules*; Van Nostrand: Princeton, 1966; p 442. (g) Mead, C. A.; Truhlar, D. G. *J. Chem. Phys.* **1979**, *70*, 2284. (h) Mead, C. A. *Chem. Phys.* **1980**, *49*, 23. (i) Keating, S. P.; Mead, C. A. *J. Chem. Phys.* **1985**, *82*, 5102. (j) Keating, S. P.; Mead, C. A. *J. Chem. Phys.* **1987**, *86*, 2152. (l) Davidson, R. E.; Borden, W. T.; Smith, J. J. *J. Am. Chem. Soc.* **1978**, *100*, 3299. (m) Mead, C. A. The Born-Oppenheimer approximation in molecular quantum mechanics. *Mathematical frontiers in computational chemical physics*; Truhlar, D. G., Ed.; Springer: New York, 1987; Chapter 1, p 1-17.

(10) (a) Salem, L. *Electrons in Chemical Reactions: First Principles*; Wiley: New York, 1982. (b) Lorquet, J. C. *Org. Mass Spectr.* **1981**, *16*, 469. (c) Koppel, H.; Domcke, W.; Cederbaum, L. S. *Adv. Chem. Phys.* **1984**, *57*, 59. (d) Whetten, R. L.; Ezra, G. S.; Grant, E. R. *Rev. Phys. Chem.* **1985**, *36*, 277.

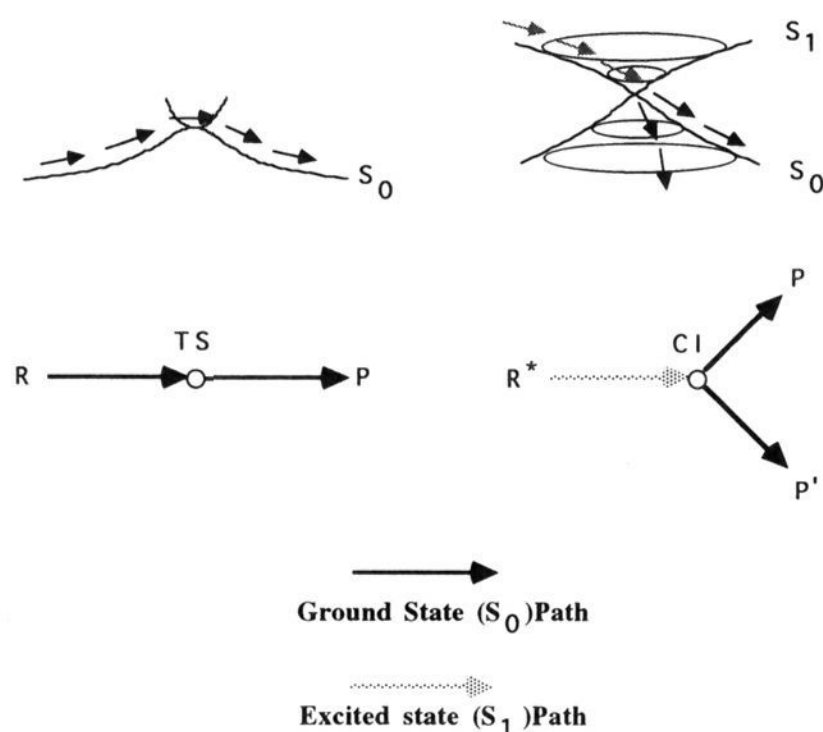
(11) (a) Bernardi, F.; De, S.; Olivucci, M.; Robb, M. A. *J. Am. Chem. Soc.* **1990**, *112*, 1737-1744. (b) Bernardi, F.; Olivucci, M.; Robb, M. A. *Acc. Chem. Res.* **1990**, *23*, 405-412. (c) Bernardi, F.; Olivucci, M.; Ragazos, I. N.; Robb, M. A. *J. Am. Chem. Soc.* **1992**, *114*, 2752-2754. (d) Bernardi, F.; Olivucci, M.; Robb, M. A.; Tonachini, G. *J. Am. Chem. Soc.* **1992**, *114*, 5805-5812. (e) Bernardi, F.; Olivucci, M.; Ragazos, I. N.; Robb, M. A. *J. Am. Chem. Soc.* **1992**, *114*, 8211-8220. (f) Palmer, I.; Bernardi, F.; Olivucci, M.; Robb, M. A. *J. Org. Chem.* **1992**, *57*, 5081-5087. (g) Domke, W.; Sobolewski, A. L.; Woywod, C. *Chem. Phys. Lett.* **1993**, *203*, 220.

(12) (a) Atchity, G. J.; Xantheas, S. S.; Elbert, S. T.; Ruedenberg, K. *J. Chem. Phys.* **1991**, *94*, 8054-8069. (b) Atchity, G. J.; Xantheas, S. S.; Elbert, S. T.; Ruedenberg, K. *Theor. Chim. Acta* **1991**, *78*, 365. (c) Muller, H.; Koppel, H.; Cederbaum, L. S.; Schmelz, T.; Chambaud, G.; Rosmus, P. *Chem. Phys. Lett.* **1992**, *197*, 599-606. (d) Manaa, M. R.; Yarkony, D. R. *J. Chem. Phys.* **1990**, *93*, 4473. (e) Manaa, M. R.; Yarkony, D. R. *J. Chem. Phys.* **1992**, *97*, 715-717.

(13) Atchity, G. J.; Xantheas, S. S.; Ruedenberg, K. *J. Chem. Phys.* **1991**, *95*, 1862.

(14) (a) Tully, J. C.; Preston, R. K. *J. Chem. Phys.* **1971**, *55*, 562. (b) Dehareng, D.; Chapuisat, X.; Lorquet, J. C.; Galloy, C.; Raseev, G. *J. Chem. Phys.* **1983**, *78*, 1246. (c) Blais, N. C.; Truhlar, D. G.; Mead, C. A. *J. Chem. Phys.* **1988**, *89*, 6204.

Scheme 2



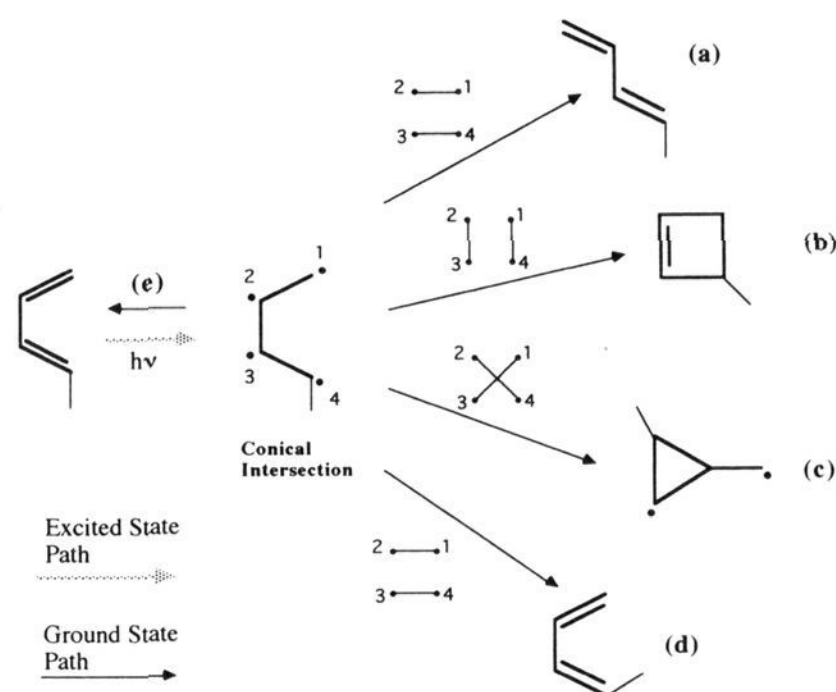
state in a thermal reaction. For a thermal reaction, the transition state corresponds to the point of the potential energy surface where the probability of passage from the reactant well to the product well is the largest. Similarly, in a photochemical reaction, a conical intersection represents the region of the excited state potential energy surface where the probability of decay to the ground state is the largest. The initial evolution of the reacting system after passage through a transition state is characterized by the transition vector (normal coordinate corresponding to the imaginary frequency) which is parallel to the reaction path that leads to products. Accordingly, the transition vector gives information on the nature of products which might be formed via that reaction pathway. For a nonadiabatic photochemical mechanism proceeding via a conical intersection, the initial direction of motion after the decay is instead determined by the direction of the velocity of the excited-state system at the moment of the decay and by the orientation of the plane $x_1 x_2$. The difference between a transition state and a conical intersection has been pictorially illustrated in Scheme 2.

By analogy with the information conveyed by the transition vector, the directions of the initial motion on the ground-state surface (S_0) may provide information on the photoproducts which originate from reaction paths in the decay region. Of course, the ground-state relaxation pathway is also determined in part by the accessibility of ground-state valleys which develop as one moves away from the apex of the conical intersection. Thus one important novel feature of a photochemical reaction, that has its origins in the decay via conical intersection, is the branching motion (to P and P' in Scheme 2). This feature rationalizes the simultaneous formation of different photoproducts that is commonly observed in organic photoreactions.^{1a,b}

To conclude this section we should comment briefly on the nature of the driving force that governs the ground-state relaxation process that begins at a conical intersection. This force is related to the electronic structure of the system at the decay point. As we have shown previously, the two butadiene conical intersections (cisoid and transoid) have a geometry and electronic structure that is essentially that of a tetraradical.^{7,11a-c} Thus at the moment of the decay from the conical intersection, the four π -electrons of the system are unpaired. Thus, the driving force leading the system along the ground-state relaxation valleys will be provided by the different electron recouplings or bond-forming processes. In Scheme 3 we have illustrated the possible electron recoupling/bond-forming schemes in the conical intersection originating from *s-cis*-butadiene (an arbitrary substituent has been added on center 4 to illustrate the process occurring along path d).

One can see that all the observed photoproducts of butadiene

Scheme 3



can in principle be formed via one of the recoupling processes that originate from a tetraradicaloid conical intersection. The total quantum yield and quantum yield ratios thus depend on the factors which make a specific recoupling scheme more probable than another. Thus, the most important factors controlling the probability of a specific (ground state) recoupling in butadienes and thus the quantum yield of the corresponding photoproducts are related to (i) the geometry of the conical intersection point and (ii) to the direction of the excited-state pathway leading to it. We will demonstrate that the substituent effects observed in butadiene photochemistry are due to the ability of the 2,3-dimethyl and 2-cyano substituents to change the probability of entering a specific ground-state relaxation pathway.

2. Computational Details

All CAS-SCF computations have been performed using the MC-SCF program distributed in Gaussian 92.¹⁵ For all calculations, the active space chosen includes all π -orbitals and π -electrons of the molecular structures under investigation. Thus, we have used a four-electrons/four-orbitals active space for butadiene and 2,3-DMB and an eight-electrons/eight-orbitals active space for 2-CNB. Location of the excited-state minima, transition structures, and mapping of the intrinsic reaction coordinates (IRC) have been carried out by using the methods available in the Gaussian package. However the rigorous location of funnels corresponding to low-lying conical intersection points requires a non-standard method¹⁶ that has been implemented in a development version of the same package. This method has been used to optimize the conical intersection structures located at the end of excited state IRC and to compute the nonadiabatic coupling (NAC) and gradient difference (GD) vectors.^{13,16} These vectors correspond to x_1 and x_2 in Scheme 1 and define the branching space at the conical intersection point.

Finally we should make a brief comment on the accuracy of the methods used. Firstly, all the orbitals are fully utilized and optimized in the computation, but only the active orbitals can have variable occupancy. Thus no assumption of σ/π separability is implied. The identification of the p^π active orbitals is merely a specification of which orbitals can have occupancy other than 2. As the geometry is changed from a planar arrangement, the optimization of the orbitals mixes σ/π orbitals to give the lowest energy. The only type of interaction that is not included explicitly at the configuration interaction level would result from single excitations of the σ backbone. However, this type of interaction is included through the Brillouin condition satisfied by the optimum MC-SCF orbitals. Our objective in this work is to document the covalent excited-state reaction paths. However, because we use a CAS expansion, the MC-SCF wave

(15) Gaussian 92. Revision B, Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1992.

(16) Ragazos, I. N.; Robb, M. A.; Bernardi, F.; Olivucci, M. *Chem. Phys. Lett.* 1992, 197, 217.

Table 1. Absolute (E) and relative (ΔE) CAS-SCF Energies for the Critical Points and Conical Intersections Located on the First Excited (S_1) State of Butadiene. The Values Reported Have Been Computed Using the 4-31G, DZ+d (values in brackets) and DZ+spd (values in square brackets) Basis Sets. The Abbreviation "CI" Indicates a Conical Intersection Point

structure	state	E (au)	ΔE (kcal/mol)
C_s s-cis min ^c	S_1	-154.5654 ^a	0.0
		(-154.8041)	(0.0)
		[-154.8055]	[0.0]
C_2 s-cis min ^c	S_1	-154.5634 ^a	1.26
		(-154.8010)	(1.94)
C_2/C_s s-cis TS ^c	S_1	-154.5622 ^a	2.01
		(-154.8006)	(2.19)
C_2/CI s-cis TS ^d	S_1	-154.5622	2.01
		(-154.8022)	(1.19)
		[-154.8037]	[1.13]
S_2 s-trans min ^c	S_1	-154.5638 ^a	1.0
		-	-
C_2 s-trans min ^c	S_1	-154.5641 ^a	0.82
		(-154.8023)	(1.13)
C_2/S_2 s-trans TS ^c	S_1	-154.5619 ^a	2.20
		(-154.8012)	(1.82)
s-cisoid CI ^e	S_1	-154.5580 ^{a,b}	-
		S_0	-154.5578 ^b
s-transoid CI ^f	S_1	-154.5696 ^{a,b}	-
		S_0	-154.5703 ^b

^a Data from ref 7. ^b CAS-SCF with state averaged orbitals. ^{c-f} The structures and main geometrical parameters are reported in Figure 1 (c), Figure 6 (d), Figure 9 (e), and Figure 10 (f).

function which results is capable of describing all the states that can arise from all possible arrangements of the electrons in the orbitals, i.e. both covalent and zwitterionic states. We shall demonstrate this subsequently by showing that the zwitterionic excited-state minimum is correctly reproduced. However, in the case of a zwitterion, the detailed energetics are sensitive to the choice of basis and the inclusion of dynamic correlation.

Since we have explored the ground and excited surfaces as well as the conical intersection region in considerable detail, we have restricted ourselves to a modest 4-31G basis set. The effect of using an extended basis with diffuse and polarization functions has been calibrated for the reference butadiene system and a discussion will be presented subsequently. Our calculations therefore offer a correct description of the excited singlet covalent surfaces which we believe to be of main importance in the photochemical processes.

3. Results and Discussion

(i) Characterization of the Excited-State Reaction Pathways for 2,3-Dimethylbutadiene (2,3-DMB) and 2-Cyanobutadiene (2-CNB). In this section we present the results of ab-initio CAS-SCF calculations on the first excited state of 2,3-DMB and 2-CNB together with data for the corresponding 2^1A_g excited state of butadiene (which has been refined from ref 7 using larger basis sets). These data will serve as a basis for discussing the effects of methyl and cyano substituents throughout the rest of this paper. The energies of all conical intersection structures and conventional stationary points are collected in Tables 1-3.

We begin with a discussion of the 2^1A_g potential energy surface of butadiene. The only true energy minima correspond to two nonplanar s-cis and one nonplanar s-trans conformers (see Figure 1). The two s-cis forms have C_2 and C_s symmetry, respectively, and are connected via a transition structure (C_2/C_s TS) which is characterized by one rotated terminal CH_2 group. The conversion of the C_2 form to the C_s form is associated with a barrier less than 1 kcal mol⁻¹ (see Table 1) while the barrier for the C_s to C_2 conversion is larger. In the s-trans region the only excited-state stationary point found using either the 4-31G or DZ+d basis sets has C_2 symmetry. However, at the 4-31G level it is also possible to locate an S_2 stationary structure (faint structure in Figure 1) which disappears using the larger basis set DZ+d. This observation is consistent with the existence of a very low-

Table 2. Absolute (E) and Relative (ΔE) CAS-SCF Energies for the Critical Points and Conical Intersections Located on the First Excited (S_1) State of 2,3-DMB. The Values Reported Have Been Computed Using the 4-31G Basis Set. The Abbreviation "CI" Indicates a Conical Intersection Point

structure	root	E (au)	ΔE (kcal/mol)
C_2 s-cis min ^b	S_1	-232.5231	1.38
C_s s-cis min ^b	S_1	-232.5253	0.0
C_s/CI s-cis TS ^c	S_1	-232.5249	0.25
C_2 s-trans min ^b	S_1	-232.5255	-0.13
S_2 s-trans min ^b	S_1	-232.5248	0.31
s-cisoid CI ^d	S_1	-232.5249 ^a	-
	S_0	-232.5254 ^a	-
s-transoid CI ^e	S_1	-232.5309 ^a	-
	S_0	-232.5327 ^a	-

^a CAS-SCF with state averaged orbitals. ^{b-e} The structures and main geometrical parameters are reported in Figure 2 (b), Figure 6 (c), Figure 9 (d), and Figure 10 (e).

Table 3. Absolute (E) and Relative (ΔE) CAS-SCF Energies for the Critical Points and Conical Intersections Located on the First Excited (S_1) State of 2-CNB. The Values Reported Have Been Computed Using the 4-31G Basis Set. The Abbreviations "CI" and "CI₂" Indicate Conical Intersection Points along Paths a, b in Figure 5 (paths a, c in Scheme 5) and Paths a, b in Figure 8 (paths b, d in Scheme 5), respectively

structure	root	E (au)	ΔE (kcal/mol)
pseudo- C_2 s-cis min ^b	S_1	-246.2495	1.44
pseudo- C_s s-cis min ^b	S_1	-246.2518	0.0
pseudo- C_s/CI s-cis TS ^c	S_1	-246.2507	0.69
pseudo- C_2/CI_2 s-cis TS ^d	S_1	-246.2462	3.51
pseudo- C_2 s-trans min ^b	S_1	-246.2497	1.32
pseudo- C_2/CI s-trans TS	S_1	-246.2489	1.82
pseudo- C_2/CI_2 s-trans TS	S_1	-246.2486	2.01
s-cisoid CI ^e	S_1	-246.2412 ^a	-
	S_0	-246.2480 ^a	-
s-transoid CI ^f	S_1	-246.2532 ^a	-
	S_0	-246.2552 ^a	-

^a CAS-SCF with state averaged orbitals. ^{b-f} The structures and main geometrical parameters are reported in Figure 2 (b), Figure 6 (c), Figure 8 (d), and Figure 9 (e) structure in Figure 10 (f).

frequency (about 50 cm⁻¹) normal mode^{7,17} of the S_2 structure at the 4-31G level so that this stationary point seems to be an inflection point of the excited-state potential energy surface rather than a real minimum. Thus the existence of the S_2 s-trans conformer is rather uncertain. On the other hand, we were able to locate a transition structure (C_2/S_2 TS) for the transformation of the C_2 s-trans minimum to the S_2 (minimum) point using both the 4-31G and the DZ+d basis set. This transition state connects the C_2 real minimum to the flat S_2 valley via a 1 kcal mol⁻¹ barrier (see Table 1). Like the s-cis C_2/C_s TS, the geometry of this transition structure has a rotated terminal CH_2 group.

The optimized (CAS-SCF/4-31G) stationary points on the excited-state surface for 2,3-DMB and 2-CNB are collected in Figure 2 and the related energetic data can be found in Tables 2 and 3. One finds minima for C_2 s-cis, C_s s-cis and C_2 s-trans conformers. In the case of 2,3-DMB an S_2 minimum similar to the S_2 structure of butadiene also exists. The molecular structures in Figure 2 and the energetic data in Tables 2 and 3 show that the energy minima found for 2,3-DMB and 2-CNB are nearly identical to those computed for the unsubstituted system.

We now discuss the excited-state reaction paths for 2,3-DMB and 2-CNB and compare this data with the butadiene reference data. For butadiene,⁷ the system undergoes facile deformation along two low-lying 2^1A_g excited-state pathways starting from the C_s s-cis and S_2 s-trans minima, respectively. Both these pathways involve disrotatory motion of the two terminal CH_2 groups and terminate in two different conical intersection points (the nature of the reaction path is illustrated schematically in

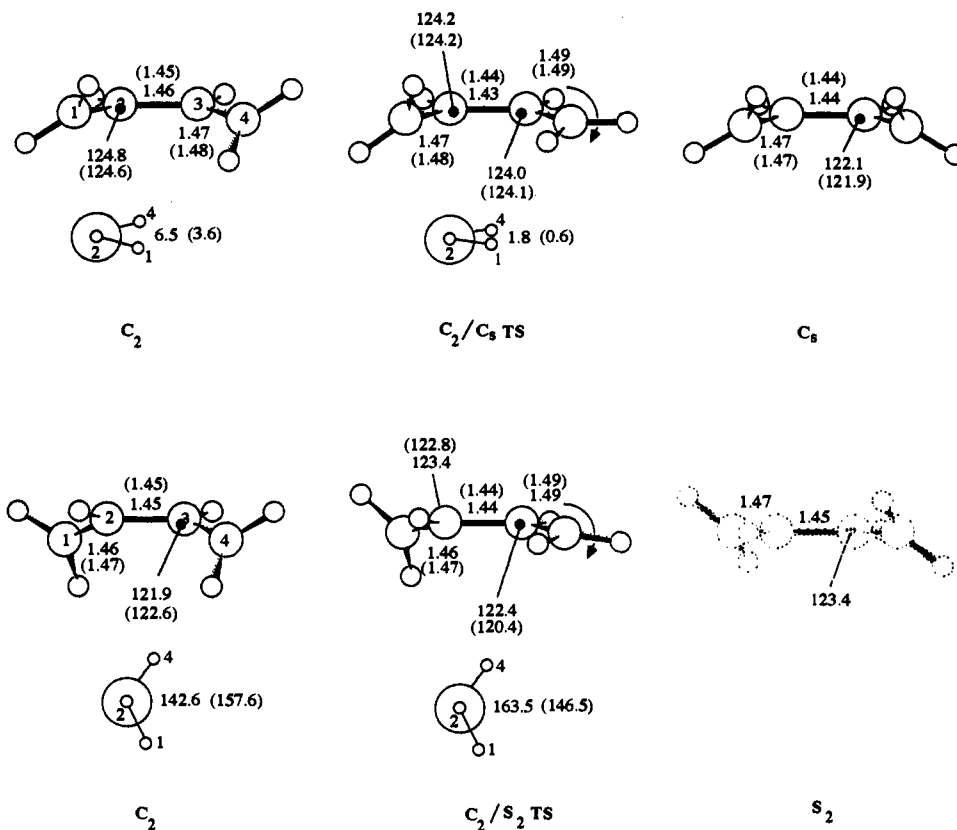


Figure 1. Optimized CAS-SCF/4-31G⁷ and DZ+d structures of the 2^1A_g excited state of butadiene. (a) *s-cis*-Butadiene equilibrium (C_2 and C_s) and transition (C_2/C_s TS) structures. (b) *s-trans*-Butadiene equilibrium (C_2 and S_2) and transition (C_2/S_2 TS) structures. The S_2 minimum (faint structure) has been located at the 4-31G level only. The values of the relevant structural parameters are given in angstroms and degrees (DZ+d parameters are in brackets).

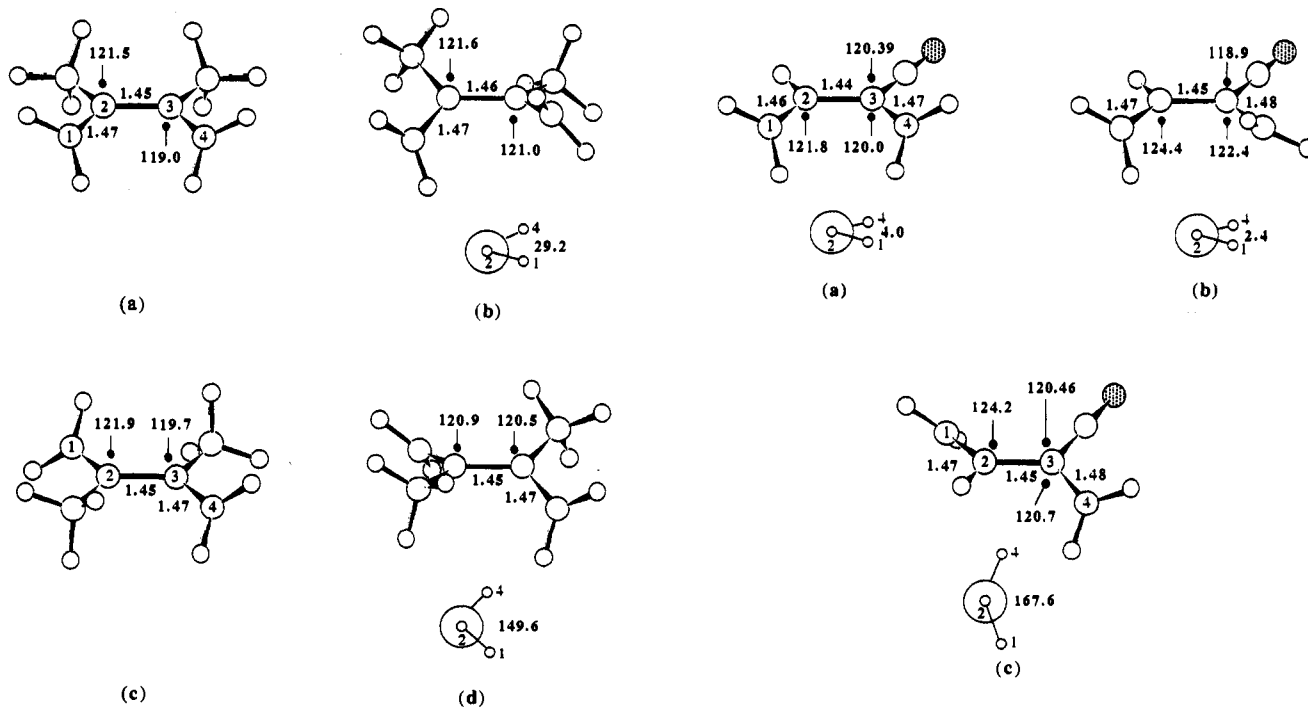
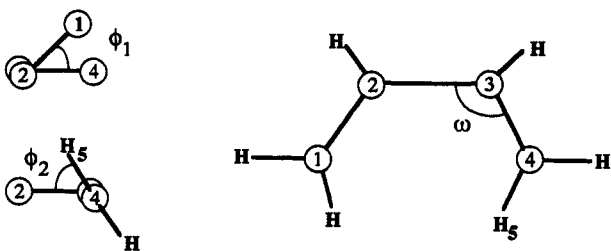


Figure 2. Optimized CAS-SCF/4-31G excited-state equilibrium structures of 2,3-DMB and 2-CNB. 2,3-DMB: (a) *s-cis* C_s , (b) *s-cis* C_2 , (c) *s-trans* S_2 , (d) *s-trans* C_2 . 2-CNB: (a) *s-cis* C_s , (b) *s-cis* C_2 , (c) *s-trans* C_2 . The values of the relevant structural parameters are given in angstroms and degrees.

Scheme 1). In contrast, from the C_2 *s-cis* and C_2 *s-trans* minima the system can access two pathways which involve conrotatory motion of the two terminal CH_2 groups. Since the increase in the energy along these conrotatory pathways is much larger than the conformational barriers (see Table 1 and Figure 5 in ref 7),

the C_2 *s-cis* and C_2 *s-trans* conformers convert rapidly to the C_s *s-cis* and S_2 *s-trans* structures. Accordingly, we will concentrate on the description of the evolution of the C_s *s-cis* and S_2 *s-trans* forms of butadiene. These reaction paths have been documented using the IRC method which provides a description of the classic

Scheme 4



(adiabatic) motion that the system undergoes on the excited state sheet. The computed IRC show that in all cases the geometrical deformation leading to the decay point is dominated by the three geometrical parameters shown in Scheme 4.

In Figure 3 we give the energy profiles for the excited state IRC starting from the C_s s-cis (Figures 3a and 3c) and starting from the S_2 s-trans (Figures 3b and 3d) regions of butadiene. The 4-31G results are from ref 7 and the DZ+d are new. The energetic values, relative to the C_s s-cis minimum (see also Table 1), have been plotted against the value of the torsional coordinate ϕ_1 in

Scheme 4. In Figures 3a and 3b, one observes a continuous decrease in energy difference between the ground and excited state along the two IRC which terminate when the two eigenvalues corresponding to the excited and ground states approach degeneracy. In these regions ($\phi_1 > 55.0^\circ$ and $\phi_1 < 120.0^\circ$) the ground- and excited-state potential energy surfaces merge in two distinct conical intersections. Figures 3c and 3d show an enlargement of the two flat excited-state energy profiles alone. The 4-31G s-cis pathway (Figure 3c) shows the presence of a transition structure about 2.0 kcal mol⁻¹ higher than the C_s minimum. The corresponding DZ+d barrier is 1.2 kcal mol⁻¹. In contrast the s-trans IRC follows a basically barrierless route from the S_2 region to the transoid conical intersection. Thus, while the DZ+d results yield a smaller barrier and a more rapid decrease in energy along the two pathways, the shape of the energy curves remains unaffected by the basis set used. Remarkably, the conical intersection point located at the termination of the s-trans path is located below all other points (see Figures 3b and 3c) and thus it corresponds to the global minimum of the excited-state surface. Since the 4-31G and DZ+d energy profiles were qualitatively similar, the larger 2,3-DMB and 2-CNB computations have been

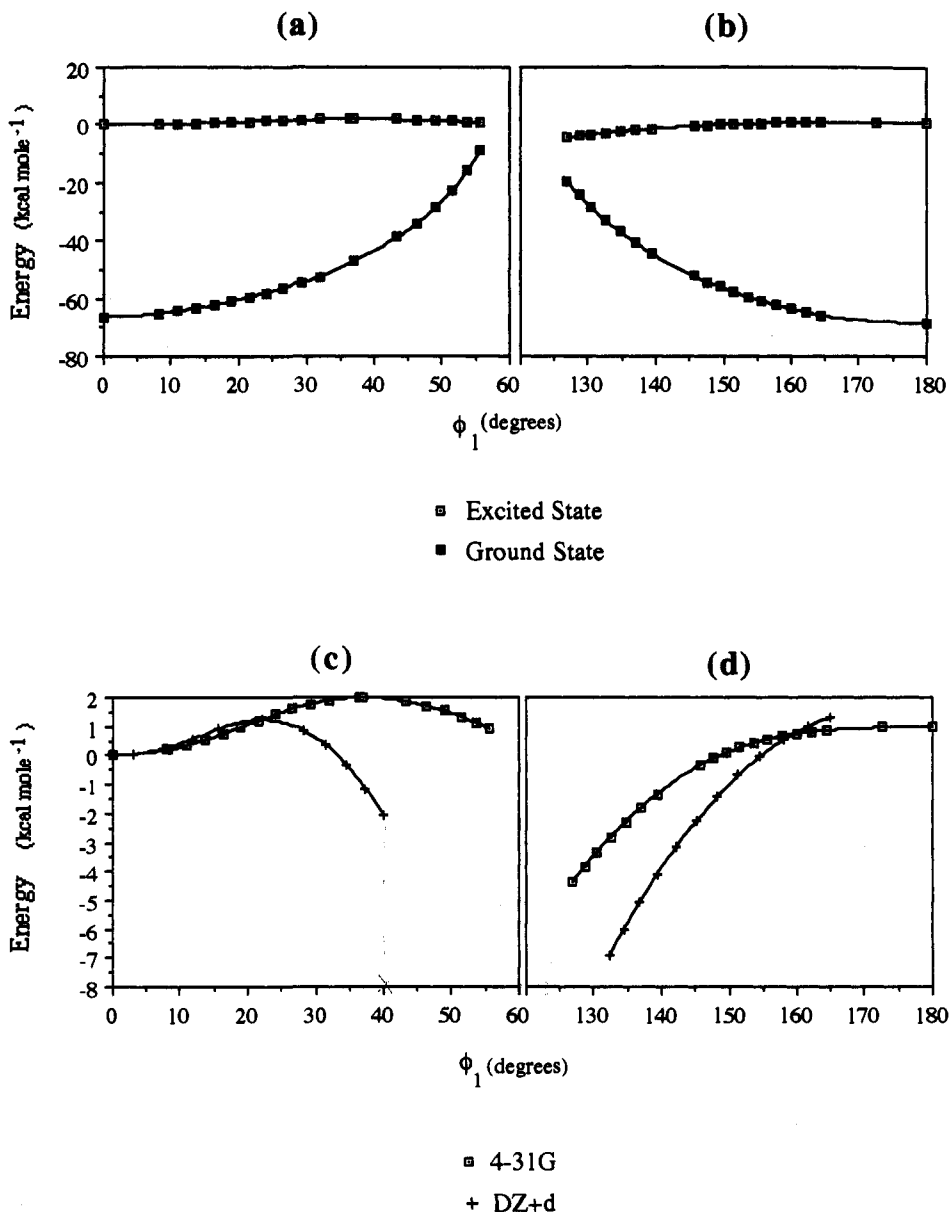


Figure 3. Excited- and ground-state energy profiles for butadiene along the excited-state s-cis (a) and s-trans (b) IRC computed at the CAS-SCF/4-31G level and plotted against the torsional angle ϕ_1 (see Scheme 4). Expanded view of the excited-state energy profiles along the s-cis (c) and s-trans (d) IRC computed at the CAS-SCF/4-31G and DZ+d levels.

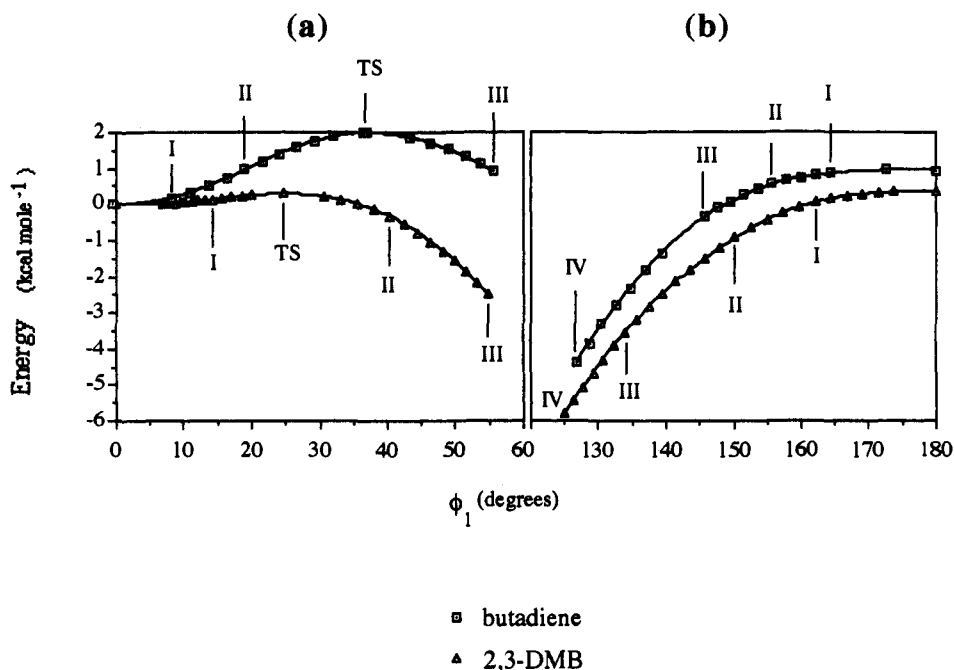


Figure 4. Comparison of butadiene and 2,3-DMB excited-state energy profiles along the *s-cis* (a) and *s-trans* (b) excited-state IRC computed at the CAS-SCF/4-31G and plotted against the torsional angle ϕ_1 (see Scheme 4).

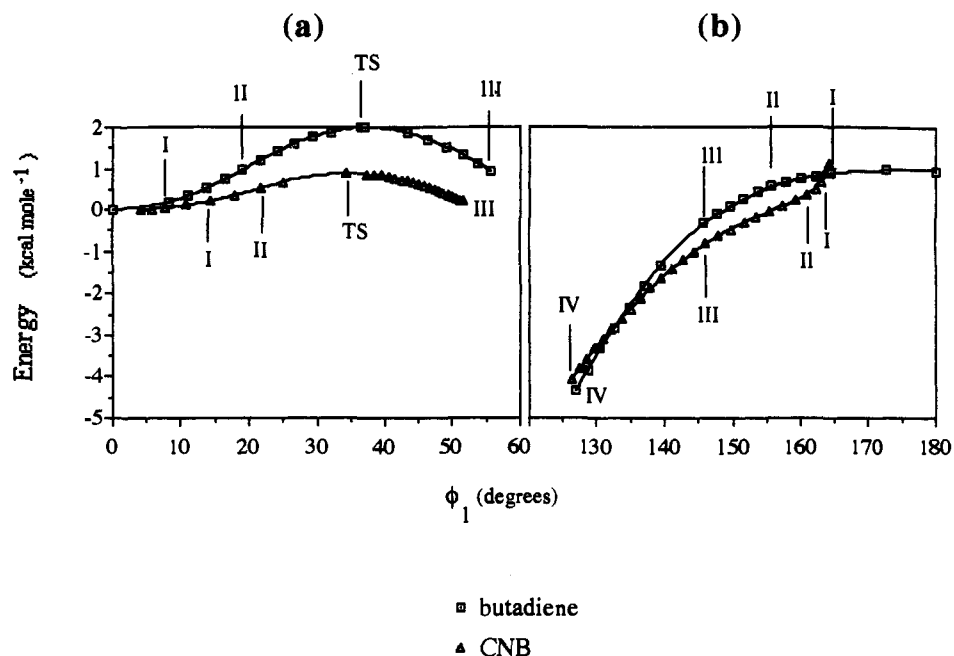


Figure 5. Comparison of butadiene and 2-CNB excited-state energy profiles along the *s-cis* (a) and *s-trans* (b) excited-state IRC computed at the CAS-SCF/4-31G and plotted against the torsional angle ϕ_1 (see Scheme 4).

carried out at the 4-31G level. Thus in the following we assume that the surface topology, including the location of the reaction pathways, is correctly represented at this level of theory.

The 4-31G IRC energy profiles computed for 2,3-DMB and 2-CNB are presented in Figures 4a, 5a, 4b, and 5b. They are qualitatively similar to the corresponding butadiene curves. However, the magnitude of the barrier and relative energies of the curves are different from the reference butadiene. Along the *s-cis*-2,3-DMB path the barrier to the conical intersection is almost 2.0 kcal mol⁻¹ lower than that of the unsubstituted system. The same behavior is observed in the *s-cis*-2-CNB pathway where there is a 1.5 kcal mol⁻¹ reduction of the barrier height. Similarly along the two *s-trans* pathways one observes a decrease in relative energies for both the substituted butadienes (in the case of 2-CNB this stabilization effect disappears at ϕ_1 values below 140°).

The evolution of the molecular structure along the different pathways is illustrated in Figure 6 for the *s-cis*-butadiene (column 1), 2,3-DMB (column 2), and 2-CNB (column 3). The corresponding data for the *s-trans* conformers are shown in Figure 7. In each case four sequential structures on the IRC are given. In Figure 6 structure I describes the initial deformation undergone by the excited state *s-cis* C₂ minima while structure III corresponds to the final IRC point before the system enters the cisoid conical intersection. Figure 7 shows the deformation along the *s-trans* pathways. Since the initial part of this pathway is extremely flat, the transition state is not detectable. The final point on the IRC before the system enters the transoid conical intersection corresponds to structure IV. One can recognize few very specific modes of deformation which are common features along all pathways. Firstly, the torsional angle ϕ_1 , defined in Scheme 4,

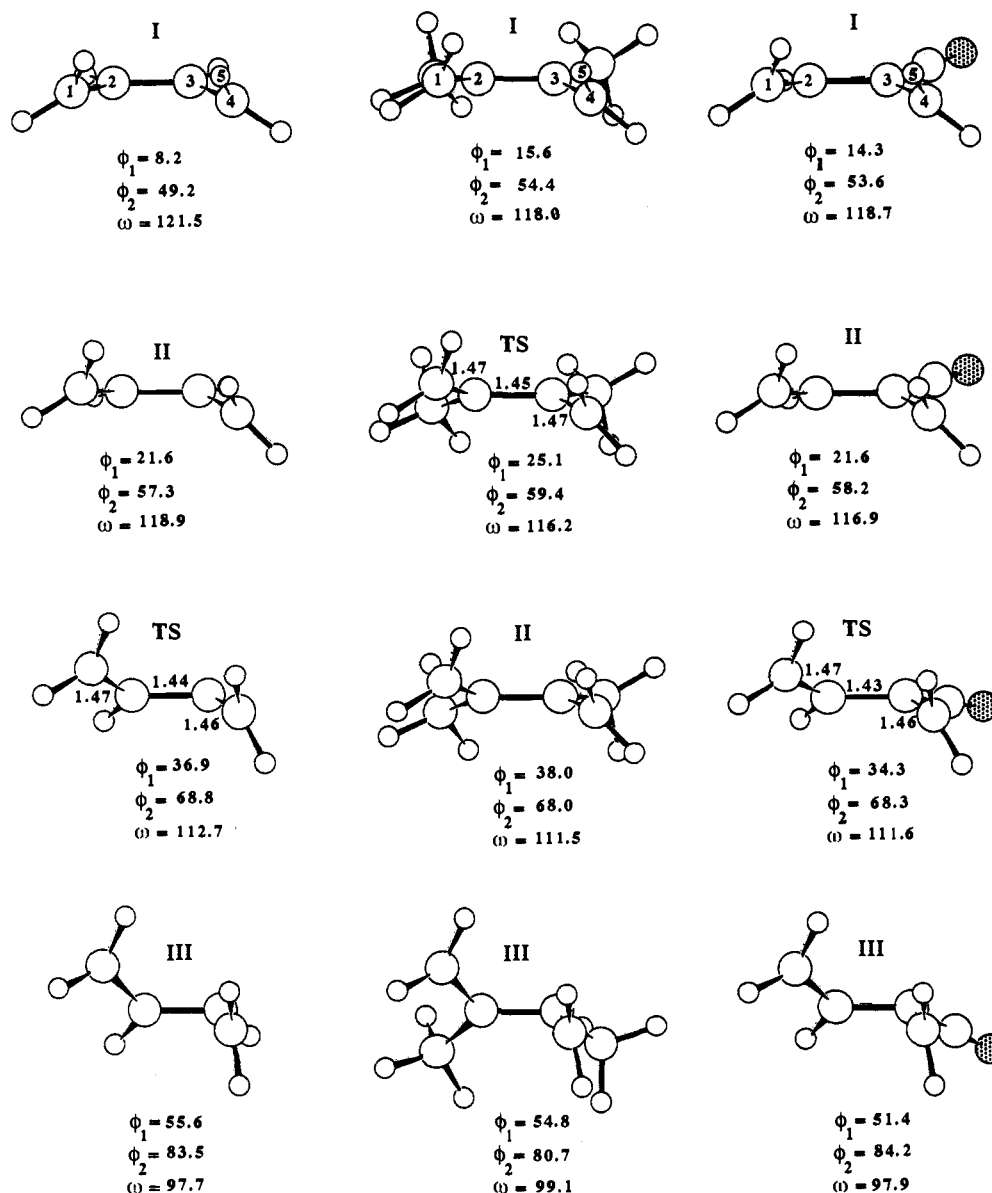


Figure 6. Selected geometries on the *s-cis* IRC profiles (CAS-SCF/4-31G) showing the evolution of the C_4 butadiene (left column), C_4 , 2,3-DMB (central column), and pseudo- C_4 , 2-CNB (right column) equilibrium structures. The values of the structural parameters ϕ_1 , ϕ_2 , and ω are given in degrees. The value of the relevant bond lengths of the three excited-state transition structures TS are given in angstroms.

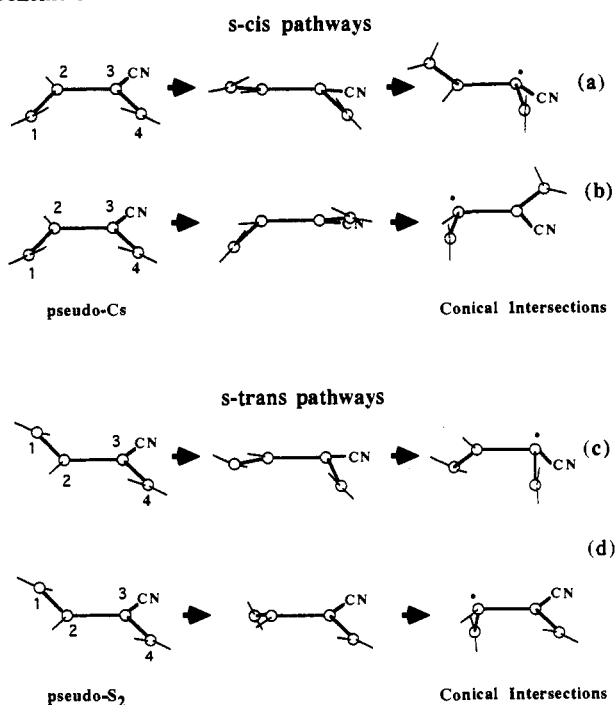
changes monotonically along the IRC. The increase in ϕ_1 along the *s-cis* pathways and the decrease along the *s-trans* pathways is mainly due to the change in the geometry at the C_4 center which passes from planar to pyramidal. This change in pyramidalization affects only the $C_1-C_2-C_3-C_4$ torsion and the substituents on centers C_2 and C_3 do not change their relative position all along the IRC. Thus one observes a striking feature in the *s-cis*-2,3-DMB pathway: two adjacent bulky methyl groups remain rigidly eclipsed from start to end. Secondly, one can observe another general feature associated with the torsional angle about the C_3-C_4 bond, ϕ_2 , defined in Scheme 4. Along the pathways the value of ϕ_2 changes from about 50° (130° for the *s-trans* forms) to 90° , leading to a twisted terminal CH_2 group. The increase of the value of the two torsions ϕ_1 and ϕ_2 leads to a rather large electron unpairing effect along the C_3-C_4 and C_2-C_3 bonds. Thus, along the excited-state pathways the system gradually increases its tetradical character. This is the most important feature of the electronic structure of the conical intersection found in butadienes. Finally, one can observe a rapid decrease of the value of the bending angle ω (see Scheme 4) in the last part of the IRC. The value of ω changes from that of an sp^2 angle (i.e. about 120°) to a value of about 90° . This deformation certainly will introduce a large amount of strain

energy in the system. Further, it permits a non-negligible overlap of the p-orbitals centered on C_2 and C_4 which will be important for the bicyclobutane formation (path c in Scheme 3).

The increase of electron decoupling along the excited-state pathways and the corresponding formation of incipient radical centers create an electronic structure which is sensitive to the presence and position of conjugating substituents. This effect can be seen in 2-CNB and gives rise to chemically distinct excited-state pathways for both the *s-cis* and *s-trans* excited-state regions. The structural changes along these pathways are pictorially illustrated in Scheme 5.

While the IRC corresponding to a and c are similar to those found in butadiene and have already been given in Figures 6 and 7, paths b and d correspond to alternative *s-cis* and *s-trans* pathways where the position of the cyano substituent with respect to the butadiene moiety distortion is different. While in a and c the CN group is connected to a carbon center (i.e. center 3) which rapidly develops radical character along the IRC, in b and d this center remains part of a loose π -system due to the small twisting about the C_3-C_4 bond. The different sequence of structures that lie along the paths a, c and b, d has a major effect on the energy profile of the corresponding CAS-SCF/4-31G IRC. In Figures 8a and 8b we give the result of IRC computations

Scheme 5



along paths b and d. In contrast with the data previously reported (see Figures 5a and 5b) we can see that the presence of the CN group causes a 3–4 kcal mol⁻¹ destabilization with respect to the corresponding pathways of butadiene. In Figures 8c and 8d we have given the geometries and structural parameters of the transition state (TS) and last point (IV) along the two IRC.

The direction of the motion leading to the conical intersection (i.e. to the decay point) is of some relevance to the subsequent reaction path followed on the ground state after decay. If the system arrives at the conical intersection with non-zero momentum then some momentum on the ground-state surface will exist in this direction. This direction of motion can be estimated by examining the direction (a vector) of the IRC computed at the last point (i.e. structure III or structure IV). In Figures 9a and 10a we report two different views of the main components (carbon atom motions) of the IRC vector for the last s-cis and s-trans structures of butadiene, respectively. These IRC directions are qualitatively identical for all reactions (butadiene, 2,3-DMB, and 2-CNB) and exhibit components along ω , ϕ_1 , and ϕ_2 .

The actual structure of the cisoid and transoid butadiene, 2,3-DMB, and 2-CNB conical intersections which are entered via the pathways described above has been fully optimized and characterized using the method described in ref 16. The directions of the NAC and GD vectors (x_1 and x_2 in Scheme 1) have also been determined. In Figures 9b and 10b we show the optimized structure and the major (carbon atom) components of the NAC and GD vectors for the cisoid and transoid conical intersection structures in butadiene. These vectors are qualitatively identical for all reactions (butadiene, 2,3-DMB, and 2-CNB) and exhibit components mainly along the C–C stretching. The geometrical parameters of the various conical intersection structures confirm that they indeed correspond to the end point of the IRC (compare the geometrical parameters in part a and b of the figures). Again, the structural features of the 2,3-DMB (values in brackets) and 2-CNB (values in curly brackets) conical intersection geometries are similar to those of the corresponding butadiene conical intersections.

The NAC and GD vectors provide information about the structure of the potential energy surface surrounding the conical intersection points by defining the orientation of the associated branching space. The most significant point (Figures 9b–10b)

is that the NAC and GD vectors are dominated by various stretching motions of the carbon framework with smaller components in the various torsions. An excited-state system entering the conical intersection with an infinitely slow motion (i.e. neglecting the effect of the motion along the IRC) will emerge on the ground-state sheet moving exclusively in the plane defined by NAC and GD. Thus the initial direction of motion on the ground state will be dominated by stretching motion of the carbon framework.

From the preceding discussion it is now clear that the existence of two excited-state pathways leading to decay via low-energy conical intersections is a general feature of the mechanism of butadiene photolysis and remains basically unaffected by 2,3-dimethyl or 2-cyano substitution. In the following two subsections we discuss the way in which the particular molecular deformation and electronic nature of the excited-state pathways can account for the observed substituent effects in the relative quantum yields and other experimental observations.

(ii) **Rationalization of the Photochemistry of 2,3-Dimethylbutadiene (2,3-DMB) and Related Systems.** In Scheme 1 we have given the general model for the excited-state part of the mechanism of butadiene photolysis that has been confirmed by the numerical data presented in the previous subsection. The actual energy profile between the excited state reactant and the conical intersection depends on whether the reactant is s-cis or s-trans and is sensitive to substituent effects. However, the molecular structures at the conical intersection points, the nature of the NAC/GD vectors and the IRC directions at the moment of decay are basically unaffected by substituents. The nature of the initial ground-state reaction path after decay via the conical intersection will be controlled by dynamical considerations. After the decay, the initial direction of motion on the ground state will be parallel to the direction of the velocity of the system (i.e. to the excited state IRC) but with some component in the plane $x_1 x_2$ in order to conserve total energy at the surface hop. Subsequently, the ground-state relaxation pathway is determined by ground-state valleys which develop as one moves away from the apex of the conical intersection. Thus the energy profile along the IRC in the region of the conical intersection will play an important role. A steep approach to the conical intersection will imply that a large amount of momentum in the IRC direction will be retained in the initial motion on the ground state.

We start our discussion on 2,3-DMB photochemistry by using our data to rationalize some aspects of the general behavior of acyclic butadienes. The s-cis/s-trans isomerization process is well documented in butadiene photochemistry.^{1,3} Remarkably the s-trans \rightarrow s-cis isomerization is 10 times more efficient than s-cis \rightarrow s-trans isomerization in 2,3-DMB as demonstrated by Squillacote and Sample.² After the decay the system needs to conserve a certain amount of the original excited-state motion (i.e. the motion along the IRC) or the absolute quantum yield of s-cis/s-trans isomerization would be negligible. Thus the system needs to rotate on the ground state well beyond the 50° C₁–C₂–C₃–C₄ twisting angle at the conical intersection point to complete the s-trans/s-cis isomerization. If we now examine the IRC energy profiles in Figure 3c,d and the corresponding data for the 2,3-DMB (Figure 4a,b) we can explain why the s-trans to s-cis isomerization should be more efficient than the s-cis to s-trans process in acyclic butadienes. The s-trans pathway to decay is always barrierless and much steeper than the s-cis. Thus the decaying system will enter the ground-state sheet with a higher velocity along the s-trans route.

The major effect of the 2,3-dimethyl substitution in butadiene is the inversion of the ratio of s-cis/s-trans isomerization and cyclobutene formation quantum yields. Matrix isolation experiments have shown that during the photolysis of s-cis 2,3-DMB² production of cyclobutene is strongly favored in complete contrast to the behavior observed for butadiene. Our data show that the

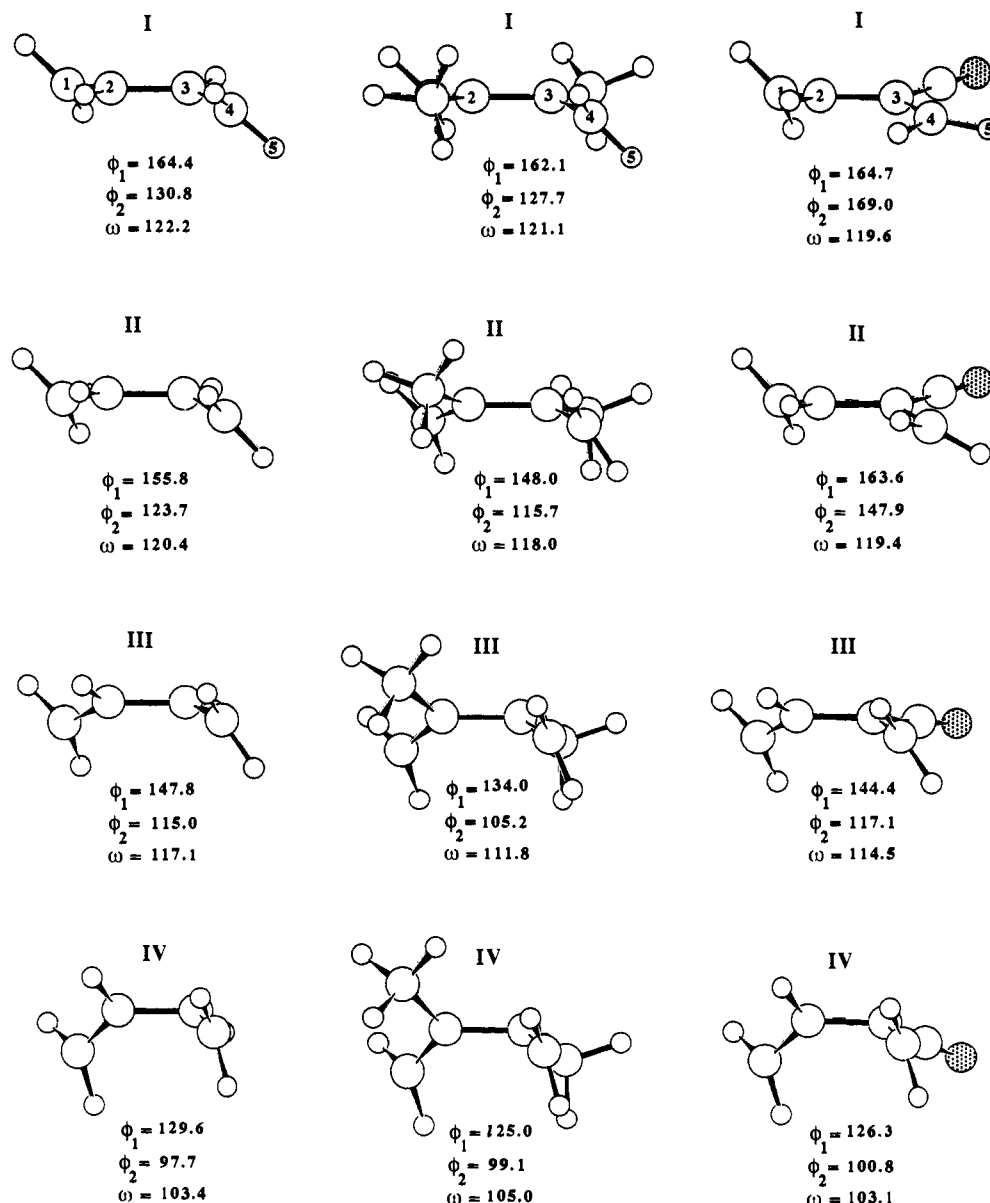


Figure 7. Selected geometries on the *s*-trans IRC profiles (CAS-SCF/4-31G) showing the evolution of the S_2 butadiene (left column), S_2 2,3-DMB (central column) equilibrium structures, and pseudo- C_2/S_2 TS of 2-CNBD (right column). The values of the structural parameters ϕ_1 , ϕ_2 , and ω are given in degrees.

s-cis-2,3-DMB excited-state energy profile (see Figure 4a) is almost barrierless and ends up at a point (point III in Figure 4a) where the energy relative to the *s*-cis reactant is 4.0 kcal mol⁻¹ more stable than for the butadiene system. Such a change in energetics will cause a decrease in the lifetime of the 2,3-DMB excited state C_1 intermediate. Further, the fact that the 2,3-DMB cisoid conical intersection lies in a deeper well than the butadiene cisoid conical intersection implies that the ground-state momentum directed along the excited-state IRC will be larger for 2,3-DMB. From Figure 9a it is clear that the IRC direction is described by components that correspond to both cyclobutene formation and *s*-cis/*s*-trans isomerization. Thus one should observe a general increase in the *total* quantum yield of these photoproducts, but this effect alone does not rationalize the observed change in the quantum yield ratio. Rather the latter effect is explained by a subtle dynamic effect that has its origin in the excited-state motion of the substituents connected to C_2 and C_3 . We now proceed to discuss this point in detail.

During the excited-state motion the substituents on C_2 and C_3 remain essentially eclipsed all along the pathway up to the conical intersection point (see Figure 9b). Thus they accumulate little or no kinetic energy (see also the IRC vector in Figure 9a).

However, the *s*-cis/*s*-trans isomerization of the butadiene moiety requires a 180.0° rotation about the central C_2 - C_3 bond and the substituents on C_2 and C_3 must therefore undergo rotation from the eclipsed (*syn*) to the staggered (*anti*) position on the ground-state surface after decay. At the conical intersection point only a negligible amount of this process has occurred. Thus, after the decay, the substituents connected to C_2 and C_3 must accelerate in opposite directions about the C_2 - C_3 bond. Further each CH_3 group will rotate in the same direction of the terminal CH_2 group connected to the same carbon atom. The driving force which sets the two substituents in motion will be provided by the sudden change in force field experienced by the system after the decay. In fact the high degree of pyramidalization achieved at C_3 during the excited state motion results in a highly strained ground state geometry which rapidly relaxes by moving the substituent on C_3 as illustrated in Scheme 6 (see arrow on decay point structures).

However, the moment of inertia of a CH_3 group is roughly 35 times larger than that of a H atom thus a CH_3 group accelerates 35 times slower. Thus acceleration of 2,3-DMB in the *s*-cis/*s*-trans direction will be much less than in butadiene and the alternative ring-closure process results highly favored. This model would predict efficient *s*-cis/*s*-trans isomerization if there were

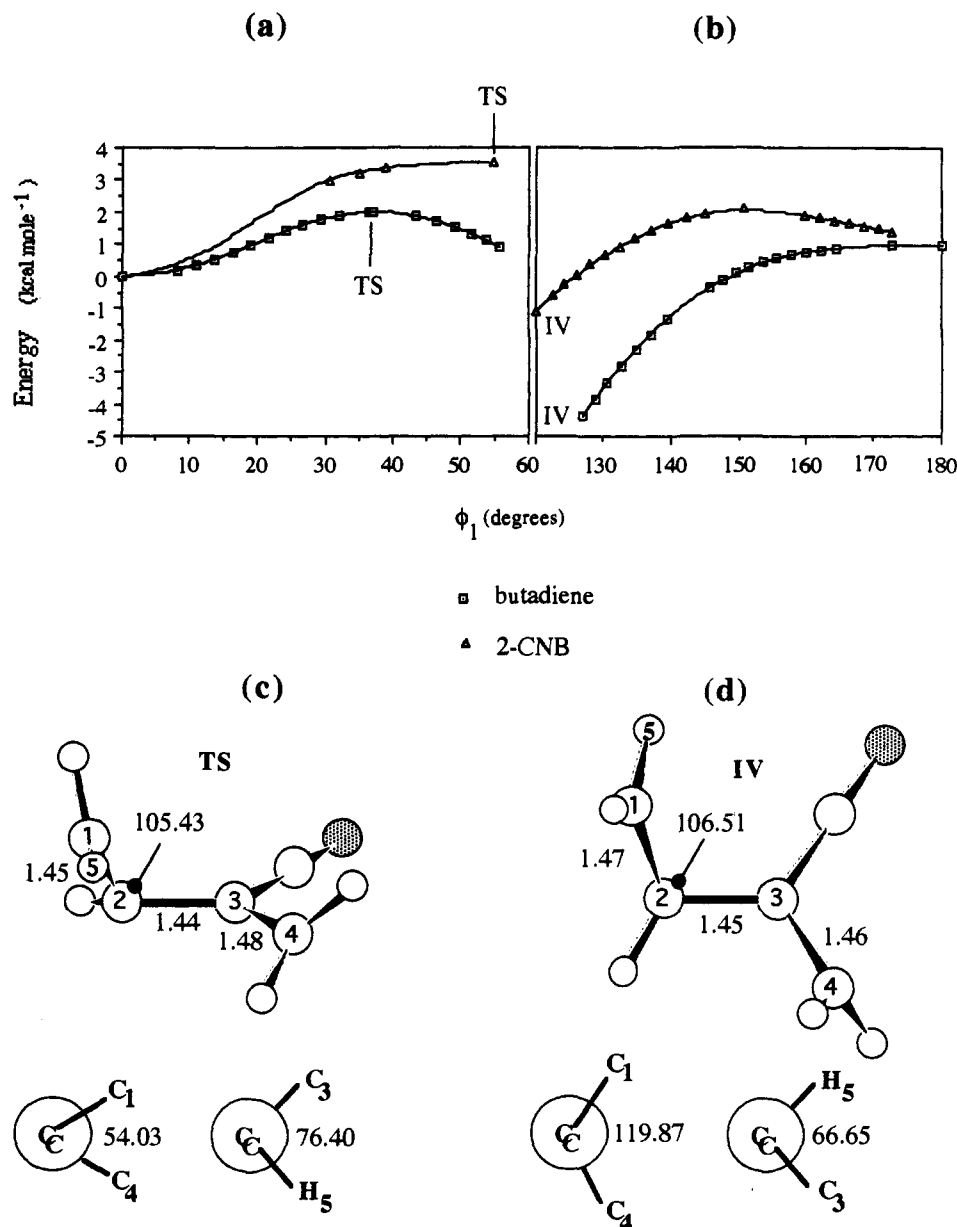


Figure 8. Comparison of butadiene and 2-CNB excited-state energy profiles along the excited-state alternative *s-cis* (a) and *s-trans* (b) IRC computed at the CAS-SCF/4-31G and plotted against the torsional angle ϕ_1 (see Scheme 4). Structure c is the transition state "pseudo- C_2/C_3 -*s-cis* TS" occurring along path b in Scheme 5 and structure d is the last optimized point along the *s-trans* IRC corresponding to path d in Scheme 5. The relevant structural parameters for these structures are given in angstroms and degrees.

at least one H in position 2 or 3. Indeed, the experimental results for the photolysis of isoprene (2-methylbutadiene) and 2-isopropylbutadiene (an even larger substituent) agree with this prediction.^{2,3} Thus, on the one hand the IRC direction at the cisoid conical intersection has components in both the directions of ring-closure and *s-cis/s-trans* isomerization and one should observe a basically unchanged photoproduct quantum yield ratio. On the other hand, the preference for ring-closure in 2,3-DMB is explained by the large inertia of the eclipsed CH_3 substituents at C_3 and C_2 which inhibits motion along the *s-cis/s-trans* isomerization path.

The low quantum yield observed when the *s-cis*-butadiene moiety is constrained also merits discussion. This situation arises when carbon C_2 and C_3 are connected by short hydrocarbon chains (1 or 2 CH_2 units) or by a ring system which results in small C_2 - C_3 -chain (α_1) and chain- C_2 - C_3 (α_2) bending angles^{16,18,19} as illustrated in Scheme 7 (the reported values of α_1 have been computed using MM_2 molecular mechanics calculations). The

observations of Aue¹⁸ in the series 1,2-bismethylenecyclobutane, 2,3-bismethylenecyclo[2.2.1]heptane, 1,2-bismethylenecyclopentane, 1,2-bismethylenecyclohexane are summarized in Scheme 7. The quantum yield for the production of cyclobutene decreases as the values of α_1 and α_2 are decreased in the corresponding reactant.

The same trend has been observed by Leigh^{16,19} in the photochemistry of 1,2-bismethylenecycloalkanes. In the case of 1,2-bismethylenecyclobutane¹⁸ and 1,2-bismethylenecyclobutane¹⁶ no product has been detected. Again this behavior finds a convincing explanation in the deformation of the butadiene moiety along the *s-cis* pathway observed for the parent butadiene and 2,3-DMB (Figure 6). Along this pathway the value of one of the bending angles (ω in Scheme 7) must change from the sp^2 equilibrium value (120°) at the C_2 , minimum to 90.0° at the conical intersection. If the adjacent bending angle (α_1 in Scheme 7) is already highly strained, the energy must rise very rapidly on distorting the system toward the conical inter-

(18) Aue, D. H.; Reynolds, R. N. *J. Am. Chem. Soc.* 1973, 95, 2027.

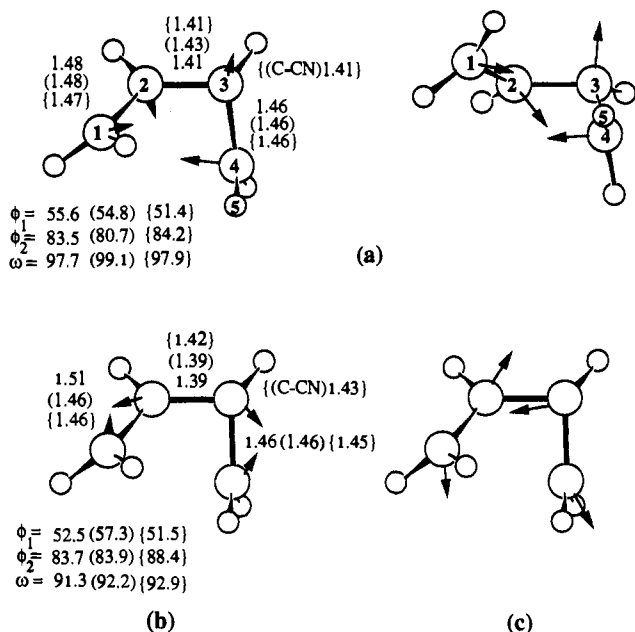


Figure 9. (a) Different views of the structure of the last optimized point along the *s-cis*-butadiene, 2,3-DMB (values in brackets), and 2-CNB (values in curly brackets) IRC (structures III in Figure 6). The sets of arrows indicate the main atomic displacements corresponding to the IRC vector evaluated at this point. (b) Optimized CAS-SCF/4-31G conical intersection structure from excited-state *s-cis*-butadiene 2,3-DMB (values in brackets), and 2-CNB (values in curly brackets). The arrows indicate the direction of the main atomic displacements corresponding to the NAC vector. (c) Same as b but the arrows indicate the direction of the main atomic displacements corresponding to the GD vector. The values of the more relevant structural parameters are reported in angstroms and degrees.

section. This will increase both the barrier to the conical intersection and the lifetime of the excited-state intermediate. This theoretical interpretation predicts a regular increase in product quantum yields by gradual relaxation of the α_1 and α_2 angles in accordance with the trend¹⁸ shown in Scheme 7 and with the work of Leigh.^{16,19} Thus highly strained α_1 and α_2 angles may actually impair the production of all butadiene photoproducts by increasing the excited-state barrier to the conical intersection. The consequent increase in excited-state lifetime should also cause an increase in fluorescence quantum yield.

Finally, we remark on the general efficiency of double-bond *cis/trans* isomerization. This process is undoubtedly the most efficient photochemical reaction in open-chain butadienes and is unaffected by substituents on C₂ and C₃. Deuterium labeling experiments show that double-bond *cis/trans* isomerization occurs 500 times and 150 times faster than *s-cis/s-trans* isomerization in *s-trans*-2,3-DMB and *s-cis*-2,3-DMB, respectively.² The same trend is also observed in other substituted systems.^{16,20,21} The details of the molecular structures along the IRC for butadiene and 2,3-DMB shown in the Figures 6 and 7 give a theoretical rationalization of these observations. The ϕ_2 torsional angle (see Scheme 4) describing *cis/trans* isomerization of one of the two double bond of butadiene increases along the excited state pathway up to a value of about 90.0° at the decay point. Thus the decay of the excited state at the conical intersection occurs at a geometry where the double bond is completely broken by twisting. This geometry corresponds to that of a thermal *cis/trans* isomerization transition structure.

The mechanism described above for the double-bond *cis/trans* isomerization involves the evolution of the system along the same

(19) Leigh, W. J.; Zheng, K. *J. Am. Chem. Soc.* 1991, 113, 4019. *Errata: Ibid.* 1992, 114, 796.

(20) (a) Squillacote, M. E.; Semple, T. C. *J. Am. Chem. Soc.* 1987, 109, 892. (b) Squillacote, M. E. Private communication.

(21) (a) Vanderlinden, P.; Boué, S. *J. Chem. Soc. Chem. Commun.* 1975, 932. (b) Boué, S.; Srinivasan, R. *J. Am. Chem. Soc.* 1970, 92, 3226.

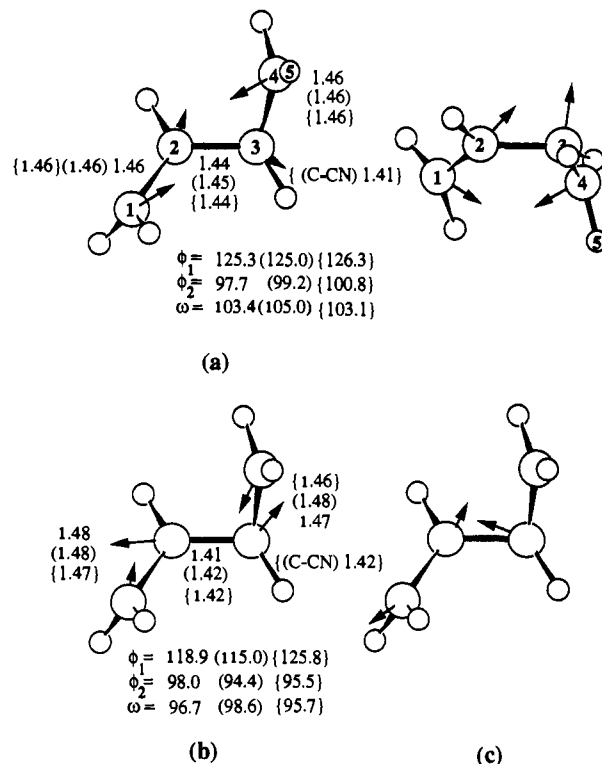


Figure 10. (a) Different views of the structure of the last optimized point along the *s-trans*-butadiene, 2,3-DMB (values in brackets), and 2-CNB (values in curly brackets) IRC (structures IV in Figure 7). The sets of arrows indicate the main atomic displacements corresponding to the IRC vector evaluated at this point. (b) Optimized CAS-SCF/4-31G conical intersection structure from excited-state *s-trans*-butadiene, 2,3-DMB (values in brackets), and 2-CNB (values in curly brackets). The arrows indicate the direction of the main atomic displacements corresponding to the NAC vector. (c) Same as b but the arrows indicate the direction of the main atomic displacements corresponding to the GD vector. The values of the more relevant structural parameters are reported in angstroms and degrees.

²Ag excited state pathway leading to the other 2,3-DMB photoproducts. In contrast to this mechanistic view, Squillacote and Semple propose a different reaction scheme² in which the double-bond *cis/trans* isomerization occurs via an independent excited state route involving the formation of an allyl cation methyl anion intermediate. Our results definitely show that zwitterionic character does not develop along the IRC starting from either the *s-cis*- or *s-trans*-butadiene minima. However, this does not preclude the existence of different relaxation pathways starting near the Franck–Condon region. In the vicinity of the Franck–Condon region the system could indeed “branch” along two different reaction coordinates, one leading to the covalent ²Ag potential energy surface,²³ the other continuing on the ionic ¹Bu surface into a zwitterionic intermediate well.

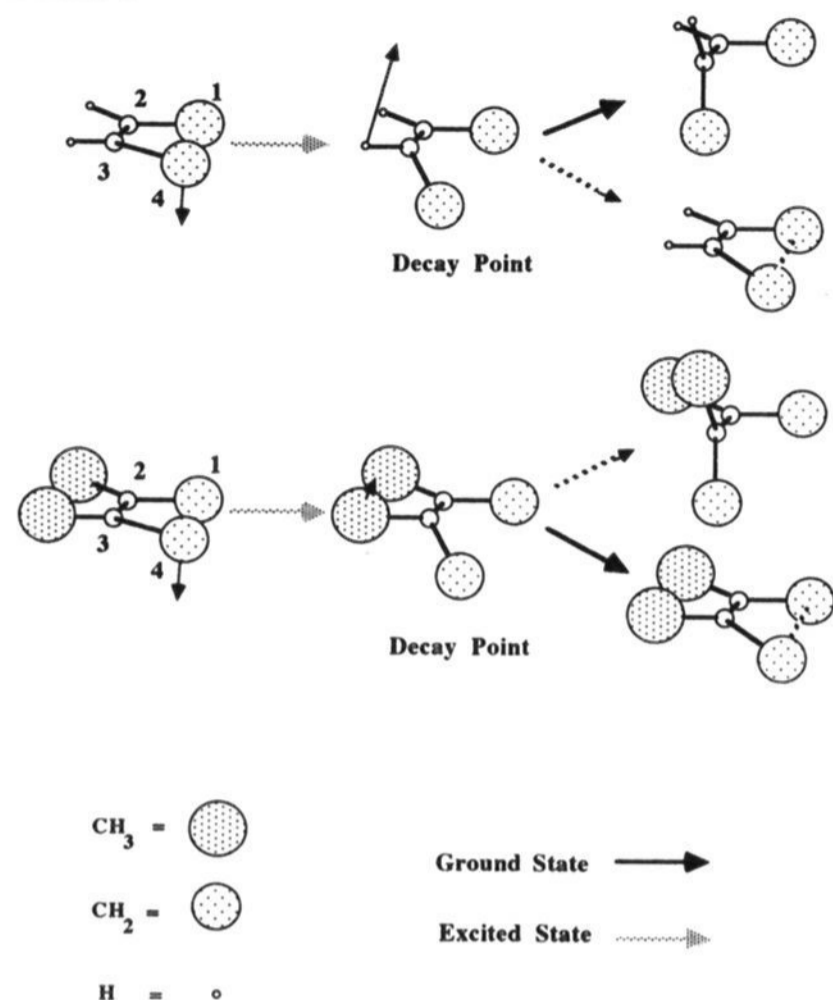
Careful theoretical investigation of the excited-state zwitterionic structures of butadiene have been reported by other workers.^{22,24} Recent results²² indicate that there is a rather small difference in excitation energy between the ¹Bu spectroscopic

(22) Serrano-Andres, L.; Merchan, M.; Nebot-Gil, I.; Lindh, R.; Roos, B. O. *J. Chem. Phys.* 1993, 98, 3151–3162.

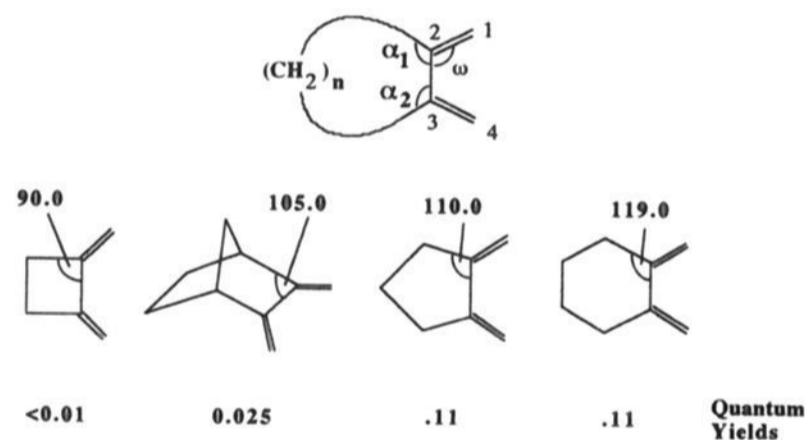
(23) In the case of isoprene it has been seen that after photoexcitation the system crosses from the spectroscopic (1Bu) state to the covalent 2Ag state. This crossing occurs in a few femtoseconds under a very small geometrical distortion from the vertical excitation region (Trulson, M. O.; Mathies, R. A. *J. Phys. Chem.* 1990, 94, 5741–7). The authors of this study also suggest that any significant geometrical distortion, including *cis/trans* isomerization, must occur on the 2Ag (covalent) potential surface.

(24) (a) Bruckmann, P.; Salem, L. *J. Am. Chem. Soc.* 1976, 98, 5037. (b) Bonacic-Koutecky, V.; Persico, M.; Dohnert, D.; Sevin, A. J. *J. Am. Chem. Soc.* 1982, 104, 6900. (c) Aoyagi, M.; Osamura, Y.; Iwata, S. *J. Chem. Phys.* 1985, 83, 1140. (d) Aoyagi, M.; Osamura, Y. S. *J. Chem. Phys.* 1989, 111, 470. (e) Ohmine, I. *J. Chem. Phys.* 1985, 83, 2348.

Scheme 6



Scheme 7



state and the forbidden 2^1A_g state in *s-trans*-butadiene (few kcal mol⁻¹). Further, Aoyagi, Osamura et al.^{24c,d} have used ab-initio CAS-SCF with MIDI-4+ diffuse function basis sets to optimize the geometrical structure of the excited-state zwitterionic intermediates Z_1 (allyl cation methyl anion). Z_1 shows a highly pyramidalized 90° twisted methyl anion and a planar allyl cation where the positive charge is almost completely localized on the carbon adjacent to the negative center. However, at this zwitterionic structure, the excited-ground state energy gap is too large to explain the rapid radiationless decay and lack of fluorescence observed in butadiene. Ohmine has documented (MRDCI with Dunning basis set) a surface-crossing mechanism^{24e} involving facile allyl cation to methyl anion H-shift that could account for fast radiationless decay. We have redetermined the Z_1 zwitterion structure using CAS-SCF with a much better basis set (DZ+ d-type polarization and sp-type diffuse functions). Our computations confirm the results of Ohmine et al. At this zwitterionic minimum, the ground state lies about 30 kcal mol⁻¹ lower in energy and the 2^1A_g state (which has a diradical structure) is located 45 kcal mol⁻¹ higher in energy. Thus in this region the S_1 state is definitely of zwitterionic nature and correlates with the spectroscopic state 1^1Bu . We have also found that the zwitterion lies basically at the same energy of the region of the $S_1 2^1A_g$ -minima in Figure 1.

The hypothesis of the involvement of an excited state zwitterionic intermediate in the photochemistry of butadienes has

also been tested experimentally. For instance, Dauben has observed the trapping of an intermediate capable of adding CH₃-OH during the photolysis of cyclic butadienes held in a *s-transoid* conformation.^{25a,b} However, other experimental results indicate that no direct photoaddition of CH₃OH occurs in acyclic butadienes but that in these systems the reaction takes place in the ground state of bicyclobutane (one of butadiene photoproducts) and also requires the presence of small quantities of acid.^{25c,d} Squillacote et al. have reported indirect evidence for the intermediacy of an allyl cation methyl anion intermediate during the double-bond *cis/trans* isomerization of 1-methylbutadiene (1,3-pentadiene).^{20a} Their observation indicates that the fastest rotating terminal methylene is the unsubstituted one, in agreement with the existence of such intermediate (i.e. the CH₃ group stabilizes the allyl cation part). On the other hand this observation can be also simply explained on the basis of a momentum of inertia argument similar to the one we have used above for explaining the ratio of *s-cis/s-trans* isomerization and cyclobutene formation quantum yields. In other words the less-substituted methylene rotates faster. This interpretation seems to be in complete agreement with the 2^1A_g reaction pathways reported in this work. On the other hand the same author has recently found that in 1,1,1-trifluorohexa-2,4-diene the heavier group (CHCF₃) rotates faster than the lighter group (CHCH₃).^{20b} This observation could be taken as evidence for a zwitterionic mechanism since CF₃ could stabilize the negative charge of a Z_1 zwitterion.

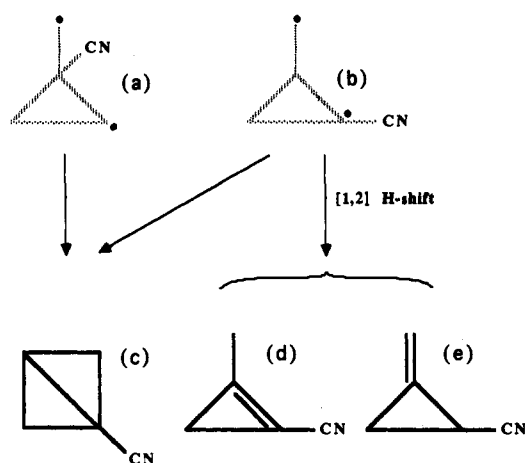
In this work we concentrate on the covalent excited-state reaction paths. However, one must recognize that the possible existence of a competitive zwitterionic route to photochemical double-bond *cis/trans* isomerization in butadienes cannot be excluded and the question remains open as to the relative populations of the zwitterionic channel and the one documented in this work. An answer to this question can only be provided by further computational and experimental investigation. As mentioned in section 2, a rigorous description of the relationship between the zwitterionic and the covalent pathways will require the evaluation of the dynamic correlation contribution to the electronic energy of the system.

(iii) **Rationalization of the Photochemistry of 2-Cyanobutadiene (2-CNB).** The photoproduct quantum yield ratios of butadiene depend, in part, on the relative efficiency of the different ground-state electron recoupling processes shown in Scheme 3. Obviously electron recouplings requiring highly strained conformations of the butadiene moiety and/or large ground-state deformation of the geometry at the decay point will be unfavored. Thus the quantum yield of the photoproducts generated via these kinds of processes will be very low. This situation is expected for three-membered ring photoproducts (see path c in Scheme 3) like cyclopropenes²¹ and even more in production of strained bicyclic systems like bicyclobutanes.^{5,21} However, both these species have been detected in very low quantum yields in acyclic butadienes.

As we have discussed previously, there are two types of 2-CNB excited-state reaction paths: one (lowest energy, corresponding to a and c in Scheme 5) involves the pyramidalization of the carbon bearing the CN (carbon C₃), the other (at higher energy, corresponding to b and d in Scheme 5) involves the pyramidalization of the unsubstituted carbon (carbon C₂). The CN group causes a 1 kcal mol⁻¹ decrease of the barrier along the *s-cis* pathway and an about 0.5 kcal mol⁻¹ stabilization of the *s-trans* route. However, this fact alone cannot explain the preference for photochemical reactivity of 2-CNB to give the bicyclobutane 1-CNBCB.⁴ A rather simple explanation can be derived on the basis of the fact that, as pointed out in section 3, carbon C₃ develops, during the excited-state motion, a radical character.

(25) (a) Dauben, W. G.; Poulter, C. D. *Tetrahedron Lett.* **1967**, 3021. (b) Dauben, W. G.; Spitzer, W. A. *J. Am. Chem. Soc.* **1968**, *90*, 802. (c) Barltrop, J. A.; Browning, H. E. *Chem. Commun.* **1968**, 1481. (d) Dauben, W. G.; Hart Smith, J. H.; Saltiel, J. *Org. Chem.* **1969**, *34*, 261.

Scheme 8



Since the CN group is known to favor formation and stability of radical centers it might be the primary cause of both the energetic changes computed along the excited-state pathways and of the observed increase in quantum yield of 1-CNBCB. Thus the CN group simply stabilizes the radical center on C_3 at the beginning of ground-state relaxation. This stabilization effect will hinder the subsequent radical pairing to C_4 or C_2 required to lead to *s-cis*/*s-trans* isomerization and reactant back-formation (see a and d in Scheme 3) or cyclobutene formation respectively (see b in Scheme 3). Rather, 2-cyano substitution would enhance production of the ground state 1,3-diradical intermediate (see c in Scheme 3) which is a precursor to both bicyclobutane (from *s-trans*-butadienes²⁶) and 1-methylcyclopropene (from *s-cis*-butadienes²¹). We should note that because the CN group affects the stability of the radical center on C_3 , the ground-state force field will be modified as will the shape of the ground-state potential energy surface near the decay point. Thus in the case of a 2-CNB the substituent effect seems to be due to a change in the driving force for the ground-state relaxation.

The computational study of the ground-state pathways leaving the conical intersection region is extremely difficult due to the lack of stationary point in this region. Despite our efforts, it has not yet been possible to clearly document the pathways leading to 1,3-diradical species. Further, the location of the 1,3-diradical intermediate has also been problematic. The result of a series of CAS-SCF/4-31G optimization attempts has indicated that these intermediates correspond, for both 2-CNB and butadiene, to flat inflection points on the potential energy surface which ultimately evolve to bicyclobutanes. Thus 1,3-diradicals are actually transient species (indicated as dashed structures a and b in Scheme 8) on a concerted (asynchronous) pathway to bicyclobutanes.

Evidence for a cyano-substituent effect on the stability of the excited-state decay routes of 2-CNB has already been documented in section 3i above. In Scheme 5 we have schematically reported four possible *s-cis* and *s-trans* excited-state pathways (path a, b, c and d) for 2-CNB. These pathways lead to different conical intersection structures where the highly pyramidal radical center on C_3 is either substituted (path a and c) or unsubstituted (path b and d). The corresponding IRC energy profiles (see Figures 5a,b and Figures 8a,b) show that when carbon C_3 does not bear a CN group the corresponding energy profile is 4 kcal mol⁻¹ higher in energy. While this feature provides support to the hypothesis of radical stabilization at the C_3 center, the data presented are also consistent with an efficient production of only one type of "transient" ground state 1,3-diradical corresponding to structure b in Scheme 8.

This theoretical prediction cannot be tested on the basis of the available experimental results on 2-CNB photochemistry. However, a search for direct or indirect evidence supporting this prediction is highly desirable as this would increase one's confidence in the general validity of the idea that conical intersection mechanisms control butadiene photochemistry. A realistic possibility would involve matrix isolation photolysis of *s-cis*- and *s-trans*-2-CNB, search and characterization of 1-methylcyclopropenes (d) and/or 1-methylenecyclopropanes (e) in the product mixture.

4. Conclusions

In this article we have documented the details of a general model (Scheme 1) for the excited-state part of the mechanism for the photolysis of butadienes. While the general features of the model (the molecular structures at the conical intersection points, the nature of the NAC/GD vectors, and the IRC directions at the moment of decay) are not sensitive to substituent effects at C_2 and C_3 , the actual energy profile between the excited-state reactant and the conical intersection depends on whether the reactant is *s-cis* or *s-trans* and is sensitive to substituent effects. The nature of the ground-state reaction after decay via the conical intersection will be controlled mainly by the direction of the velocity of the excited-state system at the moment of the decay (i.e. by the direction of the final part of the excited-state IRC), and by the nature of the ground-state valleys which develop as one moves away from the apex of the conical intersection. Consequently, the effect of substituents is mainly related to both dynamical features and nature of the (ground-state) force field.

The *s-cis* and *s-trans* pathways located on the first excited state of butadiene, 2,3-DMB, and 2-CNB all describe a similar evolution of the photoexcited reactants. Along the *s-cis* pathways which connect the (C_2) reactant well to an asymmetric (cisoid) conical intersection structure there is a transition state with a rather low (2.0–0.2 kcal mol⁻¹) barrier. In contrast the *s-trans* pathway, which starts in a very flat S_2 region, is barrierless and ends in a (transoid) conical intersection point that corresponds to the lowest energy point (i.e. the absolute minimum) on the excited-state surface. In 2,3-DMB the reaction paths are stabilized relative to butadiene due to the relief of steric repulsion along both the *s-cis* and *s-trans* pathways. Along the 2-CNB pathways the substituent effects reflect the fact that the CN group is actually part of the reactant π -system. Indeed the photoexcited 2-CNB can enter, from both the *s-cis* and *s-trans* reactant wells, two distinct pathways which differ in the position of the CN group respect to the deformation of the butadiene moiety as shown in Scheme 5. Our results suggest that when the center connected to the CN group develops a radical character along the pathway (C_3 along paths a and c in Scheme 5) the corresponding energy profile is stabilized respect to that of the unsubstituted system. In contrast if the CN group is connected to a carbon center which does not develop this character (C_2 along paths b and d in Scheme 5) the energy profile is destabilized.

Substituents mainly affect the ground-state relaxation process occurring just after the decay and are related to the specific type of structure and momentum that the photoexcited reactant assumes during the path to the conical intersection. Along this path the main structural features are (i) one of the two central carbons (say C_3 in Scheme 4) of the butadiene moiety becomes highly pyramidalized while the other remains basically planar, (ii) the terminal methylene connected to the pyramidalized carbon center (C_3 in Scheme 4) rotates by almost 90°, (iii) the bending angle $C_2-C_3-C_4$ decreases continuously down to a value near 90°, (iv) the substituents on C_2 and C_3 remain basically eclipsed (in *s-cis*-butadienes) or staggered (in *s-trans*-butadienes) during the excited-state motion. The latter structural feature gives rise to a dynamic effect in *s-cis*-2,3-DMB photochemistry. During ground-state relaxation, the heavy CH_3 group accelerates about

(26) (a) Dauben, W. G.; Wipke, W. T. *Pure Appl. Chem.* 1964, 9, 539. (b) Bartrop, J. A.; Browning, H. E. *J. Chem. Soc. Chem. Commun.* 1968, 1481. (c) Dauben, W. G.; Ritscher, J. S. *J. Am. Chem. Soc.* 1970, 92, 2925.

35 times slower than a H atom so that the *s-cis* → *s-trans* isomerization motion in 2,3-DMB is substantially hindered causing a decrease in the production of the *s-trans* form and an increase in the production of 1,2-dimethylcyclobutene. This change in photoreactivity is consistent with the effects observed in both the *s-trans*-butadiene/cyclobutene quantum yield ratio and the absolute quantum yield of cyclobutene which changes from 0.04 in butadiene²⁷ to 0.12 in 2,3-DMB.¹⁸

The nature of ground-state valleys which develop as one moves away from the apex of the conical intersection seems to control the nature of the substituent effect in 2-CNB. The observed changes in the relative quantum yield of bicyclobutane and cyclobutene are related to an effect of the cyano substituent on the energetic stability of the ground-state pathways leading to these two products. The CN group is known to stabilize a radical center which in turn results in the development of ground-state

valleys leading to the transient 1,3-diradical intermediate shown in Scheme 3 and thus to bicyclobutane. The same effect should also lower the production of cyclobutene from *s-cis* butadienes. In fact the more-stable radical center on C₃ makes the electron recoupling between the C₂ and C₃ (necessary to the formation of cyclobutene; see b in Scheme 3) energetically less favored. The intermediacy of 2-cyanomethylenecyclopropane (see a in Scheme 8) rather than 1-cyanomethylenecyclopropane (see b Scheme 8) transient diradicals may be tested as suggested in the previous section.

Acknowledgment. This research has been supported in part by the SERC (UK) under grant number GR/G 03335. The authors are also grateful to IBM for support under a Joint Study Agreement. All computations were run on an IBM RS/6000. The authors are also grateful to I. N. Ragazos who performed some of the computations and to W. J. Leigh for supplying preprints of unpublished work.

(27) Boue, S.; Rondelez, D.; Vanderlinden, P. in *Excited State in Organic Chemistry and Biochemistry*; Pullmann, B., Goldblum, N., Eds.; Reidel: Dordrecht, 1977; p 119.