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On the Effects of Methyl Substitution on the Excited States of Butadiene

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Abstract: The effects of methyl substitution on the excited-state properties of butadiene are studied. Hyperconjugation and inductive effects are considered in detail and it is shown that the semiempirical parametrization normally used to account for the latter may be justified on the basis of ab initio calculations. The spectroscopic red shift resulting from methyl substitution in butadiene has two origins. In 1-methylbutadiene it is due to hyperconjugation while in 2-methylbutadiene inductive mixing between the optically forbidden A_g^- state and the allowed B_u^+ state is found to be important. The description of these effects within the framework of MO theory requires that doubly excited configurations be included in the CI scheme; however, they are intuitively obvious from consideration of valence bond structures. Charge distributions are strongly affected by the inclusion of doubly excited configurations and the A_g^- and B_u^+ states are found to have reverse directions of polarization. The CNDO/S method is shown to be incapable of properly treating inductive effects and may be replaced, for the compounds under consideration, by a π electron scheme in which the π orbitals of the methyl group have been appropriately parametrized.

Introduction

Methyl substitution in conjugated molecules has pronounced effects on absorption spectra. These often arise from conformational changes induced by steric hindrance[2] as is the case, for example, in retinals, the chromophore of the visual pigments.[3] In addition, there are always intrinsic changes in electronic structure leading generally to 5–10-nm red shifts per methyl group (Woodward's rules[4]). Synthetically modified retinals where methyl groups have been added or deleted have been used extensively in visual pigment research and large spectroscopic and photochemical effects have been observed.[5] Our interest in understanding these effects has led us to consider the modifications in the excited-state properties of polyenes that result from methyl substitution.

Theoretical studies of methylation in olefins have been primarily concerned with ground-state properties and have been based both on semiempirical and ab initio calculations employing single determinental wave functions.[6-8] Using propene and methylacetylene as prototypes it was found, for example, that in the absence of steric hindrance the main effect of methylation is the polarization of the π molecular orbitals of the chromophore such that substituted positions lose electron density.[6-8]

In the present paper we take *trans*-butadiene as a prototype of linear polyenes and discuss charge distributions and spectral shifts in its methylated derivatives. Some spectroscopic effects can be understood in terms of ground-state properties while in others a detailed description of excited states is required. Of particular interest is the influence of doubly excited configurations on the calculated quantities. Attempts to account for the spectroscopic effects of methyl substitution have been reported previously.[9-11] However, no general agreement seems to exist as to the relative importance of the inductive and hyperconjugation effects and this question and the related consequences of double excitations are treated here in some detail.

The main absorption band in essentially all polyenes corresponds to a transition from the ground state to an excited state of B_u^+ symmetry. This state has generally been considered to be the lowest singlet; however, recent experimental studies on a number of polyenes have revealed a weakly allowed transition at longer wavelengths than the main band[12] (see also below). π electron calculations which include doubly excited configurations in the CI scheme predict the existence of a state of A_g^- symmetry below the B_u^+ state[13] (although calculations using only single excitations place the A_g^- state at significantly higher energies). Thus there seems to be excellent agreement between theory and experiment for the longer polyenes.

The situation for the shorter polyenes such as butadiene is less clear since no absorption band at longer wavelengths than the main transition has been detected experimentally.[41] However, π electron calculations on butadiene indicate that the A_g^- state is still below the B_u^+ with a small energy difference separating the two states.[13] A number of extensive ab initio calculations have also been carried out on butadiene.[14]

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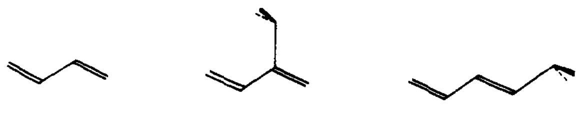


Figure 1. Butadiene, 2-methylbutadiene, and 1-methylbutadiene.

In agreement with the π electron studies the A_g^- state is also placed below the B_u^+, although there is uncertainty as to the identity and character of the strongly allowed B_u^+ state. The implications of these results for our own study will be considered in more detail below.

In this paper we show that the effect of methylation on the excited states of butadiene includes the mixing of the A_g^- and B_u^+ states, particularly for interior positions. This is found to have important spectroscopic consequences. Since our ultimate aim is to treat the effects on longer polyenes, including visual pigments where unusually large methyl induced shifts have been observed,[3,5] we have attempted to develop a reliable parametrization for the methyl group within π electron theory. For molecules somewhat smaller than retinal CNDO/S[15] calculations are feasible and these should in principle be preferred since all valence electrons, including those of the methyl group, are explicitly taken into account. However, we show below that all CNDO-like theories in their standard form offer little improvement over π electron calculations in their treatment of methyl substitution.

In Appendix A we develop a PPP parametrization which is found to be equivalent to the CNDO/S method in its treatment of methyl substitution in π electron systems. The nature of this study has required that we employ a number of parametrization schemes. For example, it has been shown[13] that different parameters are required by PPP calculations using either singly or doubly excited configurations and these of course are different than those used in the CNDO/S method. However, we have, as much as possible, attempted to make the PPP calculations compatible with the CNDO/S calculations. Valence bond calculations have also been carried out so as to illustrate the effects of methyl substitution on particular states in graphical terms.

Definition of the Inductive Effect and Hyperconjugation

Apart from any conformational changes, the effects of methyl substitution involve both inductive interactions and hyperconjugation.[16-18] We first show that if these are defined in quantitative terms then the inductive effect is not invariant under transformation of basis.

Consider butadiene and two of its methylated derivatives (Figure 1). All three molecules have the same plane of symmetry so that it is possible, in each case, to decompose the Fock matrix into two distinct blocks. One block contains the σ orbitals while the other contains the π orbitals including those of the methyl group. These include one p_π orbital centered on the methyl carbon and another pseudo-p_π orbital constructed from the two out-of-plane hydrogenic orbitals. Since most of the information concerning π electron transitions may be extracted from the π block of the Fock matrix, it is convenient to have a definition of hyperconjugation and inductive effects with reference to this block.[19] Hyperconjugation results from nonzero off-diagonal matrix elements between π orbitals of the chromophore with the π (or pseudo-π) orbitals of a methyl group. The largest interaction is of course with the carbon atom bonded to the methyl. The inductive effect may be defined as the change in the diagonal matrix elements of the chromophore's π orbitals induced by the presence of the methyl group.[18] Obviously the inductive effect involves both the σ and π charge distributions, as well as other factors,[6,19] and is therefore a complicated concept whose magnitude is not easy to predict.

Considerable controversy has surrounded the uncertainty as to the relative importance of hyperconjugation and the inductive effect.[16-21] With respect to the definitions given above it appears that a major difficulty involves the sign of the inductive effect. That is, if i denotes a p_π orbital adjacent to a methyl and j denotes a p_π orbital located further away, one wants to know which of the two matrix elements, F_{ii} or F_{jj}, is larger. The semiempirical approach, as based, for example, on ionization potential data,[11] normally assumes that methyl substitution increases F_{ii} in the substituted position (in most cases this means a decrease in absolute value) and this may be shown, as expected, to result in a decrease in electron density at that position. However, in a detailed study of methylacetylene, Newton and Lipscomb[7] have shown the opposite; the diagonal matrix element of the substituted position had a larger negative value even though the unsubstituted position was richer in electron density.

The discrepancy is, however, only an apparent one, and results from the fact that a different basis set is employed in both cases. In order to illustrate this point we have carried out STO-3G calculations on propene. Expressing the F_{ii} in terms of Slater orbitals we find, in agreement with Newton and Lipscomb,[7] that the diagonal element for the substituted position (-2.44 eV) is more negative than that of the unsubstituted position (-2.19 eV), even though the π charge density is lower ($p_{ii} = 1.031$ for the unsubstituted position and 0.97 for the substituted position). However, Slater orbitals constitute a nonorthogonal basis set while semiempirical calculations tacitly employ an orthogonal basis (albeit undefined). Thus a more appropriate comparison should be made between semiempirical parameters and ab initio results transformed into an orthogonal basis. Indeed, when the Fock matrix for propene is transformed into Lowdin orbitals F_{ii} for the substituted position now exceeds F_{ii} for the unsubstituted position by over 0.4 eV while the charge distributions remain essentially the same.[22] Thus both the sign and magnitude of the inductive effect normally assumed in semiempirical calculations[9-11] are consistent with ab initio results.

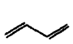
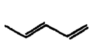
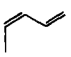
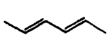
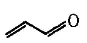
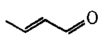
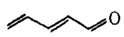
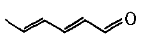
We conclude that ab initio calculations, when expressed in terms of orthogonalized orbitals, justify the semiempirical approach to treating inductive effects that result from methyl substitution. In the following we will then assume that the standard method, of increasing the value of the ionization potential at the substituted position, is a reasonable one.

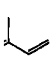
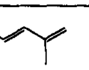
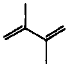
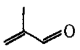
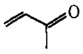
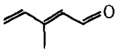
UV Absorption Spectra of Methylated Polyenes

We wish to determine the relative importance of hyperconjugation, inductive effects, and doubly excited configurations on the excited states of polyenes. Previous studies have considered these factors separately, but there has been no detailed attempt to assess their relative contributions. In the following we report the results of PPP and CNDO/S calculations on butadiene and its methylated derivatives. A simple model for hyperconjugation can be easily incorporated into the PPP scheme by including the π orbitals of the methyl group in the calculations (see Appendix A) while inductive effects require a reparametrization of the one-center integrals. Both types of interaction can, in principle, arise intrinsically in the CNDO/S calculations since both σ and π orbitals of the methyl group are explicitly included in the basis set. It is therefore of some interest to determine the extent to which the CNDO/S method is successful in treating substituent effects without additional parametrization.

Hyperconjugation. Table I presents PPP and CNDO/S calculations of the lowest allowed singlet–singlet transitions in several butadiene derivatives. Thirty singly excited configurations are included in the CNDO/S calculations; the excitations involve both σ and π orbitals. For the PPP calculations, all singly excited configurations, including those involving the π orbitals of the methyl, were considered. The ionization po-

Table I. Absorption Maxima of Methylated Polyenes[k]

								
CNDO/S	211	6.5	7.5	12	201	8	245	9
PPP	209	7	7.1	13	203	10	256	10
exptl	209[a]	6[a]	7,[b] 1,[c] 7[d]	13[a]	203[e] cyclohexane 203[f] isooctane	11[g] cyclohexane 10[f] isooctane	250[h] hexane	10[i] isooctane

						
CNDO/S	2	8	3	8	2	2
PPP	3	8	3.5	8	−2	3
exptl	7[a]	8[a] 11[j]	11[a]	12[g] cyclohexane 10[h] cyclohexane	2[f] isooctane	9[h] hexane

[a] Taken from ref 14b. [b] A.P.I. Research Project 44, cited in ref c. [c] L. C. Jones and L. W. Taylor, *Anal. Chem.*, **27**, 228 (1955). [d] L. E. Jacobs and J. R. Platt, *J. Chem. Phys.*, **16**, 1137 (1948). [e] E. S. Stern and C. J. Timmons, "Electronic Absorption Spectroscopy in Organic Chemistry", Edward Arnold, London, 1970. [f] A. E. Moskvin, *Theor. Exp. Chem.* (*Engl. Transl.*), **2**, 469 (1966). [g] E. Elkik, *Bull. Soc. Chim. Fr.*, **1**, 283 (1968). [h] E. E. Boehm and M. C. Whiting, *J. Chem. Soc.*, 2541 (1963). [i] E. M. Kosower and T. S. Sorenson, *J. Org. Chem.*, **28**, 692 (1963). [j] Reference 18, p 225. [k] λ_{max} are given for the parent molecules, and the shifts in λ_{max} are shown for the derivatives. All values in nanometers. Unless specified otherwise, gas-phase values are quoted. CNDO/S parametrizations: as in ref 15 except that the Mataga formula was employed for the repulsion integrals, and β for the oxygen was changed to 31.5 so as to improve the fit of CNDO/S calculations to polyene aldehydes (R. Blout and M. Fields, *J. Am. Chem. Soc.*, **70**, 189 (1948)). Bond lengths were varied after each iteration according to the bond order-bond length relationship of M. J. S. Dewar and T. Morita (*J. Am. Chem. Soc.*, **91**, 796 (1969)). The VESCF method [R. Brown and M. Heffernan, *Trans. Faraday. Soc.*, **54**, 757 (1958)] was applied to modulate the effective core charge at each iteration.

tentials of all the chain carbon atoms were taken to be identical so that inductive effects were explicitly supressed at this stage.

The top panel of Table I presents results for a set of molecules in which the substituted position is a terminal one. As is clear, Woodward's rules[4] are well reproduced, i.e., ca. 5-nm red shift in polyenes and 10 nm in aldehydes. PPP and CNDO/S calculations produce similar results. Since no inductive effect was introduced into the PPP scheme, it follows that hyperconjugation alone can explain the red shift resulting from methyl substitution at the terminal position. This is a typical case of a weak mesomeric effect[18] which is most simply correlated with a destabilization of the HOMO.

When interior carbons are methylated there are significant discrepancies between theory and experiment as can be seen from the bottom panel of Table I. The calculated red shifts are smaller than the experimental ones and this trend is common to both the PPP and CNDO/S calculations. In part these discrepancies are due to conformational changes since dimethylbutadienes and monosubstituted acroleins contain an appreciable amount of cisoid conformers which will red shift the absorption band.[23-26] However, 2-methylbutadiene has only a small (~11%) percentage of s-cis conformers,[25,27,28] and curve fitting indicates that these cannot account for the observed red shift. It appears therefore that hyperconjugation alone cannot account for the effects of methyl substitution in interior positions. This in fact is expected on the basis of a perturbation analysis[18] which shows that butadiene should be rather insensitive to hyperconjugation involving the 2 position since the coefficient of the corresponding atomic orbital is small in the HOMO and LUMO. The sensitivity of the terminal position may be understood in terms of its larger contribution to the HOMO/LUMO. This trend may be seen from the calculated orbital energies. For 1-methylbutadiene, we calculate that the HOMO is destabilized by 0.3 eV relative to that of butadiene, while for 2-methylbutadiene the destabilization is only 0.1 eV. These numbers are in close agreement with the experimental ionization potentials;[29] 9.03, 8.61, and 8.89 for butadiene, 1-methylbutadiene, and 2-methylbutadiene, respectively.

Inductive Effects. It is of interest that the CNDO/S method which explicitly considers all valence electrons gives results very similar to PPP calculations that do not incorporate inductive effects at all (Table I). This shortcoming follows (as shown in detail in Appendix B) from the basic assumptions underlying all CNDO-type methods which implicitly introduce a complete suppression of inductive effects. Thus, for the simple conjugated hydrocarbons considered here, CNDO/S has no advantage over the simpler PPP scheme in its treatment of the π electron manifold.

The extent to which PPP CIS calculations succeed in accounting for the spectral effects of methyl substitution, even qualitatively, is strongly dependent on the set of parameters employed. There is one report in the literature,[9b] using CIS, which reproduced the 1-methylbutadiene and 2-methylbutadiene red shift but the particular set of parameters that was introduced was found to be inadequate in additional applications.[9c] Here, using a representative set of π electron parameters, we are unable to reproduce both the 1-methylbutadiene and 2-methylbutadiene red shift, even when the inductive effect is incorporated into the calculations. In any case, it now seems clear[13] that it is necessary to include double excited configurations (CID) in any treatment of polyene spectra. When CID is introduced into our calculations of butadiene, the optically forbidden A_g^- state is found to be 218 nm above the ground state while the strongly allowed B_u^+ state appears at 205 nm. (The corresponding values using only CIS are 209 nm for the B_u^+ and 168 nm for the A_g^-.)

PPP calculations for 1-methylbutadiene and 2-methylbutadiene were also carried out and all singly and doubly excited configurations constructed from both the diene and methyl orbitals were included. Figure 2 shows the results as a function of ΔI where ΔI is the depression in absolute value of the ionization potential at the substituted position and is thus a measure of the inductive effect. The top of the figure displays λ_{max} while the bottom panel shows the contributions of the configuration $V_{3\to4}$ to both the A_g^- and B_u^+ states. This configuration represents the one-electron strongly allowed transition from the HOMO to the LUMO and is the most important, intensity determining, configuration of the B_u^+ states in the butadiene derivatives.

As is clear from Figure 2a, the introduction of CID has little effect on the situation for 1-methylbutadiene. There is a 5-nm red shift in the B_u^+ transition (210 nm compared to 205 nm calculated for unsubstituted butadiene), which is almost entirely due to hyperconjugation. There is only a weak depen-

Table II. Charge Densities in Ground and Excited States of Dienes[a]

	butadiene					1-methylbutadiene					2-methylbutadiene				
	ΔI	P_1	P_2	P_3	P_4	ΔI	P_1	P_2	P_3	P_4	ΔI	P_1	P_2	P_3	P_4
GS	0.	1.012	0.988	0.988	1.012	0.	0.998	1.010	0.988	1.018	0.	1.032	0.975	0.990	1.015
		(1.014	0.986	0.986	1.014)		(0.995	1.013	0.984	1.022)		(1.038	0.969	0.987	1.017)
						0.5	0.962	1.041	0.988	1.023	0.5	1.063	0.941	0.933	1.015
							(0.951	1.051	0.982	1.030)		(1.076	0.929	0.990	1.016)
A_g^-	0.	0.978	1.022	1.022	0.978	0.	0.994	0.983	1.068	0.982	0.	0.990	0.891	1.155	0.989
		(0.868	1.132	1.132	0.868)		(0.850	1.121	1.160	0.898)		(0.858	1.099	1.154	0.906)
						0.5	0.983	0.961	1.098	0.983	0.5	1.005	0.731	1.292	1.000
							(0.834	1.14	1.154	0.900)		(0.870	1.084	1.155	0.908)
B_u^+	0.	1.003	0.997	0.997	1.003	0.	0.968	1.044	0.986	1.032	0.	1.013	1.072	0.904	1.024
		(1.007	0.993	0.993	1.007)		(1.003	0.985	1.015	1.027)		(0.995	0.963	1.025	1.034)
						0.5	0.898	1.092	0.982	1.058	0.5	1.027	1.135	0.812	1.036
							(0.964	0.976	1.041	1.046)		(0.973	0.899	1.071	1.073)

[a] ΔI denotes the inductive effect in eV. Upper rows, without brackets, refer to CID calculations; lower enclosed rows refer to CIS calculations.

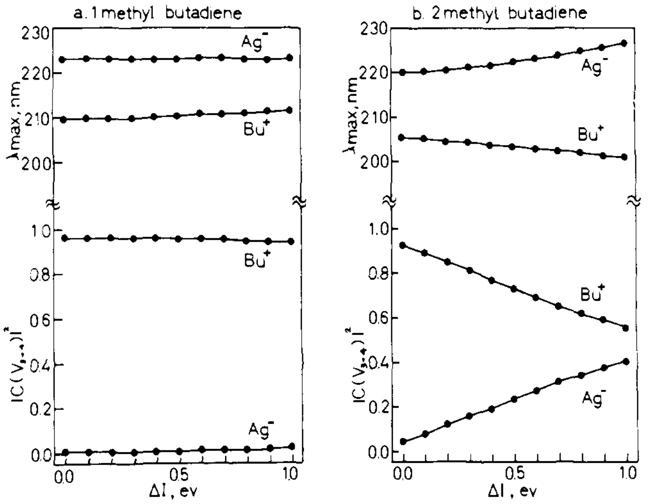


Figure 2. PPP CID calculations on 1-methylbutadiene and 2-methylbutadiene. Lower scale: contribution of the configuration $V_{3\rightarrow4}$ to the A_g^- and B_u^+ states. Upper scale: energies of the two excited states. Calculations as described in Appendix A.

dence on the inductive effect as can be seen from the insensitivity of both λ_{max} and $C(V_{3\rightarrow4})$ to ΔI. As a result, the intensities in 1-methylbutadiene are comparable to those of butadiene; the B_u^+ state is strongly allowed while the A_g^- state is essentially forbidden. The situation is very different for 2-methylbutadiene, which is extremely sensitive to the magnitude of the inductive effect. The B_u^+ state is now blue shifted as the inductive effect is increased, the A_g^- state is red shifted, and the configuration $V_{3\rightarrow4}$ (and thus the intensity) is more evenly distributed between the two excited states.

Figure 2 implies that the A_g^- and B_u^+ excited states undergo extensive mixing when a methyl group is substituted at position 2 while a terminal substitution leaves them unmixed. The relevant perturbation is due almost entirely to the inductive effect as is obvious from the figure. For example, when $\Delta I = 0$ and thus only hyperconjugation is involved, $|C(V_{3\rightarrow4})|$ is only 0.05 for the A_g^- state. Perturbation analysis shows that, for an inductive effect of 0.5 eV, the interaction matrix element between the A_g^- and B_u^+ states in 2-methylbutadiene is 0.15 eV while their energy separation is ~0.3 eV. In contrast, the interaction matrix element between these two states in 1-methylbutadiene is only 0.02 eV. Thus, for 2-methylbutadiene but not 1-methylbutadiene, it is possible to account for the spectral red shift relative to butadiene by averaging intensity of the two overlapping absorption bands. This explanation is similar to that proposed by Allinger et al.[11b] for 2-methylbutadiene, but we have shown here that 1-methylbutadiene must be understood in terms of hyperconjugation, not configurational mixing. The effect of the methyl group on 2-methylbutadiene should be distinguished from the familiar "inductive effect" in which the zeroth order molecular orbitals are modified by substitution. Here the perturbation mixes different electronic states rather than different molecular orbitals.

A difficulty with this explanation of 2-methylbutadiene is that the A_g^- state has not been unambiguously located below the main absorption band (see discussion below). However, the essential factor that determines the 2-methylbutadiene red shift remains valid even if the level ordering is reversed. If the B_u^+ state is actually lower than the A_g^-, the two will be mixed in any case by the inductive effect and this will result in a lowering of the excitation energy of the allowed B_u^+ transition. Thus, the underlying explanation of the 2-methylbutadiene red shift in terms of inductive mixing between the A_g^- and B_u^+ states seems likely to be correct, irrespective of which state is lower in energy.

As a final point in this section it would be of interest to extract an exact value for ΔI from the experimental data which could be used as a parameter in semiempirical π electron calculations. However, this turns out to be rather difficult since the spectra are rather diffuse and since the effect is relatively small. However, from Figure 2 a value of ΔI between 0.5 and 1 eV would appear reasonable and agrees well with the value obtained from the ab initio calculations reported here and standard parametrization.

Effect of Methyl Substitution on Charge Distribution

CIS and CID Results. The effect of methyl substitution on the ground states of polyenes is to induce a polarization resulting from a decrease in electron density at the substituted position. The effect involves primarily the π orbitals and has been discussed in detail by Libit and Hoffmann,[8] who described it on the basis of hyperconjugation. The top panel of Table II contains the results of PPP calculations of ground-state charge densities in butadiene, 1-methylbutadiene, and 2-methylbutadiene. Since we set $h_{ij} \neq 0$ for non-nearest-neighbors (see Appendix A) the Coulson-Rushbrooke theorem[33] does not hold and nonuniform charge densities are obtained, even for butadiene. The methyl induced polarization can be seen clearly from the CIS calculations. When $\Delta I = 0$ and only hyperconjugation is a factor there is a decrease in electron density at the substituted position and the polarization is further enhanced when an inductive effect of $\Delta I = 0.5$ eV is introduced. It should also be noted that the charge transfer from the methyl group to the chain is small,[6,7] involving about 0.01 of an electron. This and the direction of polarization are maintained upon inclusion of CID in the calculations. The major difference between the CIS and CID results is a slight decrease in the magnitude of the polarization in the latter case. That is, charge distributions are calculated to be more uniform when CID is included in the calculations.

It is clear from Table II that the ground-state polarization in substituted butadienes is not large but a rather significant effect is found for the excited state of 2-methylbutadiene. As is the case for ground states, the introduction of CID tends to produce more uniform charge distributions and again there is only a small (0.02 electrons) transfer of charge from the methyl group to the chain. However, a number of important effects are apparent from the table. (a) Dipole moments are higher in the excited states than in the ground state, particularly for 2-methylbutadiene. (b) The dipole moments of the A_g^- and B_u^+ states have opposite directions in 2-methylbutadiene. (c) The calculated dipoles are highly sensitive to the inclusion of CID. (d) Net atomic charges may change sign in going from CIS to CID. The reverse polarization of the A_g^- and B_u^+ excited states of aryl polyenes has recently been noted[34] on the basis of CIS calculations; however, the results presented here suggest that the sign (though not the existence) of the effect might have been changed had CID been included.

Valence Bond Considerations. A simple explanation for the excited-state charge distributions calculated in Table II is readily provided by VB theory. This approach is convenient here since butadiene is a small enough molecule for all (20) VB structures to be included. (There are 175 structures in the 6-orbital case.) For simplicity we consider inductive effects alone since they dominate in 2-methylbutadiene and operate in the same direction as hyperconjugation in 1-methylbutadiene.

VB calculations were carried out with the method described by Van der Lugt and Oosterhoff[35] with an inductive effect of 0.5 eV. The resulting wave functions for butadiene, 1-methylbutadiene, and 2-methylbutadine are shown in Figure 3. It is clear that methyl substitution has a much larger effect on the excited states than it does on the ground states, since methyls remove the degeneracy of ionic structures and these in turn make a greater contribution to the excited states than to the ground state. The polarization of the various states depends on the relative contributions of the ionic structures. Structures **7** and **8** are of particular interest. They are degenerate in butadiene and occur with equal (in absolute value) coefficients in each of its wave functions as is required by the zero dipole moment. In 2-methylbutadiene the degeneracy of the two structures is removed: structure **8** is now higher in energy by ΔI due to the inductive effect. Since in our calculations the A_g^- lies below the B_u^+ state, the destabilized structure **8** will make the major contribution to the B_u^+.

Consideration of the unperturbed butadiene wave functions facilitates a qualitative understanding of the effects of methyl substitution since the wave function of 1-methylbutadiene and 2-methylbutadiene may be derived from a simple perturbation analysis. The effect of the perturbation depends on the energy gap between the unperturbed states, on the weight of the various structures in the unperturbed wave functions, and on the magnitude of the destabilization of an ionic structure when a methyl group is located at a position that contains a negative charge. Structure **8**, for example, is destabilized in 2-methylbutadiene by ΔI relative to structure **7** and this leads to an interaction between the A_g^- and B_u^+ states with the typical matrix elements: $\Delta I(C_{A_g^-,8})^2$, $\Delta I(C_{B_u^+,8})^2$ and $\Delta I(C_{A_g^-,8})(C_{B_u^+,8})$. Here, $C_{A_g^-,8}$ and $C_{B_u^+,8}$ are the coefficients of structure **8** in the A_g^- and B_u^+ states, respectively. The mixing of the A_g^- and B_u^+ states will therefore be significant if the coefficients of structure **8** are large in both states, and if the inductive effect, ΔI, is not small with respect to the energy gap. The latter condition is fulfilled when $\Delta I = 0.5$ eV and, since structure **8** contributes to both the A_g^- and B_u^+ states, considerable mixing is expected. This of course was found from the MO calculations of the previous section.

The difference in the charge distribution of the two states can also be understood on this basis. As is clear from Figure 3, the result of the mixing due to methyl substitution is that structure **7** makes an increased contribution to the A_g^- state while structure **8** contributes to the B_u^+ state to a greater extent than it did in unsubstituted butadiene. Thus, negative charge will accumulate on the substituted position in 2-methylbutadiene in the B_u^+ state and will be removed from that position in the A_g^- state. That inductive effects make only a small contribution to the mixing of states in 1-methylbutadiene may also be understood in terms of Figure 3. The degenerate structures **3** and **4** could in principle mix the A_g^- and B_u^+ states but their small contribution to the A_g^- wave function leads to a particularly inefficient interaction. The weak dependence of the spectroscopic transition energy of 1-methylbutadiene on the magnitude of the inductive effect (see Figure 2) then follows.

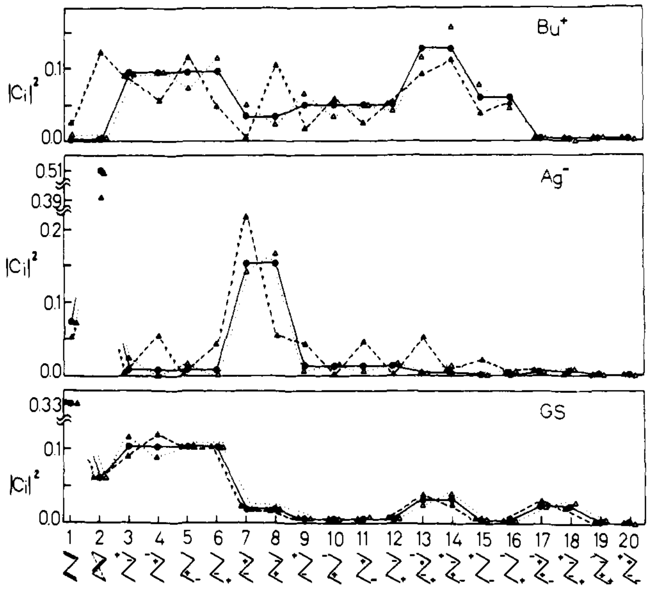


Figure 3. VB wave function of - - -●- - -, butadiene; . .△. ., 1-methylbutadiene; - - - ▲ - - -, 2-methylbutadiene. Calculations were done as in ref 32. CID parameters were used since valence bond calculations correspond to full CI. A single-bond length of 1.457 Å, double-bond length of 1.347 Å, and bond angle of 120° were used. An inductive effect of 0.5 eV was assumed.

It should be emphasized that the response of the A_g^- and B_u^+ states to methyl substitution would be reversed if the ordering of the two energy levels were reversed. For example, in this case structure **7** would make a greater contribution to the B_u^+ state than to the A_g^- state. The two states would still be polarized in a reverse direction to one another, but the direction of polarization would be opposite to that indicated in Table II. However, the existence of a strong polarization due to inductive mixing depends only on the proximity of the two states.

Discussion

In this paper we have presented a detailed analysis of the effects of methyl substitution on the lowest excited singlet states of butadiene. Both hyperconjugation and inductive effects were explicitly accounted for in the framework of PPP theory using both singly and doubly excited configurations. CNDO/S calculations were also carried out; however, it was found that CNDO-type methods in general offer little improvement over π electron theories in their treatment of inductive effects and were thus of little use insofar as the specific goals of this paper were concerned.

The spectroscopic effects of hyperconjugation result from a destabilization of ground-state orbitals which reduces the transition energy to the lowest allowed B_u^+ singlet state. This accounts for the experimental red shift seen upon methylation of the terminal carbon (position 1) and which is accurately reproduced in CIS calculations. CIS calculations fail, however, to explain the red shift resulting from methyl substitution at position 2 where hyperconjugation alone has only a small effect. Upon inclusion of CID into the SCF scheme it is found that the optically forbidden A_g^- state is close in energy to the strongly allowed B_u^+. The close proximity of these two states renders them particularly sensitive to the effects of methyl substitution. They are strongly mixed by the inductive effect arising from methyl substitution at position 2 and the red shift in 2-methylbutadiene may be understood on this basis. Position 1 is, on the other hand, relatively insensitive to inductive effects. This serves to emphasize the important point that inductive and hyperconjugation effects, though well defined theoretically, may have different experimental consequences in different molecules and in different electronic states. This is particularly obvious from Table II and Figure 3.

The validity of our description depends primarily on the assumption that the A_g^- and B_u^+ states are close in energy. McDiarmid[33] identified a weakly allowed transition on the short-wavelength shoulder of the B_u^+ state and assigned this as the A_g^-. This assignment has been questioned by Buenker et al.,[14e] whose ab initio results place the A_g^- at somewhat higher energies. Thus, the exact location of the A_g^- state in butadiene remains experimentally unresolved. Experimental studies on other polyenes strongly suggest the existence of a weakly allowed transition close in energy to the allowed transition to the B_u^+ state. The A_g^- state was first detected from high-resolution spectra of diphenyl polyenes but the extrapolation of these results to other polyenes cannot be unambiguously justified. However, recent two-photon measurements[34] have detected a weak transition slightly below the main band in retinyl polyenes containing five and six double bonds. Moreover, Christiansen and Kohler[35] have presented evidence for the presence of a low-lying excited state in a trimethylpentaene and -hexaene. Finally, Andrews and Hudson[36] have detected a forbidden transition below the main band in a tetraene, the shortest polyene in which the A_g^- state has been apparently found. The energy gap between the A_g^- and B_u^+ states is found to increase with increasing chain length as has been observed for diphenyl polyenes. For the tetraene the observed gap is only 2500 cm^{-1}. Extrapolation of these results to butadiene strongly suggests that the two states are close in energy with their ordering uncertain.[41]

Most CID calculations[13] including those reported here place the A_g^- slightly below the B_u^+ in *trans*-butadiene but there is some uncertainty in the theoretical results due to the sensitivity of CID calculations to the form of the repulsion integrals used.[37] However, the success of π electron calculations in accounting for the experimental results in longer polyenes suggests that their prediction of a small energy gap in butadiene is likely to be correct.

A number of extensive ab initio calculations have been carried out on butadiene; however, these have not as yet led to an unambiguous location of the various excited states. Hosteny et al.[14d] find the A_g^- state at 6.77 eV and a B_u^+ state slightly above it at 7.05 eV. Buenker et a.[14e] using an all valence electron CI treatment place the A_g^- at 7.02 eV and the lowest B_u^+ slightly below it, at 6.67 eV, but still significantly above the observed transition at approximately 6 eV.[33] However, this state has considerable Rydberg character and its low calculated oscillator strength led Buenker et al.[14e] to suggest that excitation to the second B_u^+, which is a valence state, corresponds to the main absorption band. This state is calculated to be 7.65 eV above the ground state and thus is in particularly poor agreement with the experimental transition energy. To account for this discrepancy, Buenker et al.[14e] suggested that nonvertical transitions to excited-state geometries in which bond lengths have inverted make the major contribution to the intensity of the main absorption band.

This assumption may not be necessary. Studies on ethylene have shown that basis set limitations and choice of configurations in the CI calculations may introduce an artificial diffuseness into the orbitals.[38] Indeed, the extensive calculations of McMurchie and Davidson[39] on ethylene, though confirming its partial Rydberg character, do suggest that the π^* transition is valence-like. Thus, it is reasonable to expect that future ab initio studies will succeed in reducing the calculated transition energy to the strongly allowed B_u^+ state in butadiene to about 6 eV. However, the position of the A_g^- state is not expected to be significantly affected by further CI.[14c] In terms of the effects considered in this paper, an energy gap of about 0.7 eV between the *theoretical* transition energy of the A_g^- state[11c] and the *experimental* value of ~6 eV for the B_u^+ state[33] would increase the magnitude of the inductive effect (ΔI) required to produce the observed red shift in 2-methylbutadiene. It is worth pointing out in this regard that the A_g^- state is stabilized even more than the B_u^+ by bond length inversion,[14b] so that, even if nonvertical transitions are important, both states would appear at significantly lower energies than those calculated. Thus, inductive mixing between the two states would still be expected to have important spectroscopic consequences.

Assuming that total intensity of the B_u^+ transition is distributed over the B_u^+ and A_g^- transitions in 2-methylbutadiene (actually this turns out to be not strictly the case), one would expect a broadening of the main absorption band with a corresponding decrease in the maximum absorbance. $\epsilon_{\max}$ does in fact decrease in 2-methylbutadiene relative to 1-methylbutadiene; however, the reported absorption bands[26] are too diffuse to detect small changes in bandwidth. High-resolution spectra on these compounds would be of interest in this regard and might help in detecting which of the two states is lowest in energy. In any case it is worth reemphasizing that the underlying cause of the spectral red shift and excited-state charge polarization depends on the proximity of the two states, not on their relative ordering.[41]

The strong inductive mixing of the A_g^- and B_u^+ states is found to have pronounced effects on their respective charge distributions. They are polarized in a different way and each responds differently to substitution at position 1 or 2. Finally, since there is good evidence that a low-lying A_g^- state is present in longer polyenes, it is likely that the effects we have found for butadiene will be of considerable importance for longer molecules as well.

Appendix A. PPP Parametrization for Methylated Polyenes

In this Appendix we present a new set of parameters which allow the introduction of methyl groups into a π electron scheme. Our approach is to use CNDO/S values wherever possible and, where necessary, to extract appropriate π electron parameters from CNDO/S calculations. The set of parameters we obtain may be used in calculations on longer polyenes (which is our ultimate aim) and will produce essentially identical results with the CNDO/S method with a considerable savings of computer time. The full set of parameters is listed in Table III. As is evident from Tables IV and I, we are able to obtain excellent agreement with the reported value of $\lambda_{\max}$ for a large number of molecules.

Chain Carbon Parameters. The PPP method was initially parametrized such that CIS calculations would reproduce the spectra of linear polyenes. The core resonance integral was calculated from

$$\beta_{ij} = \tfrac{1}{2}(\beta_i + \beta_j)S_{ij} \tag{A.1}$$

where i and j denote atomic orbitals (not necessarily neighbors) and S_{ij} is the overlap integral between them. β_i and the ionization potentials I_i were modified at each iteration by

$$\beta_i = \beta_i^0(\zeta_i/\zeta_i^0)^2 \tag{A.2}$$

$$I_i = I_i^0(\zeta_i/\zeta_i^0)^2 \tag{A.3}$$

where I_i^0 and β_i^0 are parameters to be fixed and ζ_i^0 is the

Table III. Parameters for PPP Calculations

	chain		methyl	
	carbon	oxygen	carbon	hydrogen
I^0, eV	10.90	15.10	11.60	10.00,[a] 10.50[b]
β^0, eV	10.15	18.50	10.15	21.00
γ^0, eV	11.11	13.00	11.11	8.90,[a,c] 12.85[d] 9.85,[b,c] 12.85[d]
ζ^0	3.25	4.55	3.25	1.2

[a] CIS calculations, Mataga formula for the repulsion integrals. [b] CID calculations, Ohno formula for the repulsion integrals. [c] Value used in the intraatomic repulsion $\gamma_{\mu\mu}$ (see Appendix A). [d] Value used in the interatomic repulsion integral $\gamma_{\mu\nu}$ (see Appendix A).

Slater exponent which is modified at each iteration according the method of Brown and Heffernan (see Table I). The Mataga formula was employed for the repulsion integrals and the one-center integral γ_i was modified at each iteration as

$$\gamma_i = \gamma_i^0(\zeta_i/\zeta_i^0) \tag{A.4}$$

where γ_i^0 was set equal to γ_{ii} which is calculated from the CNDO/S parametrization.

Methyl Carbons. β^0, γ^0, and ζ^0 were assigned the same value as the chain carbon atoms. The ionization potential was taken as the average value extracted from CNDO/S calculations on a number of molecules (see Appendix B).

Hydrogenic Orbitals. The ionization potential was extracted from CNDO/S calculations as was done for the methyl carbon atoms. β^0 was chosen so as to fit $\lambda_{\max}$ and the ionization potential of 1-methylbutadiene (see text and Table I).

The repulsion integrals involving the hydrogenic orbitals require additional discussion. γ_{ii} for the orbital $(\frac{1}{2})^{1/2}(1s_a - 1s_b)$ is in the ZDO approximation, $\frac{1}{2}(\gamma_{1s_a,1s_a} + \gamma_{1s_a,1s_b})$. Using the CNDO/S value for $\gamma_{1s_a,1s_b}$ and assuming a standard methyl geometry we find 8.9 eV for γ_{ii} in the Mataga approximation and 9.85 eV in the Ohno approximation (which we use in the CID calculations—see below). The repulsion integral between a hydrogenic orbital and a p_π orbital is simply given by γ_{1s_a,p_π} since for the planar molecules considered in this paper both hydrogens are equidistant from any carbon atom. This integral is calculated from either the Mataga or Ohno formula; note in this regard that $\gamma_{1s_a,1s_a}$ rather than γ_{ii} (where i is the hydrogenic π orbital) must be used for the one-center integral that appears in both equations. The Slater exponent for the hydrogenic orbitals is the CNDO/S value.

Oxygen Parameters. γ_i^0 and ζ_i^0 are the CNDO/S values. I_i^0 and β_i^0 were fixed so as to fit the spectra of acrolein and 1-methylacrolein (Table I).

CID Calculations. Schulten et al.[13] have shown that the Ohno formula rather than the Mataga formula should be used in CID calculations. This is due to the fact that the Mataga formula accounts implicitly for correlation effects which are explicitly taken into account in CID calculations. Accordingly, all repulsion integrals were calculated with the Ohno formula in the CID calculations.

Appendix B. On the Inability of CNDO-Type Theories to Account for the Inductive Effect

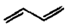
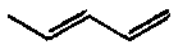
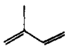
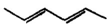
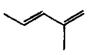
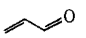
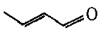
In PPP calculations, where one assumes a frozen σ core, the inductive effect may be included through appropriate parametrization. CNDO-type theories, on the other hand, treat all-valence electrons and thus, it might be concluded, account for the inductive effect explicitly. This, however, turns out not to be the case, and in fact CNDO-type theories intrinsically suppress the inductive effect as we show here for the CNDO/S method. Focusing on the π block of the CNDO/S F matrix, we are interested in how its diagonal elements are affected by the existence of a methyl group. The formal expression for F_{ii} is

Table IV. Calculated and Experimental[a] Absorption Maxima for Polyenes

	$CH_2{=}CH(CH{=}CH)_nCH{=}CH_2$					
n	0	1	2	3	4	5
calcd	209	258	300	335	363	388
exptl[a]	210	258	304	334	364	390

[a] For $n = 0$, experimental value taken from ref 33. For $n > 0$, values taken from F. Sondheimer, D. Ben Efraim, and R. Wolovsky, *J. Am. Chem. Soc.*, **83**, 1675 (1961). The first vibrational band, which is the strongest in most of these molecules, was used.

Table V. CNDO/S Calculations of I_i^π (eq B.5) for Dienes[a]

	$-I_1^\pi$	$-I_2^\pi$	$-I_3^\pi$	$-I_4^\pi$
	10.908	10.891	10.891	10.908
	10.866	11.107	10.901	10.929
	11.051	10.893	10.919	10.835
	10.926	11.084	11.084	10.926
	10.923	11.082	10.933	10.999
	10.729	11.195	11.016	15.132
	10.673	11.369	11.002	15.147

[a] All values are in eV. Parameters of the calculations as in Table II. Input geometry fixed according to standard bond lengths and angles (Table I).

$$F_{ii} = U_{ii} + \left(P_A - \frac{1}{2}p_{ii}\right)\gamma_{AA} + \sum_{B\neq A}(P_B - Z_B)\gamma_{AB} \tag{B.1}$$

where i refers to an orbital on atom A, and A, B to atoms. P is the charge and bond order matrix, P_A and P_B are the gross atomic population numbers, Z_B is the core charge of atom B, U_{ii} is the ionization potential of orbital i, and γ_{AB} are the repulsion integrals. We take i to be a P_π orbital, and separate the charge density into σ and π components, so that

$$P_A = P_A^\sigma + P_{ii} \tag{B.2}$$

Inserting eq 2 into eq 1, we have

$$F_{ii} = (U_i + P_A^\sigma\gamma_{AA}) + \frac{1}{2}p_{ii}\gamma_{AA} + \sum_{B\neq A} Q_B\gamma_{AB} \tag{B.3}$$

where Q_B is the surplus charge on atom B, $Q_B = P_B - Z_B$. If we now decompose Q_B further into its σ and π components

$$Q_B = Q_B^\sigma + Q_B^\pi \tag{B.4a}$$

$$Q_A^\pi = p_{ii} - 1 \tag{B.4b}$$

where it is understood that, for hydrogens not bearing π charges, $Q_B = Q_B^\sigma$, and define I_i^π such that

$$I_i^\pi = U_i + P_A^\sigma\gamma_{AA} + \sum_{B\neq A} Q_B^\sigma\gamma_{AB} \tag{B.5}$$

we have finally, upon substituting eq 4 and 5 into eq 3

$$F_{ii} = I_i^\pi + \frac{1}{2}p_{ii}\gamma_{AA} + \sum_{B\neq A} Q_B\gamma_{AB} \tag{B.6}$$

which is just the formal expression appearing in PPP theory.[39] However, while in PPP calculations I_i^π is input data and is assumed to be a constant, in CNDO-type calculations it is related to the σ charge developed (eq B.5) and thus varies from one center in the molecule to another. Table V gives CNDO/S calculations of I_i^π for several polyenes. It is immediately apparent that the PPP assumption of the uniformity of I_i^π is quite good. In fact, not only is I_i^π essentially unchanged from one carbon atom to another in the molecules shown, but its value is also in good agreement with the value used in standard PPP calculations. Note, however, the I_i^{π} is rather insensitive to the existence of a methyl group. In PPP calculations, inductive effects are accounted for by taking I_i^{π} at the substituted positions to be lower in absolute value than other positions by at least 0.5 eV. However, CNDO/S calculations for methylated butadienes, as shown in Table V, yield a value for ΔI of only 0.1 eV.

In fact, the depression of the inductive effect is implicit in all CNDO-type theories. For F_{ii} in these theories may be written in general

$$F_{ii} = F_{ii}{}^0 + \sum_j \left(\frac{\partial F_{ii}}{\partial q_j}\right) q_j' \qquad \text{(B.7)}$$

where q_j is the surplus charge in orbital j, $q_j = p_j - 1$. $F_{ii}{}^0$ is a fixed parameter and is the same for all orbitals of a specific type (e.g., 2s or 2p), regardless of their environment. All environmental effects are therefore buried into the summation term in eq B.7. Since this term is proportional to the charges and since these are small (in the absence of a heteroatom), the low magnitude of the inductive effect follows. Since this result is apprently incorrect, one may conclude that the assumption of fixed $F_{ii}{}^0$ is too crude. Indeed, $F_{ii}{}^0$ contains U_i, which is just the core matrix element h_{ii}. h_{ii} in CNDO-type theories does not distinguish a carbon atom bound to a methyl from a carbon atom bound to a hydrogen. This assumption is definitely not rigorous, and is apparently quite inaccurate since the inductive effect is lost. It is therefore necessary to introduce inductive effects into CNDO theories much in the same ad hoc manner that has been used previously in PPP calculations. Indeed, in the recent calculations of Lipari and Duke[40] on methyl derivatives of benzene, it was found necessary to parametrize the methyl carbon differently from other carbon atoms.

References and Notes

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