ON THE ORIGIN OF A LOW-LYING FORBIDDEN TRANSITION IN POLYENES AND RELATED MOLECULES†

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It is demonstrated that the inclusion of double-excited configurations in semi-empirical and a priori calculations of polyenes leads to a significant alteration of the spectrum. In agreement with the recent experiment of Hudson and Kohler, a forbidden (^1A_g) state appears below the strongly allowed (^1B_u) state.

The preceding paper by Hudson and Kohler [1] has presented experimental evidence for the existence in polyenes of an unsuspected excited state below that involved in the well-studied, lowest-allowed, $\pi\pi^*$ transition [2]. Their high-resolution spectra of α,ω-diphenyl octatetraene (DPO) indicate that the transition to the newly discovered state is only weakly allowed ($f = 0.06$, relative to $f = 1.5$ for the allowed $\pi\pi^*$ transition). In this communication, we outline a theoretical treatment for polyenes which demonstrates that there exists such a low-lying π-electron state; in the undistorted all-*trans* polyene, the state has ^1A_g symmetry and is, therefore, forbidden from the ground state. The nature of the state is such that it could be present in all polyenes and in many related molecules (e.g., the visual chromophore, retinal) and might play a role in their photochemical properties.

Pariser–Parr–Pople (PPP) calculations were performed with a standard program [3] which has been widely applied to polyenes and other conjugated π-electron systems. In this program, the core resonance integrals are represented by a linear approximation [4], the electron repulsion integrals are determined by the Ohno formula [5], and penetration integrals are neglected. As in most PPP calculations, the program is set up to determine SCF LCAO MO's for the ground state and to include single-excitation configuration interaction for the excited states. Table 1 in the columns headed S gives the results for the lowest singlet states of all-*trans* butadiene, hexatriene, and octatetraene obtained by use of the program; the bond lengths and bond angles were given their standard values ($R_{C=C}$ = 1.35 Å, R_{C-C} = 1.46 Å, all angles 120°). It is clear from the table that the configuration-interaction treatment with single-excited states yields the same energy level pattern for the series of molecules. In agreement with earlier calculations on these systems [2], it is found that the transition from the ground state to the lowest $\pi\pi^*$ level (^1B_u) is allowed, and that there are next two near-degenerate levels (^1A_g) that correspond to forbidden transitions from the ground state. The lower of the two ^1A_g states becomes allowed (the so-called *cis* peak) [6] in configurations of the polyene chain involving *cis* double bonds or *s-cis* single bonds that destroy the inversion symmetry of the molecule.

To improve the π-electron energy level calculations, the configuration interaction program was modified to include all double-excited configurations in addition to the single-excited configurations‡. From the results given in table 1 (columns headed S+D), the most prominent effect of this change is that one of the two ^1A_g states is significantly lowered in energy. In fact, the ^1A_g is calculated to be slightly below the

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‡ For discussions of the importance of double excitations in the benzene spectrum, see refs. [7].

Table 1
Calculated π-electron energy levels (eV) of *trans*-polyenes a)

Butadiene		Hexatriene		Octatetraene	
S	S+D	S	S+D	S	S+D
0.000(^1A_g)	0.000 b)(^1A_g)	0.000(^1A_g)	0.000 c)(^1A_g)	0.000(^1A_g)	0.000 d)(^1A_g)
5.465(^1B_u)	5.408(^1A_g)	4.633(^1B_u)	4.731(^1A_g)	4.112(^1B_u)	4.422(^1A_g)
7.371(^1A_g)	5.860(^1B_u)	6.591(^1A_g)	5.182(^1B_u)	5.926(^1A_g)	4.830(^1B_u)
7.624(^1A_g)	7.836(^1A_g)	6.672(^1A_g)	5.630(^1B_u)	6.058(^1A_g)	5.268(^1B_u)
9.582(^1B_u)	9.408(^1A_g)	7.485(^1B_u)	7.204(^1A_g)	7.010(^1B_u)	5.890(^1A_g)

a) All energies are in eV relative to the ground state as zero.
b) The ground state energy is lowered by 0.554 eV relative to the (S) calculation.
c) The ground state energy is lowered by 0.817 eV relative to the (S) calculation.
d) The ground state energy is lowered by 1.068 eV relative to the (S) calculation.

^1B_u state in the three polyenes. Furthermore, the ^1B_u and the other ^1A_g excitation energies are altered less by including the double-excited configurations, although in hexatriene and octatetraene another ^1B_u appears below the ^1A_g state. Table 2 compares the results of the (S) and (S+D) calculations with experimental data for the ^1B_u transition of the corresponding polyenes [8]; all measurements were made in organic solvents, without correction for the difference between solutions and vapor. There is reasonable agreement between the polyene experimental values and both sets of calculations, although the (S) values are somewhat better because the program parameters were obtained by fitting single excitation results to spectral data [4, 5]. The larger excitation energies in the (S+D) calculations arise primarily from the lowering of the ground state relative to the value for the (S) calculation. The α,ω-diphenylpolyenes, follow approximately the same trend as the unsubstituted polyenes, except that the ^1B_u transition is shifted to longer wavelengths for the equivalent number of double bonds in the chain [9]; e.g., for α,ω-diphenyloctatetraene, the ^1B_u transition is at 3.07 eV, as compared with the octatetraene value of 4.08 eV. As to the position of the "forbidden" transition, definitive data are available only for α,ω-diphenyloctatetraene. For this compound, extrapolation of the solution measurements to the vapor (see fig. 1 of ref. [1]) yields 0.66 eV as the energy difference between the weakly-allowed state and the ^1B_u state, while the (S+D) calculated value for the difference between the ^1A_g and ^1B_u state of octatetraene is 0.41 eV (see table 1). There is some

Table 2
^1B_u excitation energy (eV) in all-*trans* polyenes

Number of double bonds	Experiment a)	Calculations b) (S)	(S+D)
2	5.71	5.465	5.860
3	4.63	4.633	5.182
4	4.08	4.112	4.830

a) Ref. [8].
b) From table 1.

indication [9, 10] that the experimental energy difference between the two states increases with the number of double-bonds in the diphenylpolyenes: the calculations reported here do not show such an increase. Further investigation, both experimental and theoretical, of the energy difference is required. The calculations, in particular, should be improved by consideration of the details of the molecular geometry, the specific integral approximations, and the contribution of multiple-excited configurations.

One further point of interest in the experimental comparison is that Hudson and Kohler [1] concluded from their vibrational analysis of the transition for DPO in bibenzyl that the zero-zero band is present. Thus, identification of the observed transition with a ^1A_g polyene state requires that some distortion be introduced so as to make the transition weakly allowed. This could be a consequence of interactions with the matrix or possibly be inherent in the rather flexible polyene chain, particularly when substituted with

Table 3
Butadiene calculations with a priori integrals [a]

Gaussian lobe SCF MO CI [b]			Slater – VB→		
S	S+D [c]→	All [d]→	e)	f)	g)
0.00(^1A_g)	0.00(^1A_g)	0.00(^1A_g)	0.00(^1A_g)	0.00(^1A_g)	0.00(^1A_g)
9.03(^1B_u)	7.71(^1A_g)	7.69(^1A_g)	5.44(^1A_g)	7.21(^1A_g)	4.71(^1A_g)
10.99(^1A_g)	10.34(^1B_u)	10.19(^1B_u)	10.14(^1B_u)	10.34(^1B_u)	9.69(^1B_u)
12.64(^1A_g)		12.90(^1A_g)	11.57(^1A_g)	13.12(^1A_g)	11.42(^1A_g)
14.59(^1B_u)		14.58(^1A_g)	12.87(^1B_u)	14.63(^1A_g)	13.07(^1B_u)

a) All energies in eV relative to the ground state.
b) Ref. [12]; there is a state (10.24 eV, ^1A_u) involving σ-electron excitations that lies below the third ^1A_g state.
c) The ground state energy is lowered by 1.618 eV relative to the (S) calculation.
d) The ground state energy is lowered by 1.686 eV relative to the (S) calculation.
e) Ref. [13]; f) ref. [14]; g) ref. [15].

benzene rings that are twisted out of the plane [11].

It is important to compare the present results with those obtained by ab initio calculations for butadiene, the only polyene for which configuration interaction calculations including all double excitations have been reported previously. Table 3 lists the π-electron excitation energies from an a priori all-electron SCF LCAO MO CI calculation [12]† with a basis set contracted from 130 gaussian lobe functions, and those from complete minimum basis set π-electron valence-bond treatments with a priori values for the integrals. The three valence-bond calculations included in the table used somewhat different integrals and approximations for the σ-electron core [13–15]. It is seen that in all cases, the energy level ordering of the lowest four states is the same as in the (S+D) PPP calculation, although there are large quantitative differences between the a priori and PPP results and among the various a priori calculations themselves. The SCF LCAO MO CI results [12] confirm that in butadiene the most important difference between the calculation with only single excitations and with both single and double excitations is the stabilization of the ^1A_g state so that it lies below the ^1B_u state. It should be noted, also, that this calculation illustrates the fact that including all excitations produces a small change relative to that resulting from the introduction of double excitations (see columns 2 and 3 of table 3).

† These authors discussed the possibility that butadiene might have a lowest excited state of ^1A_g symmetry.

As pointed out above, the origin of the low-lying ^1A_g state is in the pair of ^1A_g states that lies above the ^1B_u state in a calculation including only single-excited configurations. In the example of butadiene, the ^1A_g states are formed from the two possible combinations of the degenerate configurations (2→4) and (1→3), where the SCF orbitals are numbered 1, 2, 3, 4 in order of increasing energy. Thus, these states can be formulated in terms of the (±) symmetry introduced by Pariser [16] for polyacene excited states. It is the minus state ($^1A_g^-$), corresponding to [(2→4) – (1→3)], that interacts with the ground state (which is $^1A_g^-$ by definition [16]) and the important $i^2 \rightarrow j^2$ double-excited states (e.g., $2^2 \rightarrow 3^2$), while the $^1A_g^+$ state does not. Also, it is the latter state ($^1A_g^+$) that gives rise to the *cis* peak in polyene isomers; e.g., for *s-cis* butadiene, the $^1A_g^+$ state goes over into an $^1A_1$ state that is allowed and has its transition moment oriented along the two-fold symmetry axis.

To obtain a more qualitative picture of the nature of the $^1A_g^-$ excited state, two alternative approaches are most useful. One of these is the valence-bond method and the other is an exciton model. Both of these, if carried to their ultimate conclusion (i.e., inclusion of all structures in the valence-bond treatment, inclusion of all configurations in the exciton treatment), would yield results identical with those from the complete SCF MO CI calculation. Their interest for the present problem is that they give the proper behavior of the ^1A_g state at a simpler level of approximation. In a valence-bond calculation for butadiene,

the ^1A_g state is the second of the two states that can be constructed in the covalent model for butadiene; that is, if we draw the two covalent structures as C=C–C=C and $\overline{C}$–C=C–$\overline{C}$, their linear combination yields the ground state and the first excited ^1A_g state. Of course, such a valence-bond model without ionic structures cannot describe the allowed transition; however, at all levels of approximations, including ionic structures, the ^1A_g state remains below the ^1B_u state [14, 15]. This suggests that a semi-empirical valence-bond approach to polyenes may be an excellent method for understanding their spectra. The exciton model of polyenes starts out with localized ethylenes and includes the ground and excited state configurations for the individual ethylenes plus charge transfer between them. In previous exciton treatments of butadiene [17], states involving only one ethylene excited at a time were considered. Such calculations approximately duplicate the single-excitation SCF MO CI calculations. What is missing is the excited state corresponding to that arising in butadiene from the pair of covalent valence-bond structures; the latter has a dominant contribution from the singlet state

$$\Phi_{VB} = (1/2\sqrt{3})[2|ab\bar{c}\bar{d}| + 2|\bar{a}bc\bar{d}| - |ab\bar{c}\bar{d}| - |\bar{a}bc\bar{d}| - |a\bar{b}c\bar{d}| - |\bar{a}b\bar{c}d|] , \quad (1)$$

which is the same as

$$\Phi_{exciton} = (1/2\sqrt{3})[2|\phi_I \phi_{I^*} \bar{\phi}_{II} \bar{\phi}_{II^*}| + 2|\bar{\phi}_I \bar{\phi}_{I^*} \phi_{II} \phi_{II^*}| - |\phi_I \bar{\phi}_{I^*} \phi_{II} \bar{\phi}_{II^*}| - |\bar{\phi}_I \phi_{I^*} \phi_{II} \bar{\phi}_{II^*}| - |\phi_I \bar{\phi}_{I^*} \bar{\phi}_{II} \phi_{II^*}| - |\bar{\phi}_I \phi_{I^*} \bar{\phi}_{II} \phi_{II^*}|] , \quad (2)$$

where

$$\phi_I = 2^{-1/2}(a+b) , \quad \phi_{I^*} = 2^{-1/2}(a-b) , \quad \phi_{II} = 2^{-1/2}(c+d) , \quad \phi_{II^*} = 2^{-1/2}(c-d) , \quad (3)$$

and a, b, c, d, are the four butadiene π orbitals. From eq. (2), the important contribution to the ^1A_g state in the exciton model has two ethylenes individually excited to a triplet state, the two triplets being coupled to yield an overall singlet†. This is not unexpected since the lowest ethylene triplet state is at 4.6 eV so that two non-interacting triplet ethylenes have an energy of 9.2 eV, near that of a one ethylene excited to a singlet state (7.6 eV)‡. The other singlet spin pairing of the two excited ethylenes (i.e., singlet in each ethylene), which is not present in the covalent valence-bond treatment, is of such a high energy that its contribution is less important. The calculated values of the contributions in an exciton model for butadiene are 0.77 and 0.02 for the triplet–triplet and singlet–singlet spin-coupling states, respectively. Extension of the exciton approach to larger polyenes is straight-forward; it requires introduction of the corresponding exciton states, limiting them in the first approximation to those having only single charge transfer and no more than two ethylenes excited at a time. However, care must be used since, even for butadiene, additional states must be included to duplicate the SCF MO CI results with the same parameters.

It is clear from the above discussion that the low-lying ^1A_g state should be present in all polyenes and related systems, since its origin is such that there is no reason for it to be restricted to the specific molecules considered in this paper. What is not certain without additional calculations is how the position of the ^1A_g state will be altered relative to the ^1B_u state when substituent or other perturbations are introduced. One might expect that, because of their different properties (e.g., transition moments), the two states could behave very differently in the presence of inductive substituents and that the ordering might well change from one compound to another. If the ^1A_g state were lowest, it would be expected to be involved in the photochemical isomerization of these molecules. Additional investigations of this problem, including consideration of other excited states and extension of the calculations to retinal and related compounds, are in progress and will be reported subsequently with a more detailed presentation of the results.

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† This interpretation has been suggested independently by I. Shavitt and W.A. Goddard III.

‡ The calculated values of the excitation energies for ethylene at the polyene C=C bond length (R = 1.35 Å) are 3.72 eV ($^3B_{1u}$) and 7.15 eV ($^1B_{1u}$).

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