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A Theoretical Investigation of Several Low-Lying States of trans, trans-1,3,5-hexatriene

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cuprate(II) is found to have strong b_{1g} (σ -type) bonding between the copper and four ligating nitrogen atoms. The b_{2g} and b_{3g} out-of-plane (π -type) bonding is also strong not only for Cu-N bonds but between the biuretato ligand components as well. The in-plane π -type Cu-N bonding is found to be very weak. It manifests itself only through the interaction of the $3d_{x^2-y^2}$ (Cu), $4p_x$ (Cu), and $4p_y$ (Cu) with the $2p_x$ (N) and $2p_y$ (N) components of the a_{1g} , b_{3u} , and b_{2u} molecular orbitals.

In order to judge if the $X\alpha$ -SW can generally predict the electronic structure and bonding of charged transition-metal complexes, more computations of the type presented above must be performed and compared with experiment. Only then would one know what molecular properties are best predicted by this technique.

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Supplementary Material Available: Table of symmetry adapted one-electron orbitals for the bis(biuretato)cuprate(II) dianion and 10 equations for the molecular \mathbf{g} tensor components in terms of molecular orbital coefficients (7 pages). Ordering information is given on any current masthead page.

Theoretical Investigation of Several Low-Lying States of *trans,trans*-1,3,5-Hexatriene

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Results from ab initio calculations concerning several low-lying electronic states of *trans,trans*-1,3,5-hexatriene are presented and compared with experimental and previous theoretical results. The lowest excited singlet state is predicted to be the 1B_u state, having essentially valence-like $\pi \rightarrow \pi^*$ character. The nominally doubly excited $2{}^1A_g$ state is found to lie approximately 0.6–0.9 eV above the 1B_u state. Results are also presented for several Rydberg states. The implications of the present results for current parametrizations of semiempirical π molecular orbital schemes are discussed.

I. Introduction

The spectroscopy of linear polyenes has been an area of intense interest for both experimentalists and theoreticians.¹ The study of such molecules is important to the understanding of the visual pigments² and has also been a testing ground for theoretical models of the electronic structure of π -electron systems.^{1,3,4} One example of the interplay between experiment and semiempirical theory in this area was the discovery^{1,4,5} that in longer polyenes the excited singlet state observed in fluorescence is not the $\pi \rightarrow \pi^*$ state of molecular orbital theory but is instead a state that can be described as doubly excited relative to the ground state. The understanding of this via the use of semiempirical molecular orbital and valence bond theories^{6,7} has led to further consideration of the importance of electron–electron repulsions in the determination of the nature of the excited states of such compounds.¹

Ab initio electronic structure techniques have been applied to several of the shorter chain polyenes.^{8–15} In the case of ethylene,^{8–10} a significant effort went into the description of the lowest $\pi \rightarrow \pi^*$ state. There, experimental evidence along with semiempirical molecular orbital calculations seemed to suggest a purely valence-like state. The present description based on accurate ab initio results seems to argue for a more diffuse ${}^1B_{1u}$ state and for significant nonvertical excitation contributions to the spectral intensity.^{8–10} Butadiene has a similar history, and only recently have ab initio methods been able to find a predominantly valence-like state near the experimentally observed intensity maximum.¹⁴ Hexatriene^{13,15} has received less attention, doubtless due to the increased size of the computations and the limited success of CI results in the description of the shorter chain species. The size of the longer chain species (decapentaene, dodecahexaene) most likely prohibits application of adequate ab initio methods to the quantitative investigation of their spectroscopy in the near future, but detailed theoretical investigations of the spectroscopy of the shorter chain species can still be helpful to both experimentalist and theoretician. For example, studies of the va-

lence–Rydberg mixing in such species could be used for the development of more accurate semiempirical schemes.

In another vein, the location of the doubly excited state (that is, the analogue of the lowest excited singlet in the long chain species) relative to the $\pi \rightarrow \pi^*$ excited state is still an open question for the short chain species. The development of accurate ab initio treatments for such systems may help to answer this question. In addition, the positions of the various Rydberg transitions are still very much in question for hexatriene, and ab initio results may be useful in this regard also, since current semiempirical methods are limited to the treatment of valence states.

With these questions in mind, we have undertaken an investigation of the low-lying electronic states of *trans,trans*-1,3,5-hexatriene by using ab initio CI wave functions. The methods employed are similar to those used in our previous study of butadiene¹⁴ and give results that are significantly different than past

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ab initio predictions^{13,15} concerning the nature and position of the 1^1B_u state. They are also significantly different from a number of semiempirical results^{6,7} for the position of the 2^1A_g state. The reasons for these differences will be discussed below.

II. Theoretical Methods

The geometry used for all results presented in Tables III–VI for *trans,trans*-1,3,5-hexatriene was the experimental geometry obtained by Traetteberg.¹⁶

The basis set used for carbon was the Dunning (4s,2p) contraction¹⁷ of the Huzinaga¹⁸ (9s,5p) basis. This basis was augmented with a set of d functions (exponent = 0.55) and two sets of p Rydberg functions (exponents = 0.021 and 0.009). For hydrogen, a (3s) contraction¹⁹ of the Van Duijneveldt (7s) basis²⁰ was used. For simplicity, for the remainder of the article we shall refer to basis functions that are symmetric with respect to reflection in the molecular plane as σ and functions that are antisymmetric with respect to reflection in the molecular plane as π . In all calculations only the π -type d functions were retained. The σ -type Rydberg functions were also discarded in all calculations which treated π Rydberg states, and in those calculations treating σ Rydberg states, the π Rydberg basis functions were discarded. The molecule is oriented to lie in the yz plane, thus the x axis is perpendicular to the molecular plane. In C_{2h} symmetry the σ orbitals have either a_g or b_u symmetry while the π orbitals have either a_u or b_g symmetry.

The above basis is somewhat different from that used in our treatment of butadiene.¹⁴ It will be shown below that the basis described above is sufficient to adequately reproduce the results obtained for butadiene¹⁴ while reducing the size of the problem. In the calculations concerning butadiene, three basis sets are used, labeled $DZ + \pi R$, $DZ + \pi PR$, and $TZ + \pi PR$. The first is the one defined above, with the exceptions that no d functions and only the first of the carbon Rydberg functions (exponent = 0.021) were included. The second is the one defined above without the second carbon Rydberg function, and the third is that used in ref 14, which is a (5s,3p) contraction¹⁹ of a (14s,9p) carbon basis of Huzinaga et al.²¹ with the above H basis, carbon d functions, and the first of the two carbon Rydberg functions.

All self-consistent field (SCF) energies reported below were from restricted Hartree–Fock (RHF) calculations obtained by using the MELD suite of codes²² developed in this laboratory. In all nonnatural orbital calculations the virtual orbitals were transformed to the K orbitals (KO) of Feller and Davidson.²³ Natural orbitals²⁴ (NO), obtained from iterating relatively small configuration interaction calculations on a given state, were also used to improve the orbital basis. For symmetries where more than one low-lying state was sought, use of average-natural orbitals²⁵ (ANO) was found to be an effective means of reducing the bias caused by choice of an orbital basis appropriate to only one of the states of interest. (For a more complete discussion of the advantages of ANO in cases such as these, see ref 14.)

Two classes of configuration interaction schemes (CI's) were used in the present study to address the correlation problem. In neither case were excitations allowed from the three lowest orbitals in a_g and b_u symmetries. These orbitals were composed of the carbon 1s cores. In addition, in both cases a perturbation-theory-based selection procedure was used to limit the size of the CI's performed. In this procedure one or more electronic configurations was chosen as a reference space. A zeroth-order wave function

TABLE I: CI Parameters

state	MO's	primary config ^a	no. of refs ^b	Z-O coeffs ^c
QCI				
$1^1A_g, 2^1A_g, 3^1A_g$	1^1A_g KO	$1a_u^2 1b_g^2 2a_u^2$	41	input
1^2A_u	1^2A_u KO	$1a_u^2 1b_g^2 2a_u^1$	15	input
1^2A_u	1^1A_g KO	$1a_u^2 1b_g^2 2a_u^1$	17	input
1^3B_u	1^3B_u	$1a_u^2 1b_g^2 2a_u^1 2b_g^1$	18	input
$1^1B_u, 2^1B_u$	1^1B_u ANO	$1a_u^2 1b_g^2 2a_u^1 2b_g^1$	24	input
$1^1B_g, 2^1B_g$	1^1B_g ANO	$1a_u^2 1b_g^2 2a_u^1 10b_u^1$ $1a_u^2 1b_g^2 2a_u^1 11b_u^1$	24	input
CI6 Type 1				
1^1A_g	1^1A_g KO	$1a_u^2 1b_g^2 2a_u^2$	9,11 ^d	diag
1^1A_g	1^1B_u ANO	$1a_u^2 1b_g^2 2a_u^2$	11	input
1^3B_u	1^3B_u KO	$1a_u^2 1b_g^2 2a_u^1 2b_g^1$	1	
1^2A_u	1^2A_u	$1a_u^2 1b_g^2 2a_u^1$	1	
$1^1B_u, 2^1B_u$	1^1B_u ANO	$1a_u^2 1b_g^2 2a_u^1 2b_g^1$ $1a_u^2 1b_g^2 2a_u^1 3b_g^1$	18	input
CI6 Type 2				
1^1A_g	1^1A_g KO	see text	11	diag
$1^1A_g, 2^1A_g$	2^1A_g NO	see text	24	diag

^aConfiguration(s) on which the QCI or CI6 treatment was based. In all configurations the σ orbital occupation $1a_g^2, \dots, 10a_g^2, 1b_u^2, \dots, 9b_u^2$ is implied. ^bNumber of functions used in the reference space for perturbation theory selection. Where only a single reference function was used all single excitations relative to that function were retained in the CI. ^cIndicates whether the zeroth-order-space coefficients for PT selection were input from a previous CI or were the result of diagonalizing the electronic Hamiltonian over the zeroth-order space. ^dThe nine reference functions were used in the calculation with $\sigma\pi$ restrictions, the 11 reference functions were used in the calculation without $\sigma\pi$ restrictions.

was defined (either by diagonalizing the electronic Hamiltonian over the reference space or by choosing fixed coefficients for the configurations based on a preliminary CI) and the second-order Rayleigh–Schroedinger (RS) perturbation-theory (PT) energy contributions of the configurations outside the reference space were calculated. The subset of all configurations having the largest RS energy lowerings was retained and treated variationally; the effect of the remaining configurations was estimated via an extrapolation procedure.²⁶

In the class of CI's denoted quadruples CI (QCI), the unselected configuration space was composed of up to quadruple excitations of the π electrons (and the σ Rydberg electron in the case of the 1^1B_g states) from one or two primary configurations. The specific primary configurations are given in Table I. Excitations of the π (σ) electrons were restricted to the π (σ) virtual space. From this class of configurations, PT selection was performed based on an expanded zeroth-order space, the size of which is also given in Table I.

The second class of CI treatment considered is termed a "CI6" CI. Here, the focus of the correlation treatment is the correlation of the π electrons with each other and with the σ electrons. For the type 1 CI6 results, the unselected configuration space is all single excitations plus all double excitations involving at least one of the π electrons relative to the primary configuration of interest. In addition, so-called "differential" $\sigma\sigma'$ excitations²⁷ into the two lowest a_u and three lowest b_g π orbitals were allowed, relative to the primary configuration. (See ref 14 and 27 for descriptions of the effects of "differential" $\sigma\sigma'$ excitations.) Except where noted, we have imposed the added restriction of not allowing $\pi\pi'$ double excitations into the σ virtual space (denoted $\sigma\pi$ res. below). In previous calculations on butadiene this approximation was shown not to affect the calculated excitation energies. Note that the CI6 results for the two 1^1B_u states are obtained from a single CI, where

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TABLE II: Basis Set Comparisons for *trans*-1,3-Butadiene

basis set ^a	state	CI type ^a	energy, hartree	ΔE , eV	(x^2) , au ²
DZ + π R	1^1A_g	CI4 full/ $\sigma\pi$ res	-155.0428		22.3
	1^1B_u		-154.8058	6.45	43.1
	2^1B_u		-154.7741	7.31	38.5
DZ + π R	1^1A_g	CI4 type 3/ $\sigma\pi$ res	-155.0419		22.3
	1^1B_u		-154.8050	6.45	43.1
	2^1B_u		-154.7734	7.31	38.6
DZ + π PR	1^1A_g	CI4 full/ $\sigma\pi$ res	-155.0861		22.2
	1^1B_u		-154.8487	6.46	34.4
	2^1B_u		-154.8156	7.36	46.2
TZ + π PR	1^1A_g	CI4 type 3/ $\sigma\pi$ res	-155.1179		22.1
	1^1B_u		-154.8801	6.47	32.7
	2^1B_u		-154.8478	7.35	48.9

^a See text for definitions of the CI types and basis sets.

the two lowest roots of the CI matrix are extracted. Thus double excitations relative to both the 1^1B_u and 2^1B_u primary configurations are included in the treatment. The size of the reference space used for perturbation-theory selection is given in Table I.

For the 2^1A_g state a slightly modified CI6 procedure was used, denoted as a type 2 CI6 calculation. Due to the multiconfigurational nature of the 2^1A_g state, no single configurational description can be used from which to generate single and double excitations and still yield unbiased results relative to the other states of interest. In this case, the set of unselected configurations was defined by (1) allowing all $\pi\pi' \rightarrow \pi^*\pi'^*$ from all configurations having the six π electrons distributed over the three lowest a_u and three lowest b_u orbitals, (2) allowing all $\sigma\sigma'$ differential double excitations into the three lowest a_u and two lowest b_g orbitals with the six π electrons distributed randomly within the five orbitals, and (3) allowing all $\sigma \rightarrow \sigma^*$ single excitations relative to all configurations having the six π electrons distributed over the four lowest a_u and four lowest b_g π orbitals. The reference configurations for PT selection were chosen on the basis of small CI's of this type. For the purposes of computing excitation energies with the 2^1A_g state, a similar calculation was also performed on the 1^1A_g state.

In the calculations on butadiene two variants of the CI4 calculations of ref 14 are employed. (A CI4 calculation is entirely analogous to the CI6 type 1 calculations defined above, there being only four π electrons in butadiene.) The "full" CI4 calculation of Table II employs all σ virtuals, the type 3 CI4 calculation only utilizes 21 a_g and 18 b_u σ -type MO's. In all cases, $\sigma\pi$ restrictions are maintained in the $\pi\pi'$ excitations, as discussed above.

Where ANO's were used for hexatriene, they were obtained from a small calculation on the two states of interest. Briefly, all double excitations involving the excited electron (that is, the electron which is in an excited molecular orbital relative to the ground-state occupation) are included, along with a subset of all single excitations relative to the SCF configuration.²⁸ The two lowest roots of this CI were used to calculate ANO's. The ANO's used in the butadiene calculations were obtained as described in ref 14.

In general, one must take account of the size inconsistency of CI calculations in order to obtain meaningful excitation energies. However, the dominant cause of size inconsistency in singles and doubles CI treatments is the neglect of quadruple excitations. Thus, for the QCI results, we have performed no size consistency correction. Past semiempirical treatments have concluded that inclusion of quadruple excitations is sufficient to avoid the bulk of size-inconsistency effects.^{6,7} Similarly, for the CI6 results on the 2^1A_g state (and the type 2 CI6 1^1A_g result), due to the multiconfigurational nature of the zeroth-order space, many of the most important quadruple excitations were included in the CI, and thus no size-consistency correction was performed. However, for the type 1 CI6 results, where one or at most two

configurations are used from which to generate single and double excitations, a perturbation-theory based estimate of the effects of higher excitations is employed.²⁹ These results are denoted with the symbol CI6+SC. The coefficients used to estimate the size-consistency correction were only those of the primary functions. We estimate the precision of the perturbation theory extrapolation and size-consistency correction to be good to within 10% of the total estimated correction. For example, the result presented below from the type 1 CI6 calculation on the 1^1A_g state treated variationally those configurations which accounted for 99.0% of the second-order energy lowering and gave an extrapolated energy of -232.08518 au. A similar calculation which treated those configurations responsible for 93.1% of the second-order energy yielded -232.08127 au, a difference of 0.1 eV. For the other type 1 CI6 calculations where a size-consistency correction was performed, the percentages of the second-order energy lowerings accounted for by the configurations retained were as follows: 3^1B_u , 98.4; 2^1A_u , 98.8; 1^1B_u , 92.8; 2^1B_u , 92.1. Thus, it is important to remember that the results are subject to some uncertainties due to the extrapolations and size-consistency corrections. For the values presented below this amounts to uncertainties of 0.15 to 0.30 eV.

Molecular properties were evaluated by using the MELD²² series of codes, as were transition moments between various states. Transition moments were calculated as matrix elements of the position operators. In the calculation of transition moments, the same set of molecular orbitals was used for the description of the ground and excited states (those appropriate to the excited state). It is expected that no serious error in the transition moments is introduced by this procedure.

III. Results

In order to examine the adequacy of the basis set used for hexatriene, several preliminary calculations were performed on butadiene. In Table II results are shown from CI's using several different basis sets on the 1^1A_g , 1^1B_u , and 2^1B_u states for *trans*-1,3-butadiene. We have chosen these three states due to the past difficulties in describing the lowest 1^1B_u states in butadiene. The aim of these calculations was to examine the sensitivity of the state descriptions and the excitation energies to the basis set used. The results labeled TZ + π PR are those from ref 14. On examination of the DZ + π R results, it is seen that truncation of the σ space in the CI has no observable effect on the excitation energies and state descriptions for these states and has only a minor effect on the total energies. On comparison of the DZ + π R and DZ + π PR results it is seen that the inclusion of $d\pi$ functions on the carbons has no perceptible effect on the excitation energies to the two lowest 1^1B_u states but significantly alters the states' characters. This is consistent with our previous multireference singles and doubles CI results¹⁴ on butadiene, which also indicated a relative insensitivity of the excitation energy to the diffuseness of the lowest 1^1B_u state. However, we note that in the DZ + π PR results, the basis set still has the flexibility to yield the diffuse state found in the DZ + π R case. The inclusion of the $d\pi$ functions nevertheless leads to a decrease in spatial extent of the lowest 1^1B_u state and a concomitant increase in size of the second 1^1B_u state. The inclusion of the $d\pi$ functions also leads to a significant drop in total energies, indicating their importance for the correlation of the π electrons. In proceeding to the TZ + π PR basis it is seen that the excitation energies are again similar to those of the two smaller basis sets, but the spatial extents of the states are much more similar to the DZ + π PR results than the DZ + π R results. While there is a small decrease in size of the 1^1B_u state relative to the DZ + π PR 1^1B_u state, the change is much smaller than that brought on by inclusion of the $d\pi$ functions. Within the accuracies we can expect from the present results we thus believe that the DZ + π PR basis is adequate to represent the states of interest in hexatriene.

The results presented in Table III are from SCF calculations on several low-lying states of hexatriene. The 1^1B_g , 2^1A_g , and 1^1B_u

(28) All single excitations relative to the SCF configuration were included except the two single excitations of electrons in the $1a_u$ and $1b_g$ orbitals into the $2a_u$ and $2b_g$ orbitals. Neglect of these two single excitations is expected to have no effect on the final results.

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TABLE III: *trans,trans*-1,3,5-Hexatriene SCF Energies

state	<i>E</i> , hartree	ΔE , eV
1^1A_g	-231.76296	
3^1B_u	-231.66092	2.78
1^1B_g	-231.57099	5.22
2^1A_g	-231.55999	5.52
1^1B_u	-231.55303	5.71
2^1A_u	-231.49619	7.26

TABLE IV: QCI Calculations for Various States of *trans,trans*-1,3,5-Hexatriene

state	orbitals	energy, hartree	ΔE^a , eV	$\langle x^2 \rangle$, au ²
1^1A_g	1^1A_g KO	-231.8615		
2^1A_g	1^1A_g KO	-231.6505	5.74	32.3
3^1A_g	1^1A_g KO	-231.6224	6.51	90.7
1^2A_u	1^1A_g KO	-231.5570	8.29	28.9
1^2A_u	1^2A_u KO	-231.5706	7.91	28.8
1^3B_u	1^3B_u KO	-231.7589	2.79	32.2
1^1B_g	1^1B_g ANO	-231.6507	5.74	43.1
2^1B_g	1^1B_g ANO	-231.6413	5.99	49.1
1^1B_u	1^1B_u ANO	-231.6341	6.19	43.9
2^1B_u	1^1B_u ANO	-231.6203	6.56	53.2

^aExcitation energies relative to the QCI energy for the 1^1A_g state.

states all are essentially Rydberg states. The 2^1A_g is obtained by using a nonorthogonal SCF procedure³⁰ to ensure a variational upper bound to the first excited state of the same symmetry as the ground state. It should be noted that the 1^1B_u excitation energy disagrees with the experimental value by approximately 0.8 eV³¹⁻³⁴ and that the first ionization potential is underestimated by over 1.0 eV at the SCF level.^{35,36} In addition, the single configurational description of the 2^1A_g state leads to a diffuse state, whereas the experimental results for the longer chain species and previous theoretical results on butadiene¹¹⁻¹⁴ and hexatriene^{13,15} are more consistent with a valencelike 2^1A_g state.¹

The results for the QCI calculations on several low-lying states of *trans,trans*-1,3,5-hexatriene are presented in Table IV. Several interesting points can be observed. Concerning the 1^1A_g type states, the 2^1A_g state has indeed become valencelike, having a spatial extent similar to the valence 3^1B_u state. The 3^1A_g state is a 3π Rydberg state.

The two results for the 2^1A_u state differ in the choice of the molecular orbital basis; the first uses the ground state of the neutral molecule's molecular orbitals, the second uses those of the ion. It is seen that a significant improvement in the ionization potential is achieved at the QCI level relative to the SCF values (experimental IP = 8.29 eV^{35,36}).

The two lowest 1^1B_g states are both Rydberg-like. Both lie in the plane of the molecule; the first pointing perpendicular to the

TABLE V: CI6 Results for Various States of *trans,trans*-1,3,5-Hexatriene^a

state	orbitals	energy, hartree	energy +SC, hartree	ΔE^b , eV	ΔE_{+SC}^b , eV	$\langle x^2 \rangle$, au ²
Type 1						
1^1A_g	1^1A_g KO	-232.0442 ^c	-232.0921 ^c			32.4
1^1A_g	1^1B_u ANO	-232.0378	-232.0909			32.4
1^1A_g	1^1A_g KO	-232.0387	-232.0852			32.2
1^3B_u	1^3A_u KO	-231.9293	-231.9809	2.98	2.84	32.3
1^1B_u	1^1B_u ANO	-231.8351	-231.8958	5.54	5.15	33.9
2^1B_u	1^1B_u ANO	-231.7967	-231.8613	6.59	6.09	55.4
1^2A_u	1^2A_u KO	-231.7469	-231.7874	7.94	8.10	28.8
Type 2						
1^1A_g	1^1A_g KO	-231.9873				32.0
1^1A_g	2^1A_g NO	-231.9784				
2^1A_g	2^1A_g NO	-231.7703		5.90		32.2

^a $\sigma\pi$ restrictions in all calculations unless otherwise specified (see text). ^bFor the type 1 CI6 calculations the ΔE values are relative to the $\sigma\pi$ restricted 1^1A_g state energies based on the 1^1A_g KO. For the type 2 CI6 results ΔE is relative to the 1^1A_g energy based on the 1^1A_g KO. ^cNo $\sigma\pi$ restrictions were imposed on the $\pi\pi'$ excitations.

molecular axis, the second parallel to it. The values of $\langle z^2 \rangle + \langle y^2 \rangle$ are 88.8 and 128.9 au² for the first and second 1^1B_g states, respectively, whereas for the 3^1B_u state the value is 51.6 au².

Finally, the QCI results suggest that the character of the two lowest 1^1B_u states is midway between valence and Rydberg. The lowest state occurs at 6.19 eV, whereas the experimental (optical absorption) intensity maximum for this state is at 4.93 eV.³²⁻³⁴ In none of the QCI calculations except those concerning the 1^1B_g states is there any consideration of the correlation of the π electrons with the σ space, and even for the 1^1B_g states, only the single σ electron arising from the $a_u \rightarrow b_u$ excitation is correlated.

In Table V results are shown from the two types of CI6 calculations performed on the low-lying states of *trans,trans*-1,3,5-hexatriene. For the type 1 calculations two energy entries are made, those obtained from the extrapolated CI's and those obtained upon application of the perturbative size-consistency correction²⁹ (+SC). We consider the values with the size-consistency correction to be the more accurate of the two. It is seen that the choice of orbital basis has only a small effect on the total energy estimate of the 1^1A_g state (<0.2 eV) and has a negligible effect on the value of $\langle x^2 \rangle$. The $\sigma\pi$ restriction discussed above also appears to be a minor one. In addition, compared to that for the 3^1B_u state, the size-consistency correction for the 1^1B_u states is significantly larger.

On comparison of Tables IV and V, the most significant points to note are the similarity of the results for the 3^1B_u , 2^1A_g , and 2^1A_u states and the complete dissimilarity of the results for the two lowest 1^1B_u states. In the cases of the 1^1B_u , 3^1B_u , and 2^1A_u states, the same orbital basis set was used in both the QCI and the CI6 calculations. In the CI6 results the 1^1B_u state is essentially a valencelike state while the 2^1B_u state is basically Rydberg in character ($3d\pi$). The excitation energy to the 1^1B_u , 5.15 eV, is near the experimental intensity maximum in the absorption spectrum³²⁻³⁴ and is actually in quite good agreement with the electron-impact intensity maximum of 5.13 eV.³¹

The calculated oscillator strengths for transitions from the ground state to the 1^1B_u and 2^1B_u states are 1.24 and 0.035, respectively.

IV. Discussion

In this section we discuss the results of section III using the experimental excitation energy to the 3^1B_u state and the experimental ionization potential as guides to the accuracy of our calculations. We then compare our results for the remaining states with the experimental assignments, semiempirical theoretical results, and previous ab initio theoretical results.

There is considerable uncertainty in the literature concerning the assignment of almost all Rydberg states of hexatriene and at least one of the low-lying valence states (2^1A_g). Thus there are few points at which we can make an evaluation of the accuracy

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(36) In ref 34a the IP is taken as the intensity maximum in the photoelectron spectrum. In ref 34b the IP is associated instead with the peak in the photoelectron which lies above the intensity maximum, at 8.45 eV. We have chosen to use the 8.29-eV value of ref 34a, which is in closer agreement with the IP estimate obtained in ref 32 based on the np Rydberg series. However, since our aim is to correlate our calculated excitation energies with the intensity maxima of the observed Rydberg transitions, one can avoid the question of the vertical IP altogether. This is true since one expects similar differences between vertical and adiabatic excitation energies for Rydberg transitions as are seen for vertical and adiabatic IP's. Thus the correction based on the 8.29-eV IP estimate can be viewed as a means of correcting our calculated excitation energies to correspond to the intensity maxima of the Rydberg transitions in the molecule.

of the current theoretical methods. Two such points are, however, the excitation energy to the 3B_u state, which is known from electron impact spectroscopy³¹ to be approximately 2.6 eV, and the experimental IP, which is 8.29 eV.^{35,36} These are convenient values to have, since they correspond roughly to the two limits of the excited states of interest here. The 3B_u state is a purely valencelike state and, thus, can give some estimate of the error in calculated excitation energies for valencelike states. The IP estimate gives a measure of the errors to be expected in the calculations involving Rydberg states. That is, a calculation on a Rydberg state involves the correlation of the N-1 localized electrons with each other and, secondarily, with the Rydberg electron in the diffuse orbital. With the positive ion we are concerned with the correlation of the N-1 localized electrons. Thus, to the extent that the CI can adequately treat the small correlation energy between the Rydberg electron and the N-1 core electrons in the neutral, the errors in excitation energies might be expected to be similar to those obtained in the IP estimate.

The excitation energies obtained for the 3B_u states were 2.79 and 2.84 eV for the QCI and CI6+SC calculations, respectively. Both excitation energies were obtained by using the SCF orbitals for the 3B_u state in calculations on the excited state and ground state orbitals in calculations on the ground state. From the experimental estimate of 2.61 eV³¹ we obtain excitation-energy errors of 0.18 and 0.23 eV, respectively. These errors can arise from several factors, among which are the incomplete one-electron basis and the limited treatment of the correlation problem. In particular, the limited correlation treatment could be important here. In the QCI calculations a reasonably high level of correlation is included in the π space but no account is made of correlation of the π and σ electrons or pure σ correlation which might differentially affect the excitation energy. Some $\sigma\pi$ correlation is included in the CI6 results, along with σ single excitations (which allow for some relaxation of the σ orbitals) but this in fact slightly raises the calculated excitation energy. However, both the QCI and CI6+SC results are certainly in reasonable agreement with experiment. We thus take the above errors as estimates of the errors to be expected in the excitation energies for what might be considered "classical" valence states in the respective types of CI's for hexatriene. These are used as corrections in the assignments presented in Table VI but are only intended as guides to compensate for the truncated CI's employed here.

In a similar way it seen that the calculated IP's based on use of the ion molecular orbitals for the 2A_u state are in error by -0.38 and -0.19 eV^{35,36} for the QCI and CI6+SC results, respectively. Of interest is the QCI result obtained by using the neutral's ground-state orbitals for the 2A_u ion, for which exact agreement with the experimental ionization potential is obtained. This last result can be viewed as the CI analogue of Koopmans' theorem. In this case, the loss of the relaxation energy at the SCF level entailed by use of the 1A_g molecular orbitals to describe the ion is approximately offset by the loss of correlation energy in the neutral (relative to the ion) caused by not considering $\sigma\sigma$ and $\sigma\pi$ correlation. Since we include up to quadruple excitations in the π space, it is reasonable to believe that the $\pi\pi'$ correlation is treated fairly accurately. It thus appears that with the present basis for hexatriene, the two effects cancel for the 2A_u ion. Therefore, as estimates of the errors in the present calculations where Rydberg states are concerned, we will apply the approximate corrections of adding 0.38 eV to the QCI excitation energies and 0.19 eV to the CI6+SC results and make no correction to the QCI results where the excited state is expanded in the molecular orbitals of the ground state. Again, these are only intended as approximate guides in an attempt to compensate for the truncation of the present CI's.

The results concerning the 1B_u state are perhaps the most surprising. It is seen that the two different types of CI's applied yield significantly different results, in terms of both the estimated excitation energies and the qualitative character of the state. Previous results for ethylene⁸ and butadiene¹⁴ have emphasized the importance of $\sigma\pi$ correlation in the description of the (presumed) valencelike $\pi \rightarrow \pi^*$ type states in those molecules. The

TABLE VI: Theoretical and Experimental Assignments for *trans,trans*-1,3,5-Hexatriene

state	type	ΔE , eV	ref source
${}^1{}^3B_u$	experiment	2.61	31
	ab initio	2.71	13, 15
	semiempirical	2.18	7
	present	2.8	
${}^1{}^1B_u$	experiment	4.93	32
	experiment	4.95, 5.13	31
	experiment	4.93	34
	ab initio	6.56	13, 15
	semiempirical	5.0	6
	semiempirical	5.1	7
${}^2{}^1B_u$ (3d π)	present ^a	4.92	
	experiment	6.52	39
	experiment	6.53	33
	experiment	6.57	31
${}^2{}^1A_g$	ab initio	6.27	15
	present ^a	6.28	
	experiment	5.7-6.45	33
	experiment	5.3	36
	ab initio	5.87	13, 15
	semiempirical	4.7	6
${}^3{}^1A_g$ (3p π)	semiempirical	4.5	7
	present ^a	5.6-5.7	
	experiment	6.22	38
	experiment	5.85	39
${}^1{}^1B_g$ (3p σ)	ab initio	6.26	15
	present ^a	6.51	
	experiment	6.2	39
	ab initio	6.0	15
${}^2{}^1B_g$ (3p σ')	present ^a	6.12	
	ab initio	6.20	15
	present ^a	6.37	

^aDenotes values adjusted based on the corrections outlined in the Discussion.

lowest $\pi \rightarrow \pi^*$ state in *trans,trans*-1,3,5-hexatriene is the ${}^1{}^1B_u$ state and it is seen that inclusion of $\sigma\pi$ correlation has a qualitative effect in this case as well. Since the CI6+SC calculation on the ${}^1{}^1B_u$ state (excitation energy of 5.15 eV and $\langle x^2 \rangle$ value of 33.9) has the freedom to produce a state at higher energies and larger spatial extent but does not, we believe that this is the more accurate result for the ${}^1{}^1B_u$ state. We attribute the errors in the QCI results to neglect of the important $\sigma\pi$ correlation effects. Given the essentially valencelike value of $\langle x^2 \rangle$ for the ${}^1{}^1B_u$ state in the CI6+SC results, we use the correction obtained above based on the 3B_u results. This leads to an estimated excitation energy to the ${}^1{}^1B_u$ of 4.92 eV (see Table VI).

It is interesting to examine the trend in the spatial extents of the $\pi \rightarrow \pi^*$ states of the polyenes as a function of chain length in the series ethylene, butadiene, and hexatriene. In the case of ethylene there is some disagreement as to the exact size of $\langle x^2 \rangle$,⁸⁻¹⁰ but for convenience we choose the CI2 values of ref 8, which are most consistent with the CI4 values for butadiene of ref 14 and the CI6 values presented here. For ethylene the value of $\langle x^2 \rangle$ for the lowest $\pi \rightarrow \pi^*$ state is approximately $5.5 a_0^2$ larger than that for the ground state.⁸ For butadiene¹⁴ the lowest $\pi \rightarrow \pi^*$ excited state has $\langle x^2 \rangle$ values larger than the ground state by 4 and $10.5 a_0^2$ for the cis and trans isomers, respectively. In *trans,trans*-1,3,5-hexatriene the difference in $\langle x^2 \rangle$ values between the ground state and the ${}^1{}^1B_u$ state has decreased to $1.5 a_0^2$. That is, the ${}^1{}^1B_u$ state has become essentially a pure valence state at this level of treatment. The $\pi \rightarrow \pi^*$ valence states can be described as ionic states using valence bond arguments and it has been argued that this ionic character may be the cause of the large spatial extents of the $\pi \rightarrow \pi^*$ states.^{11,14} In any event, the electronic repulsion effects responsible for the expanded ${}^1{}^1B_u$ states in the shorter polyenes appear to decrease in importance as chain length is increased. However, it should be noted that at the SCF level the ${}^1{}^1B_u$ state is still completely Rydberg-like, and only upon inclusion of $\pi\pi'$ and $\sigma\pi$ correlation does the description of the ${}^1{}^1B_u$ state decrease in size. On the basis of these results we expect that the ${}^1{}^1B_u$ states of the longer polyenes will also be relatively

more valencelike states than those of the shorter polyenes.

The other valencelike excited state, the 2^1A_g state, is much less sensitive to the effects of $\sigma\pi$ correlation, as can be observed by comparison of the QCI and CI6+SC results. Both the calculated excitation energies and the values of $\langle x^2 \rangle$ are in reasonable agreement. Applying the valence state corrections obtained above for the 3^1B_u states leads to estimated excitation energies of 5.56 eV (QCI) and 5.67 eV (CI6+SC). These corrections are expected to be somewhat less reliable when applied to the 2^1A_g state, given its qualitatively different nature from the singly excited 3^1B_u state. In addition, the QCI 2^1A_g results are from a calculation which uses the ground-state molecular orbital basis to describe the 2^1A_g state. In general one might expect a further decrease in the calculated excitation energy were the molecular orbitals appropriate to the 2^1A_g state used in the QCI calculations. An upper limit to this value of about 0.2 eV can be estimated by comparing the two different QCI 2^1A_u results. Nevertheless, either set of results predicts the 2^1A_g state to lie above the 1^1B_u state for vertical excitation. We estimate that the vertical excitation energy for the 2^1A_g state is in the range of 5.5–5.8 eV.

Turning to the Rydberg-like states, we can apply similar corrections using those obtained from the 2^1A_u states. In these cases however, only one set of calculations was performed (or is useful) for each state. In the cases of the 3^1A_g state and the two 1^1B_g states, only QCI calculations were performed. While both types of CI's were performed for the 2^1B_u state, only those from the CI6+SC calculations should be considered, due to the sensitivity of the 1^1B_u state to the inclusion of $\sigma\pi$ effects. The corrected assignments for these states are shown in Table VI. For the 3^1A_g state no correction to the calculated QCI excitation energy was made. Since the 3^1A_g state is a pure Rydberg state and was expanded in the molecular orbital basis of the ground state, we felt it was most similar to the 2^1A_u result expanded in the ground state molecular orbitals, which led to no correction. The energy ordering of the three 3p Rydberg components in the present calculation then is $1^1B_g(3p\sigma) < 2^1B_g(3p\sigma') < 3^1A_g(3p\pi)$.

The present results provide a significantly different picture of the low-lying singlet valence states of *trans,trans*-1,3,5-hexatriene than past theoretical results (see Table VI). In comparison with semiempirical results for the 1^1B_u state we are actually in quite good agreement, with values near 5.0 eV.^{6,7} No comparison can be made with our calculated oscillator strengths since the previous calculations did not provide estimates of oscillator strengths for the 1^1B_u state. For the 2^1A_g state however, we are in qualitative disagreement with the semiempirical results, since the semiempirical theories obtain the 2^1A_g at 4.5 eV⁶ and 4.7 eV,⁷ either of which is below the 1^1B_u state. Since the present ab initio results cannot claim to be definitive, one cannot assess a priori which result is the most accurate. However, several lines of evidence suggest the present result may be more accurate. First, longer polyenes, where the 2^1A_g state lies below the 1^1B_u state, are known to fluoresce from the 2^1A_g state.¹ No fluorescence is observed from the shorter polyenes, *trans,trans*-1,3,5-hexatriene included,³⁴ thus suggesting that the 2^1A_g lies above the 1^1B_u state even at their respective relaxed excited-state geometries. In addition, it has been shown above that an accurate representation of the 1^1B_u state is dependent upon inclusion of $\sigma\pi$ correlation effects. Since the σ electrons are treated as a frozen core in the CI's in the semiempirical theories of refs. 6 and 7, these effects must be included through modified parameters (electron–electron repulsion and electronic hopping integrals) in the semiempirical scheme. The fact that the 1^1B_u state is estimated accurately indicates that this has been done. However, it was also shown above that the 2^1A_g state and the 3^1B_u state are much less sensitive to $\sigma\pi$ correlation and use of the same parametrization to describe the 1^1B_u state and the 2^1A_g or 3^1B_u states might lead to an underestimation of the excitation energies for the latter two states. Indeed, the calculated excitation energy of the 3^1B_u state from ref 7 is 2.18 eV, 0.43 eV lower than the experimental value.³¹ Thus we would suggest that the present results are most likely more accurate in describing the energy ordering of the two lowest singlet excited states.

Our results are also different from the previous ab initio investigation of the low-lying electronic state of *trans,trans*-1,3,5-hexatriene. In regard to the 1^1B_u state, the lack of $\sigma\pi$ correlation in ref 13 and 15 most likely accounts for a portion of the discrepancy with the present results. A second difference may be the use of ANO's to describe the 1^1B_u states in the present study, whereas in ref 13 and 15 the 1^1B_u SCF orbitals were used. In studies on butadiene the use of ANO's rather than the more diffuse ground state molecular orbitals was found to qualitatively affect the state description of the 1^1B_u state,¹⁴ and a similar effect may be operative here. The predicted excitation energy from ref 13 and 15 for the 2^1A_g is in quite good agreement with the present results, suggesting that our inclusion of $d\pi$ polarization functions was not an important effect for the 1^1A_g – 2^1A_g excitation energy. Their estimates of the three 3p Rydberg states are somewhat lower than our corrected values. Differences in basis set probably account for these small discrepancies.

Perhaps the most striking result of the present study is the good agreement achieved with experiment for the 1^1B_u state. Even the uncorrected value of 5.15 eV is only 0.2 eV away from the optical intensity maximum^{32,34} and is essentially the same as the intensity maximum in the electron scattering experiments (5.13 eV).³¹ As discussed in the methods section, due to the uncertainties inherent in the calculations the nearly exact agreement obtained for the excitation energy should be regarded with some caution. However, the calculations do obviously obtain a valencelike state near 5.0 eV. The valencelike character of the 1^1B_u state is consistent with the minimal shift between gas- and solution-phase spectra of hexatriene.¹ Our oscillator strength for the 1^1B_u state is significantly larger than the experimental value for dimethylhexatriene in hexane (0.74)^{34,37} but is consistent with the predominantly valencelike character of the state. Comparison with experiment concerning the 2^1A_g state is somewhat difficult due to the range of experimental estimates, but the most recent value³⁸ places the 2^1A_g at approximately 5.3 eV, near where it is predicted here. The position of the vertical transition energy is still an open question.

Our assignments of the 3p Rydberg states (3^1A_g , 1^1B_g , 2^1B_g) and the 2^1B_u ($3d\pi$) state are different from previous results presented in Table VI. The results are in agreement with those of Doering et al.³⁹ for the 1^1B_g ($3p\sigma$, $3p\sigma'$) states, but we assign the 6.52 eV feature to the 3^1A_g ($3p\pi$) Rydberg feature rather than the 2^1B_u ($3d\pi$) Rydberg state, which we calculate to lie at 6.3 eV. Most surprising is the prediction that the 2^1B_u ($3d\pi$) state is actually below the 3^1A_g ($3p\pi$) state. An effect of this type could arise from an interaction between the 2^1A_g valencelike state and 3^1A_g ($3p\pi$) state which would lie quite close in energy before mixing of the two configurations. The 1^1B_u and 2^1B_u ($3d\pi$) states are expected to lie significantly farther apart before mixing due to the drop in energy of the 1^1B_u valence component with chain length. However, based on comparison with experimental spectra this prediction should be regarded with caution.

In C_{2h} symmetry, one-photon transitions to the 3p Rydberg states are forbidden, whereas one-photon transitions to the $3d\pi$ states are allowed. The present results would predict a sharp absorption near 6.3 eV due to the 2^1B_u ($3d\pi$) state and weak transitions at 6.2 and 6.5 eV due to the 3p Rydberg states. The optical absorption spectrum in the 6.1–6.6 eV region shows weak bands near 6.2 eV while a sharp feature is found near 6.5 eV.³³ In addition, in electron impact spectra no strong features are observed at 6.3 eV, and the 6.22 eV feature increases in intensity relative to the 1^1B_u peak with increased scattering angle,³⁹ a behavior normally associated with a symmetry- or spin-forbidden transition. It is possible that the current results are in error concerning the relative ordering of the 3^1A_g ($3p\pi$) and 2^1B_u ($3d\pi$) states. Possible causes of these errors may be overestimates of the effects of size consistency in the 2^1B_u excitation energy and use of ground state MO's to describe the 3^1A_g state. In addition,

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use of a subset of all quadruple excitation relative to the 1^1A_g state to describe the three lowest 1^1A_g states may artificially bias the excited states toward higher excitation energies.

Concerning the transition at 6.22 eV, both the present results and those of ref 39 are in disagreement with the polarized two-photon studies of ref 40 which present quite a strong case for assigning the 6.22-eV peak to the 3^1A_g state. Resolution of this discrepancy must await further experimental investigation, perhaps via the use of two excitation sources to make an unequivocal symmetry assignment. However, it should be stressed that the present ab initio results, as would be true of any theoretical methods applied to such an extended system, are dependent on a large cancellation of errors for even semiquantitative accuracy. At present one can hope to achieve internal consistency from theoretical results (for example, regarding state orderings) and semiquantitative accuracy for excitation energies, but firm estimates of excitation energies, accurate to within 0.1 eV, are surely more than one can expect from theory at the present time.

Nevertheless, the picture obtained of the low-lying electronic states of *trans,trans*-1,3,5-hexatriene is in quite good overall agreement with that obtained from experiment. The ordering of the valence excited states relative to the Rydberg states, the ordering of the valence states relative to one another, and even the estimated excitation energies of the valence states are reproduced quite well. On this basis, we are currently examining the effects of geometric variations in the excited states on excitation and fluorescence emission energies for butadiene and hexatriene.

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as well as extending the present treatment to other polyenes.

V. Conclusions

The present study has shown the utility of ab initio methods to the description of the low-lying electronic states of *trans,trans*-1,3,5-hexatriene. The most significant results obtained are (1) the 1^1B_u state is found to be basically valence-like and to be of $\pi \rightarrow \pi^*$ character, (2) the 2^1A_g state is calculated to lie above the corrected excitation energy for the 1^1B_u state by from 0.6 to 0.9 eV, and (3) the 3^1A_g ($3p\pi$) Rydberg state appears to be somewhat higher in energy than might be expected when compared with the $3p\sigma$ Rydberg states, perhaps due to an interaction with the close-lying 2^1A_g state.

In comparison with experiment we find good agreement for the 1^1B_u state, apparently good agreement for the location of the 2^1A_g state, and fair agreement with the location of the Rydberg states. In particular, our assignment of the 3^1A_g is in disagreement with the experimental assignment of ref 40. Further experimental studies of the spectrum of *trans,trans*-1,3,5-hexatriene in the 6.0-7.0 eV region would be quite helpful in resolving this discrepancy.

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LO-TO Effects in the Single-Crystal Raman Spectra of Urea

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Single-crystal Raman studies in urea in 90°- and 45°-cut crystals demonstrate LO-TO splitting on some (crystal) B_2 modes but not on E. A possible origin of this difference is discussed.

In a recent communication, we have demonstrated by a combination of single-crystal Raman and incoherent inelastic neutron scattering spectra and the spectra of chemical compared to physical isotopomeric mixed crystals that intermolecular vibrational coupling occurs in crystalline urea, at least for some vibrations.¹ In the solid, urea, a planar molecule of C_{2v} symmetry, occupies a C_{2v} site within a crystal of D_{2d} symmetry ($P42_1m$, D_{2d}^3).² The correlations between C_{2v} and D_{2d} (Table I) mean that at the factor group level of approximation, the presence of intermolecular vibrational coupling is not expected to change the peak count in the infrared spectrum of the crystal and in the Raman only to be manifest in a splitting of (molecular) A_1 modes into (crystal) A_1 and B_2 components in the single-crystal spectra (provided, of course, that the molecular A_1 modes are appreciably intermolecularly vibrationally coupled). Because of the absence of a center of symmetry in the D_{2d} point group, no additional information on intermolecular vibrational coupling is available from a comparison of infrared and Raman frequencies. Likewise, while inelastic neutron scattering studies are capable of exploring dispersion, itself related to intermolecular vibrational coupling,³ in

TABLE I: Comparison of Site and Factor Group Raman Activities

site (C_{2v})	factor (D_{2d}^3)
A_1 ($x'x', y'y', z'z'$)	A_1 ($zz, xx + yy$) + B_2 (xy)
A_2 ($x'y'$)	B_1 ($xx - yy$)
B_1 ($x'z'$)	E (xz, yz)
B_2 ($y'z'$)	E (xz, yz)

TABLE II

LO-TO features	0° cryst expts	45° cryst expts
B_2 (TO)	$x(yx)y$	
B_2 (LO)	$z(xy)z$	
E(TO)	$x(yz)\bar{x}$ and $y(xz)\bar{y}$	
E(TO) + E(LO)	$x(zx)z$ and $y(zy)z$	$z + y(z[x + y])y - x$
B_2 (LO) + E(TO)		$x + z(y[x + z])x - z$ and $y + z(x[y + z])y - z$
B_2 (TO) + E(LO)		$x + z(y[x + z])z - x$ and $y + z(x[y + z])z - y$

practice it is not possible to use data on polycrystalline samples in other than in a corroborative role. Only isotopic chemical and physical mixed crystals, by a distinction between limiting one-mode and two-mode behaviors, can provide immediately accessible data

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