THE EXCITED ELECTRONIC STATES OF ALL-*TRANS*-1,3,5-HEXATRIENE [*]

Marco A.C. NASCIMENTO [**] and William A. GODDARD III

Arthur Amos Noyes Laboratory of Chemical Physics [‡], *California Institute of Technology, Pasadena, California 91125, USA*

Received 10 August 1978

Extensive configuration interaction calculations based on ab initio wavefunctions including diffuse basis functions are reported for all-*trans*-1,3,5-hexatriene. Using these results we have assigned the one-photon spectra of Gavin and Rice and the electron-impact spectra of Kuppermann, and we have confirmed the assignment of the two-photon spectra of El-Sayed. The valence $2\,^1A_g$ state is found to lie above the strongly allowed valence $1\,^1B_u$ state.

In recent years there has been considerable interest in the photochemistry of polyenes, motivated partly because of their relation to the chemistry of visual pigments [1]. *Trans*-1,3-butadiene (hereafter butadiene) has been studied experimentally [2–7] and theoretically [8,9], with moderate agreement concerning the character, assignment, and ordering of most states. Several experimental techniques [10–13] have been applied to all-*trans*-1,3,5-hexatriene (hereafter hexatriene). Accurate ab initio calculations have not previously been reported for hexatriene, and there is considerable uncertainty concerning the character, location, and assignment of the hexatriene states. We report extensive ab initio calculations on both the valence and Rydberg excited states of hexatriene, including high-order electron correlation effects.

All calculations were carried out for the experimental ground state geometry [14]. The molecule is in the yz plane (z along the C_3–C_4 axis) with x per-pendicular to the molecular plane. The calculations [15] [‡] used a valence double zeta basis plus diffuse s and p functions [16]. Hartree–Fock calculations were carried out on the ground state, the $(\pi \rightarrow \pi^*)$ ^1B_u excited state, and the four lower singlet Rydberg states ($\pi_{2a_u} \rightarrow 3s, 3p_y, 3p_x, 3d_{xy}$). Using the appropriate set of SCF orbitals we carried out extensive configuration interaction (CI) (all quadruple excitations plus all lower excitations) among the 18 π basis functions (for valence and π Rydberg states) or among the 12 valence π functions plus lowest six σ Rydberg functions [‡‡] (for σ Rydberg states). In either case, the 19 core or sigma bonding orbitals were kept unexcited.

The length of the long axis ($\bar{z}$) of the hexatriene molecule is comparable to the size of the Rydberg orbitals, leading to some modifications in the usual sequence of orbitals. The lowest 3p orbital is in the plane of the molecule but perpendicular to $\bar{z}$ and is hereafter denoted as $3p_{\bar{y}}$. The lowest 3d orbital is π-like and is oriented perpendicular to the central C_3–C_4 bond (or to the z axis) and is hereafter denoted as $3d\pi_{xy}$. The 3s state (5.97 eV) is essentially degenerate with the $3p_{\bar{y}}$ state (6.00 eV). The remaining two

Table 1
Excited electronic states of the all-*trans* hexatriene molecule

State (present work)	Theoretical results (eV) (present work) a)	Gavin and Rice [10,20]	Experimental results (eV)	
			Flicker et al. [11]	others
$1\,^3B_u$	2.71		2.61 (1.9–3.5)	2.58 [21]
$1\,^3A_g$	4.32		4.11 (3.6–4.6)	4.2 [13]
$1\,^1B_u$ $(\pi \rightarrow \pi^*)$		4.93	4.95, 5.13, 5.5, 5.7	(5.1–5.7)[13]
$2\,^1A_g$ $(\pi \rightarrow \pi^*)$	5.87			
$1\,^1A_u$ (3s)	5.97	5.94 ($2\,^1A_g$, $2\,^1B_u$, $3\,^1A_g$)	6.06	
$1\,^1B_g$ ($3p_y$)	6.00			
$2\,^1B_g$ ($3p_z$)	6.20			
$3\,^1A_g$ ($3p_x$)	6.26			6.23 [12]
^1B_u ($3d_{xz}$)	6.27	6.28 ($2\,^1A_g$, $3\,^1A_g$, $2\,^1B_u$)	6.25	6.2 [13]
^1B_u $(\pi \rightarrow \pi^*)$ valence	6.56	6.53 ($2\,^1B_u$)	6.57	
^1B_u ($3d_{xy}$)	6.68	6.68		
$2\,^1A_u$ ($3d_{z^2}$)	6.72	6.73 ($2\,^1B_u$, ν_2)	6.75	
$3\,^1A_u$ ($3d_{yz}$)	6.80	6.90 ($2\,^1B_u$, ν_1)	6.93	6.9 [13]
$4\,^1A_u$ ($3d_{x^2-y^2}$)	7.00	7.06 ($2\,^1B_u$, $\nu_3 + \nu_5$)	7.08	
^1B_u ($4d_{xz}$)	7.26	7.26 ($2\,^1B_u$, $\nu_1 + \nu_2 + \nu_3$)	7.25	
^1B_u ($4d_{xy}$)	7.42	7.37		
^1A_u ($4d_{z^2}$)	7.44	7.46		
^1B_u ($5d_{xz}$)	7.68	7.68		
^1A_u ($5d_{z^2}$)	7.75	7.71 ($5p_x$)	7.77	
^1B_u ($5d_{xy}$)	7.76			
^1B_u ($6d_{xz}$)	7.90	7.88 ($6p_x$)	7.93	
^1B_u ($6d_{xy}$)	7.93	7.98 ($7p_x$)		
^1A_u ($6d_{z^2}$)	7.94			
^1B_u ($7d_{xz}$)	8.01	8.05 ($8p_x$)	8.06	8.0 [13]
^1B_u ($7d_{xy}$), ^1A_u ($7d_{z^2}$)	8.04			
^1B_u ($8d_{xz}$)	8.09	8.10 ($9p_x$)		
^1B_u ($8d_{xy}$), ^1A_u ($8d_{z^2}$)	8.11			
9d	8.18	8.13 ($10p_x$)		
10d	8.21	8.15 ($11p_x$)		
11d	8.23	8.17 ($12p_x$)		
∞d	8.33	8.27 (∞p_x)		
^1B_g $(\sigma \rightarrow \pi^*)$	9.18		9.1	9.2 [13]
			9.7	9.6 [13]
			10.5	10.7 [13]
^1A_u $(\sigma \rightarrow \pi^*)$	11.51			

a) The energies for the states assigned as 4d and higher Rydberg levels are obtained using the quantum defect formula with the quantum defect being obtained from the ab initio calculations on the 3d levels.

3p states are at 6.20 and 6.26 eV and are nearly degenerate with the $3d\pi_{xz}$ states, while the remaining four 3d states are in the range 6.68 to 7.00 eV.

The $2\,^1A_g$ excited state at 5.62 eV has the charac-ter of the broken-bond valence bond structure (but orthogonalized to the ground state), leading to a CI wavefunction that is dominated by double excitations from the ground state (when expressed in terms of

the ground state molecular orbitals). Including σ correlation effects, this excitation energy increases to 5.87 eV.

The ^1B_u state corresponds mainly to the $\pi_{2a_u} \rightarrow \pi^*_{2b_u}$ transition, leading to a high oscillator strength. As for the corresponding states of ethylene and butadiene, the calculated vertical transition energy in hexatriene is significantly above the peak in the observed spectrum (0.6, 0.67, and 1.2 eV, respectively).

Table 1 shows the results of our calculations and compares them with the available experimental results. There is good agreement between our calculated theoretical values and the experimental results of Gavin and Rice [10] and Flicker et al. [11].

From observation of two-photon absorption and polarization studies, El-Sayed et al. [12] have assigned the state observed at 6.23 eV as ^1A_g. This is in excellent agreement with our results for the $3\,^1A_g$ ($\pi_{2u} \rightarrow 3p\pi_x$) state at 6.26 eV. We find two nearby ^1B_g states ($\pi_{2u} \rightarrow 3p_\sigma$) at 6.00 and 6.20 eV. In order to assess the experimental assignment, we calculated the relative cross sections for the two-photon absorption into these three states. The two-photon intensities of the transition to the ^1A_g ($3p\pi_x$) state relative to the ^1B_g state ($3p_{\bar{y}}$, $3p_{\bar{z}}$)$[\omega_{A_g \rightarrow A_g}/\omega_{A_g \rightarrow B_g}]$ are 18.65 ($3p_{\bar{y}}$) and 12.05 ($3p_{\bar{z}}$), respectively, for circularly polarized light and 46.90 ($3p_{\bar{y}}$) and 31.35 ($3p_{\bar{z}}$), respectively, for linearly polarized light $^\ne$. Thus the ^1B_g states would have been difficult to detect in the El-Sayed experiment [12] and we concur with his assignment.

There have been suggestions that the 2^1A_g valence state might occur below the strongly allowed ^1B_u state for larger polyenes [18,19]. However, for hexatriene our calculations indicate that the $2\,^1A_g$ state lies at 5.87 eV, which is well above the observed ^1B_u state ($\approx$4.9 eV). [Relaxation of the geometry of the $2\,^1A_g$ state should lead to lower transition energy; however, it seems highly unlikely that detectable features of the $2\,^1A_g \leftarrow X\,^1A_g$ ($v = 0$) transition will be found below the ^1B_u ($v = 0$) $\leftarrow X\,^1A_g$ ($v = 0$) absorption in hexatriene.] A good experimental test here would be a multiphoton absorption experiment as in

$^\ne$ In these calculations the summation over intermediate states was performed using the complete set of improved virtual orbital (IVO) states. This result was then corrected for CI effects. The CI corrections are based on similar calculations for the butadiene molecule using states generated at full π-CI level.

the El-Sayed study [12]. Using CI wavefunctions we calculate that for $2\,^1A_g$ ($\pi \rightarrow \pi^*$) $\leftarrow X\,^1A_g$ the two-photon absorption transition rate is 7.1×10^{-51} F^2 s^{-1} for linearly polarized light and 1.2×10^{-50} F^2 s^{-1} for circularly polarized light (where F is the photon flux in photons/cm^2 s). For the observed $3\,^1A_g \leftarrow X\,^1A_g$ transition our estimated transition rates are 9.3×10^{-52} F^2 s^{-1} for linearly polarized light and $2.7 \times 10^{-51} F^2$ s^{-1} for circularly polarized light ‡‡.

The bands at 5.70 to 6.40 eV in the UV spectrum were assigned [10] to the $2\,^1A_g$ and $3\,^1A_g$ states and more recently to a $2\,^1B_u$ state [20]. Our calculations place the $2\,^1A_g$ ($\pi \rightarrow \pi^*$) and the $3s\,^1A_u$ and $3d_{\overline{xz}}\,^1B_u$ Rydberg states in this region. The transitions at 6.53—7.25 eV in the UV spectrum were assigned [10] to a $2\,^1B_u$ state and more recently to a $\sigma \rightarrow \pi^*$ [20] state. We find several allowed Rydberg transitions in this region, but the $\sigma \rightarrow \pi^*$ states are at much higher energies.

The states at higher energies can be understood in terms of (at least) three sets of d-like allowed Rydberg series, as will be fully discussed in the full-length publication.

Summarizing, we find that
(a) the spectrum of the hexatriene molecule can be understood in terms of a few valence states plus a series of Rydberg states, and
(b) the valence $2\,^1A_g$ state is found to lie above the ^1B_u state responsible for the strong optical absorption.

‡‡ The calculated intensity is to the manifold of vibrational levels of the excited state. For the Rydberg states, most of the intensity is into a few of the vibrational levels. A big uncertainty in observing the absorption to the $2\,^1A_g$ state concerns how broad the Franck—Condon envelope is and how much structure it has.

References

[1] B. Honig and T. Ebrey, Ann. Rev. Biophys. Bioeng. 3 (1974) 151;
R.A. Morton and G.A. Pitt, Advan. Enzymol. Related Subj. Biochem. 32 (1969) 97;
E.W. Abrahamson and S.E. Ostroy, Progr. Biophys. Mol. Biol. 17 (1967) 179.
[2] R. McDiarmid, J. Chem. Phys. 64 (1976) 514;
K.K. Innes and R. McDiarmid, J. Chem. Phys. 68 (1978) 2007.
[3] O.A. Mosher, W.M. Flicker and A. Kuppermann, J. Chem. Phys. 59 (1973) 6502;

W.A. Flicker, O.A. Mosher and A. Kuppermann, Chem. Phys. 30 (1978) 307.

[4] P.J. Johnson, J. Chem. Phys. 64 (1976) 4638.

[5] J.H. Moore Jr., J. Phys. Chem. 76 (1972) 1130.

[6] C. Sandorfy, J. Mol. Struct. 19 (1973) 183.

[7] K.B. Wiberg, K.S. Peters, G.B. Ellison and J.L. Dehmer, J. Chem. Phys. 66 (1977) 2224.

[8] R.P. Hosteny, T.H. Dunning Jr., R.R. Gilman, A. Pipano and L. Shavitt, J. Chem. Phys. 62 (1975) 4764.

[9] S. Shih, R.J. Buenker and S.D. Peyerimhoff, Chem. Phys. Letters 16 (1972) 244;
R.J. Buenker, S. Shih and S.D. Peyerimhoff, Chem. Phys. Letters 44 (1976) 385.

[10] R.M. Gavin Jr. and S.A. Rice, J. Chem. Phys. 60 (1974) 3231.

[11] W.M. Flicker, O.A. Mosher and A. Kuppermann, Chem. Phys. Letters 45 (1977) 492.

[12] D.H. Parker, S.J. Sheng and M.A. El-Sayed, J. Chem. Phys. 65 (1976) 5534;
D.H. Parker, J.O. Berg and M.A. El-Sayed, Chem. Phys. Letters 56 (1978) 197.

[13] F.W.E. Knoop and L.J. Oosterhoff, Chem. Phys. Letters 22 (1973) 247.

[14] M. Traetteberg, Acta Chem. Scand. 22 (1968) 628.

[15] M.A.C. Nascimento, Ph.D. Thesis, California Institute of Technology (1978).

[16] T.H. Dunning Jr. and P.J. Hay, in: Modern theoretical chemistry: Methods of electronic structure theory, Vol. 3, ed. H.F. Schaefer (Plenum Press, New York, 1977) pp. 1–27.

[17] W.J. Hunt and W.A. Goddard III, Chem. Phys. Letters 3 (1969) 414.

[18] B.S. Hudson and B.E. Kohler, Chem. Phys. Letters 14 (1972) 299.

[19] G.R. Holtom and W.M. McClain, Chem. Phys. Letters 44 (1976) 436;
H.L.B. Fang, R.J. Thrash and G.E. Leroi, J. Chem. Phys. 67 (1977) 3389;
H.L.B. Fang and G.E. Leroi, Paper MG9, 32nd Symposium on Molecular Spectroscopy, Columbus, Ohio (1977);
W.M. Hetherington III, B.S. Hudson and J. Diamond, Paper MG6, 32nd Symposium on Molecular Spectroscopy, Columbus, Ohio (1977).

[20] M. Karplus, R.M. Gavin Jr. and S.A. Rice, J. Chem. Phys. 63 (1975) 5507.

[21] D.F. Evans, J. Chem. Soc. (1960) 1735.