

Photoelectron Spectra and Molecular Properties. LIII.¹

Methyl-substituent Effects on the Hexatriene π System

E. E. ASTRUP,^{a*} H. BOCK,^a K. WITTEL^a and P. HEIMBACH^b

^a Chemisches Institut der Universität, D-6 Frankfurt, Theodor-Stern-Kai 7, Germany and ^b Max-Planck-Institut für Kohlenforschung, D-433 Mülheim, Kaiser-Wilhelm-Platz 1, Germany

The photoelectron (PE) spectra of *trans*-hexatrienes-1,3,5 with methyl groups in 2, 3, 1/1, 1/2 or 1/6 positions are reported. The first three bands are assigned to π -ionizations according to SPINDO calculations. The shifts caused by methyl substitution are small relative to those observed for butadiene, a finding, that may be explained by assuming a "buffer quality" of larger π systems which obscures the substituent effects. First and second order methyl group perturbations of the hexatriene π system are discussed, considering as well the accuracy of photoelectron spectroscopically determined ionization potentials.

The effect of methyl substituents on π systems has been the subject of many photoelectron spectroscopic investigations.²⁻¹¹ The observed lowering of the π ionization energies is best rationalized by first and/or second order perturbations,^{2,12} *i.e.* inductive and/or hypercon-

jugative effects, respectively. Therefore, it has been repeatedly attempted to determine characteristic perturbational parameters. For methyl butadienes a simple LCBO MO approach only considering occupied orbitals proved to be successful: Beez, Bieri, Bock and Heilbronner² have shown that ionization energies can be satisfactorily predicted within this model by first order perturbation, and that considerable improvement is achieved by incorporating "through space" interactions¹³ between butadiene π orbitals and the pseudo- π methyl group orbitals into the LCBO MO treatment.² For illustration, Fig. 1 displays the π -orbital movements for the mono-methyl hexatrienes as predicted by a first order perturbation²

$$\delta IE_j = (c_{j\mu})^2 \delta A' \quad (\delta A' = 0.8 \text{ eV}) \quad (1)$$

and, in addition by a "through space" hyperconjugation ($\Delta IE \sim 0.25 \text{ eV}$).³ Obviously, only for 2- or 3-methyl hexatriene isomers a further

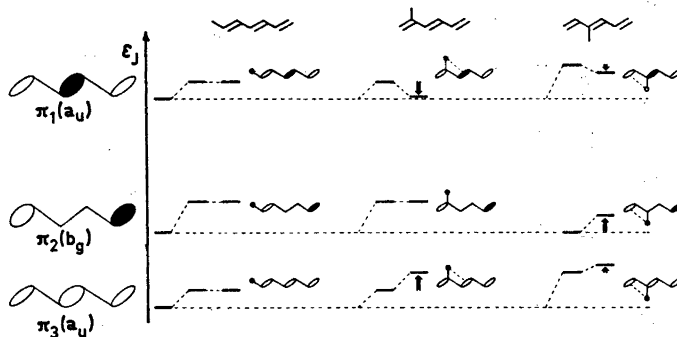


Fig. 1. π Orbital energy differences for mono-methyl hexatrienes as predicted by first and second order perturbations within an LCBO MO model.

stabilization or a counteracting destabilization is possible, while for all-*trans* 1-methyl hexatriene structural requirements are not met, which would justify an inclusion of this additional perturbation. To elucidate how well the above specified LCBO MO π model is suited for larger polyenes, the photoelectron spectra of some methyl and dimethyl hexatrienes are investigated.

The PE spectra of 2, 3, 1/1, 1/2 and 1/6 methyl substituted hexatrienes are reproduced in Fig. 2; Table 1 contains the vertical ionization potentials and includes also those of hexatriene² and 1-methyl hexatriene.²

All the PE spectra exhibit more or less the same overall picture: two isolated bands with one vibrational progression each at lower energies followed by a broad "mountain" of overlapping bands between 11 eV and 16 eV. The spectra of the disubstituted derivatives show even less structure in this region due to the additional σ ionizations caused by the second methyl group. Obviously, only the position of the first two bands can be read off with sufficient accuracy, and therefore will be included in the following discussion.

SPINDO calculations¹⁴ yield the three π orbitals as highest occupied ones (Fig. 2) contrary to the assignment by a comparison of ethylene and hexatriene^{2,15} on the basis of an LCBO MO model. But as already pointed out, the third PE bands - π or σ - will not be included in the discussion, due to the poor resolution of the spectra.

The SPINDO orbital energies (Fig. 2) are in reasonable agreement with the experimental ionization potentials, although this semiempirical method is parametrized to reproduce ionization potentials of planar hydrocarbons. Except for the lowest orbital energy $\epsilon_1^{\text{SPINDO}}$ for disubstituted derivatives, all other π orbital energies are calculated to lie slightly below the experimental ionization energies. This can be traced back to the definition of "vertical IPs" as "weighted mean" of the vibrational progression, which probably deviates from the parametrization using the "highest peak" of each band. Judging from the SPINDO eigenvalues, the orbital sequence for all-*trans*-hexatriene is $\pi_1, \pi_2, \pi_3, \sigma$ with the latter two nearly degenerate. As pointed out above, bands 3 and 4

overlap strongly in all PE spectra (Fig. 2 and Ref. 2). Therefore, an assignment $\pi_1, \pi_3, \sigma, \pi_2$ - in good agreement with the one for the *cis*-isomer and resulting in a nearly symmetrical split for the three π orbitals² - cannot be excluded. An unsymmetrical π split, following from the assumption of a $\pi_1, \pi_2, \pi_3, \sigma$ sequence, may however be understood within an LCAO MO model, since the first unoccupied π^* orbital also belongs to the irreducible representation b_g as does π_2 .

Experimentally observed shifts of the π_1 and π_2 ionization potentials on methyl substitution of hexatriene are compared in Fig. 3 to the ones calculated by the LCBO MO model perturbation (cf. Fig. 1), e.g. for 2-methyl hexatriene

$$\begin{aligned} IE_1(2\text{-Me-C}_6\text{H}_7) &= IE(\text{C}_6\text{H}_6) + c_{23}^2 \delta_A' \\ &= 8.45 - 0.5^2 \times 0.8 \\ &= 8.24 \text{ eV} \end{aligned} \quad (2)$$

Fig. 3 shows for example that the observed IE_1 shift of 2-methyl hexatriene relative to hexatriene is slightly smaller than the calculated LCBO MO perturbation (1), in agreement with an assumed stabilization of the π_1 orbital due to a bonding "through space" interaction (Fig. 1). On the contrary, a corresponding split for π_2 expectedly (Fig. 1) can be neglected. More pronounced are the observed differences for 3-methyl hexatriene relative to hexatriene: ΔIE_1 is larger than $\Delta \pi_1$ and ΔIE_2 smaller than $\Delta \pi_2$, the shifts predicted by LCBO MO perturbation; corrections by "through space interactions", i.e. bonding stabilization for π_1 and antibonding destabilization for π_2 , point in the right direction. Analogous arguments may be used for most π ionizations of the disubstituted derivatives. Obviously, incorporation of "through space" interactions between π orbitals of hexatriene and pseudo π orbitals of the methyl group improve agreement between observed and calculated shifts (Fig. 3 and 1).

Although the extended LCBO MO model seems to allow reasonable rationalization of the π ionization differences on methyl substitution of hexatriene, nevertheless, several limiting remarks are necessary. Thus comparison with methyl substitution effects on smaller polyenes^{2,7} demonstrates that the hexatriene

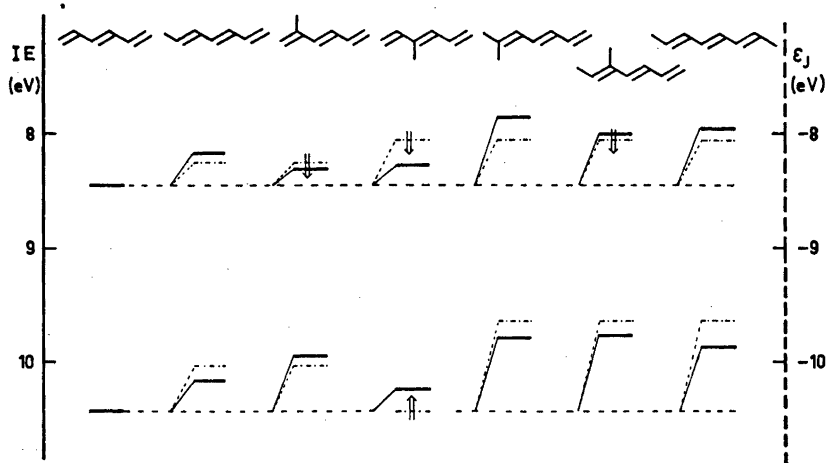
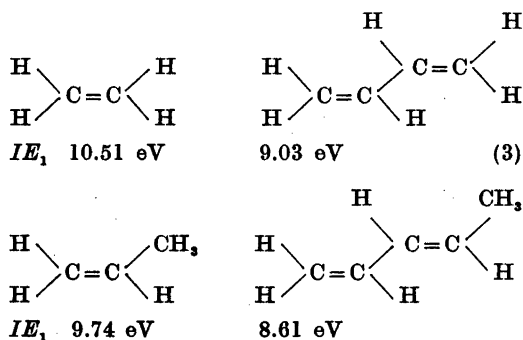


Fig. 3. Comparison of ionization potentials $IE_{1,2}$ of methyl substituted hexatrienes with calculated LCBO MO perturbations of the hexatriene π system (— measurement, - - - - perturbation calculation).



perturbation is only a relatively small one. In addition, a thorough examination of the correlation diagram (Fig. 3) reveals, that a pronounced influence of substituent position cannot be detected. Within the mono-substituted derivatives the experiment shows no differences between the 1-, 2-, or 3-substituents for the π_1 orbital and only a minimal distinction of 0.2 eV between the 1- and 2- substituents for the π_2 orbital. The same applies to the dimethyl hexatrienes, expectedly exhibiting an approximately doubled shift. But on the other hand, the largest difference $\Delta IE_1 \sim 0.15$ eV observed for 1,2- and 1,1-dimethyl isomers, is only a moderate one. Summarizing with respect to the experimental data, and comparing with the "through space" interaction model developed for methyl butadienes, there is mostly agreement, but as the observed effects for methyl

hexatrienes are much smaller, an unequivocal support hardly seems possible.

Regarding the experiment, the reproducibility is estimated to be about 0.02 eV.¹⁶ The uncertainty in the reading off is even for sharp peaks at least of the same order of magnitude. The calibration, using xenon and argon (12.13 eV and 15.76 eV) is outside the π ionization region discussed. Furthermore, whether the vertical ionization potentials are determined as the "highest peak" or the "weighed mean" of the fine structure will add to the uncertainty, since the bands do not possess the same shape, and this may amount to one vibrational spacing, *i.e.* to $\sim 0.1 - 0.2$ eV. All these uncertainties may add up to the same order of magnitude as the observed differences for the hexatriene derivatives investigated. Based on the relatively great number of ionization potentials observed, an attempt has been made to determine a set of optimal parameter values in the expression for the total methyl perturbation:

$$\delta IE_J = (c_J \mu)^2 [\Delta \alpha + \beta^2 / (\alpha_{\text{CH}_3} - IE_J^0)] \quad (4)$$

with $\Delta \alpha$ as the inductive parameter, β the resonance integral, and α_{CH_3} the Coulomb integral for the methyl group pseudo π orbital. By use of a least-squares method, the difference between the observed and the calculated perturbation was minimized. Unfortunately, only a very shallow minimum is obtained, and ob-

viously, wrong values for the parameters (4) satisfy the minimum criterion within the limits of errors. The minimum is for HMO eigenfunctions at $\Delta\alpha = -0.5$ eV, $\beta = -3.8$ eV, $\alpha_{CH_3} = -17.6$ eV with $V = \sum(\delta\epsilon_j^{exp.} - \delta\epsilon_j^{calc.})^2 = 0.08$, but allowing an only slightly larger $V = 0.095$, a range of $\Delta\alpha$ from -1.0 to $+0.8$ eV is covered. Variation of the method, *i.e.* starting the optimization from SPINDO or LCBO orbital coefficients $c_{j\mu}$ did not change the overall result. An explanation for this failure is offered by a strong correlation between the calculated parameters (4); thus any values of the "best" parameters would become meaningless.

In conclusion, it should be pointed out, that the methyl substitution effects on the hexatriene π system are in accord with independent investigations concerning compounds of comparable molecular size.^{10,17} The dependence of properties on the methyl substitution position is disappointingly small. This observation can be explained by assuming a kind of "buffer" quality for most of the larger π systems, which internally compensates for smaller donor or acceptor perturbations.

SYNTHESES

The *trans*-2- and 3-methyl hexatrienes have been prepared by Hofmann elimination of the corresponding dimethylbenzylhexadienyl ammonium bromide according to literature procedures¹⁹ followed by gaschromatography separation of the two isomers.²⁰ All *trans*-octatriene-2,4,6 has been obtained by isomerization of octatriene-1,3,5²¹ and purified by recrystallization from ethanol.²⁰ *trans,trans*-5-Methyl heptatriene-1,3,5 has been synthesized from butadiene and butine-2 using a cobalt catalyst²² and separated by distillation in a spinning band column.²⁰ Purity of all compounds has been checked by usual spectroscopic methods.²⁰

PE SPECTRA

The PE spectra of methyl substituted hexatrienes (1 to 5) are recorded on a Perkin Elmer PS 16 spectrometer. Argon and xenon have been used for calibration, and the resolution of the apparatus was about 25 mV. Vertical ionization potentials for fine structured bands are quoted as weighed mean,¹⁸ *i.e.*

$$IE_v = \sum_n IE_n I_n / \sum_n I_n$$

For unstructured bands, the value for the maximum is given.

Acta Chem. Scand. A 29 (1975) No. 9

CALCULATIONS

SPINDO calculations have been performed on the UNIVAC 1108 of the Hochschul-Rechenzentrum at Frankfurt University. We get results for hexatriene slightly different from those in Ref. 2, but cannot offer an explanation. The card deck has been checked against some published calculations.

Acknowledgements. Dr. Lindholm and Dr. Åsbrink (Royal Institute of Technology, Stockholm) kindly supplied the SPINDO program and Miss Pohlenz (University of Frankfurt) helped in recording the spectra. One of us (E. E. A.) wishes to acknowledge a research grant from the Alexander von Humboldt-Stiftung.

REFERENCES

1. Part LII: Stafast, H. and Bock, H. *Tetrahedron. In print.*
2. Beez, M., Bieri, G., Bock, H. and Heilbronner, E. *Helv. Chim. Acta* 56 (1973) 1028; *cf.* also Sustmann, R. and Schubert, E. *Tetrahedron Lett.* (1972) 2739.
3. Mollère, P., Bock, H., Becker, G. and Fritz, G. *J. Organomet. Chem.* 46 (1972) 89.
4. Klessinger, M. *Angew. Chem.* 11 (1972) 544; *Int. Ed.* 11 (1972) 525.
5. Weidner, U. and Schweig, A. *J. Organomet. Chem.* 39 (1972) 261.
6. Dewar, M. J. S. and Worley, S. D. *J. Chem. Phys.* 50 (1969) 654.
7. Frost, D. C. and Sandhu, J. S. *Indian J. Chem.* 9 (1971) 1105.
8. Ensslin, W., Bock, H. and Becker, G. *J. Amer. Chem. Soc.* 96 (1974) 2757.
9. Brogli, F., Clark, P. A., Heilbronner, E. and Neuenschwander, M. *Angew. Chem.* 85 (1973) 414; *Int. Ed.* 12 (1973) 422.
10. Turner, D. W., Baker, C., Baker, A. D. and Brundle, C. R. *Molecular Photoelectron Spectroscopy*, Wiley-Interscience, London 1970, p. 281.
11. Bischof, P. K., Dewar, M. J. S., Goodman, D. W. and Jones, T. B. *J. Organomet. Chem.* 82 (1974) 89.
12. Libit, L. and Hoffmann, R. *J. Amer. Chem. Soc.* 96 (1970) 1370.
13. Hoffmann, R. *Accounts Chem. Res.* 4 (1971) 1.
14. Fridh, C., Åsbrink, L. and Lindholm, E. *Chem. Phys. Lett.* 15 (1972) 282.
15. Bock, H. and Ramsey, B. G. *Angew. Chem.* 85 (1973) 773; *Int. Ed.* 12 (1973) 734.
16. Turner, D. W., Baker, C., Baker, A. D. and Brundle, C. R. *Molecular Photoelectron Spectroscopy*, Wiley-Interscience, London 1970.
17. Methyl substituted naphthalenes have been investigated by E. Heilbronner and co-

- workers; personal communication E. Heilbronner.
18. Smith, W. L. *Mol. Phys.* 26 (1973) 361.
 19. Hwa, J. C. H., deBenneville, P. L. and Sims, H. J. *J. Amer. Chem. Soc.* 82 (1960) 2537.
 20. Scholz, K.-H. *Thesis*, University Bochum 1974.
 21. Kloosterziel, A. and van Drunen, I. A. A. *Rec. Trav. Chim. Pays-Bas* 88 (1969) 1084.
 22. Kopp, W. *Thesis*, University Bochum 1970.

Received March 3, 1975.