

# PHOTOELECTRON SPECTRA OF NONBENZENOID CYCLIC CONJUGATED $\pi$ -ELECTRON SYSTEMS

EDGAR HEILBRONNER

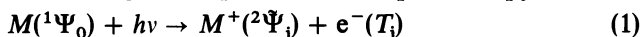
*Physikalisch-chemisches Institut, Universität Basel, Switzerland*

## NOTE

The material presented at the Second International Symposium on the Chemistry of Nonbenzenoid Aromatic Compounds has either been published or been submitted for publication. Therefore only a short synopsis of the topics covered is given here.

## INTRODUCTION

The primary process investigated in photoelectron spectroscopy, i.e.



(where M is a closed-shell molecule in its singlet ground state,  $M^+$  the corresponding radical cation in a doublet state  $^2\Psi_j$  and  $e^-$  the photoelectron of kinetic energy  $T_j$ ) is traditionally discussed in terms of Koopmans' approximation<sup>1</sup>:

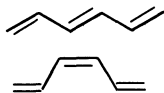
$$E(^2\tilde{\Psi}_j) - E(^1\Psi_0) = -\varepsilon_j \quad (2)$$

In (2),  $\varepsilon_j$  is the orbital energy of the vacated canonical SCF orbital  $\psi_j$  of  $M(^1\Psi_0)$ . Changes in vibrational and/or rotational quantum numbers which accompany process (1) have been disregarded. The implications, shortcomings and the danger inherent in an indiscriminate use of (2) are discussed<sup>2</sup>.

Naïvely one might have expected that 'aromatic' molecules yield photoelectron spectra which differ significantly from those of pseudo-, homo-, anti-, or otherwise non-'aromatic' molecules, e.g. in the absolute values of the ionization energies  $I_j = -\varepsilon_j$ , in typical patterns and/or spacings  $I_j - I_k$  between the  $\pi$ -bands of the  $\pi$ -band system or in the Franck-Condon shapes of the individual bands. This does not seem to be the case, as shown for example by a comparison of the photoelectron spectroscopic results obtained for the trienes 1 to 4<sup>3</sup>.



1



2



3

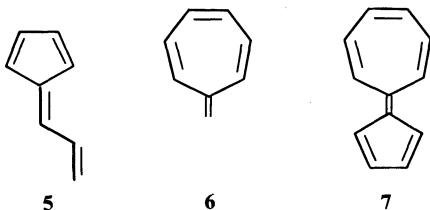


4

With these limitations in mind the photoelectron spectra of three types of nonbenzenoid systems have been discussed.

**(1) CROSS-CONJUGATED, NON-ALTERNANT  $\pi$ -SYSTEMS**

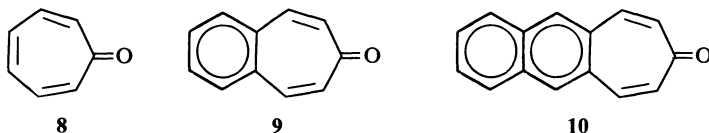
The photoelectron spectra of 6-vinyl-fulvene **5**, its 6-, 7- or 8-monomethyl derivatives, of heptafulvene **6** and of sesquifulvalene **7** are discussed<sup>4</sup>. The



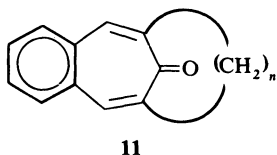
spectra are consistent with expectation values derived under the assumption of strongly localized double bonds, if the electron rearrangement in the radical cations  $5^+(1a_2^{-1})$  and  $7^+(2a_2^{-1})$  (i.e.  $5^+$  and  $7^+$  in the  ${}^2A_1$ -state with singly occupied  $\pi$ -orbitals  $1a_2$  or  $2a_2$  respectively) are taken into account, as has been discussed previously for alkyl-substituted fulvenes **3**<sup>5</sup>.

**(2) BENZOLOGUE TROPONES**

The photoelectron spectra of tropone **8**, 4,5-benzotropone **9**, 4,5-(2',3'-naphtho)-tropones **10** and a series of alkyl-substituted derivatives are presented<sup>6</sup>. In particular the dependence of the 'observed'  $\pi$ - and lone-pair



orbital energies on the ring-size of the bridging polymethylene chain in the derivatives **11** of **9** ( $n = 5, 6, 7, 9, 12$ ) is discussed in detail. The increasing

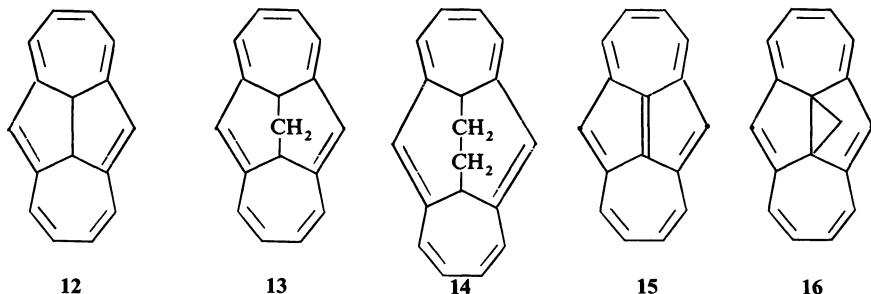


departure from coplanarity of the  $\pi$ -system of **11** with decreasing  $n$  is reflected in the characteristic changes of both the  $\pi$ - and the oxygen lone-pair ionization energies. Their dependence on  $n$  can be rationalized in terms of simple molecular orbital models through the use of correlation diagrams.

**(3) BRIDGED [14]ANNULENES AND DICYCLOHEPTA[cd,gh]PENTALENE**

The  $\pi$ -ionization energies of the 1,6; 8,13-alkanediylidene-[14]annulenes **12** to **14** show a dependence on the size of the bridging groups which is the

resultant of a complicated and not uniquely definable interplay of inductive and conjugative effects<sup>7</sup>. In contrast the photoelectron spectrum of **15** can be



rationalized by straightforward molecular orbital calculations. Finally the molecule **16** occupies a situation intermediate between **12** and **15**, because of the presence of a three-membered ring, the Walsh orbitals of which play a similar role to that of the  $\pi$ -orbital of the central double bond in **15**<sup>7</sup>.

From the set of ionization energies observed for **12** to **16** it is possible to derive estimates for the ionization energies of a hypothetical all-*cis* [14]-annulene.

It is fortunate that the photoelectron spectroscopic data known to date for benzenoid hydrocarbons<sup>3,8,9</sup>, linear polyenes<sup>3</sup>, azulenes<sup>8,10</sup>, bridged [10]annulenes<sup>11</sup> and the systems presented in this synopsis do not allow the formulation of yet another 'aromaticity' criterion.

## REFERENCES

- <sup>1</sup> T. Koopmans, *Physica*, **1**, 104 (1934).
- <sup>2</sup> E. Heilbronner, 'Some aspects of UPS', in: *The World of Quantum Chemistry*, R. Daudel and B. Pullman (eds.), D. Reidel Publishing Company: Dordrecht (1974); *Pure Appl. Chem.* **40**, 549 (1974).
- <sup>3</sup> D. W. Turner, C. Baker, A. D. Baker and C. R. Brundle, *Molecular Photoelectron Spectroscopy*, Wiley-Interscience: London (1970);  
L. Åsbrink, E. Lindholm and O. Edqvist, *Chem. Phys. Letters*, **5**, 609 (1970);  
E. Heilbronner, R. Gleiter, H. Hopf, V. Hornung and A. de Meijere, *Helv. Chim. Acta*, **54**, 783 (1971);  
M. Beez, G. Bieri, H. Bock and E. Heilbronner, *Helv. Chim. Acta*, **56**, 1028 (1973).
- <sup>4</sup> F. Brogli, E. Heilbronner and M. Neuenschwander, to be submitted to *Helv. Chim. Acta*.
- <sup>5</sup> F. Brogli, P. A. Clark, E. Heilbronner and M. Neuenschwander, *Angew. Chem.* **85**, 414 (1973); *Angew. Chem. Internat. Ed.* **12**, 422 (1973).
- <sup>6</sup> M. Allan, E. Heilbronner and E. Kloster-Jensen, *J. Electron Spectrosc.* **6**, 181 (1975).
- <sup>7</sup> C. Batick, E. Heilbronner and E. Vogel, *Helv. Chim. Acta*, **57**, 2288 (1974).
- <sup>8</sup> J. H. D. Eland and C. J. Danby, *Z. Naturforsch.* **23a**, 355 (1968).
- <sup>9</sup> F. Brogli and E. Heilbronner, *Angew. Chem.* **84**, 551 (1972); *Angew. Chem. Internat. Ed.* **11**, 538 (1972);  
P. E. Clark, F. Brogli and E. Heilbronner, *Helv. Chim. Acta*, **55**, 1415 (1972);  
R. Boschi, J. N. Murrell and W. Schmidt, *Disc. Faraday Soc.* **54**, 116 (1972).
- <sup>10</sup> E. Heilbronner, T. Hoshi and J. L. von Rosenberg, in preparation.
- <sup>11</sup> R. Boschi, W. Schmidt and J.-C. Gfeller, *Tetrahedron Letters*, 4107 (1972).