CHEMISTRY LETTERS, pp. 1081-1086, 1974. Published by the Chemical Society of Japan

PHOTOELECTRON SPECTRUM OF DISPIRO[2.2.2.2]DECA-4,9-DIENE. CONJUGATION OF WALSH ORBITALS OF CYCLOPROPANE RINGS WITH ORBITALS OF DIENE

Yoshiya HARADA*, Koichi OHNO*, Kazuhiko SEKI**, and Hiroo INOKUCHI**
* Department of Chemistry, College of General Education
The University of Tokyo, Komaba, Meguro-ku, Tokyo 153
** The Institute for Solid State Physics, The University of
Tokyo, Roppongi, Minato-ku, Tokyo 106

To study the interaction between the Walsh orbitals of cyclopropane rings and its adjacent π-orbitals the photoelectron spectrum of dispiro[2.2.2.2]deca-4,9-diene has been measured by using the 21.22 eV helium resonance line. The first four bands in the PE spectrum have been assigned on the basis of a modified CNDO/2 approximation.

INTRODUCTION

It is well known that the orbitals of cyclopropane ring conjugate with the π-orbitals of unsaturated substituents.1) The recent progress in the technique of photoelectron spectroscopy has made it possible to study the effect of this conjugation in some detail.2-4)

To obtain further information concerning the conjugation we have carried out the analysis of the photoelectron spectrum of dispiro[2.2.2.2]deca-4,9-diene (Fig. 1).

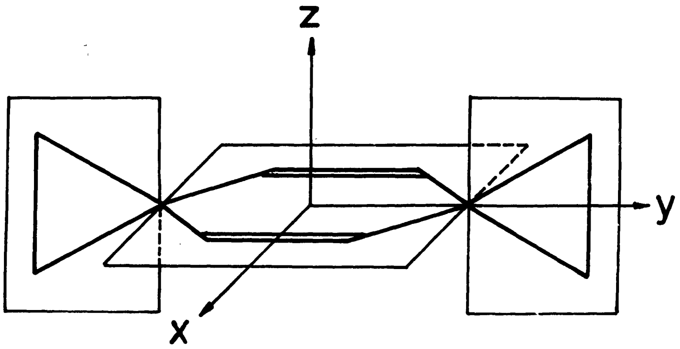


Fig. 1. Dispiro[2.2.2.2]-deca-4,9-diene.

EXPERIMENTAL

Photoelectrons were obtained by illuminating the gaseous molecules with monochromatic light of energy 21.22 eV. The source of radiation is a differentially pumped dc discharge in helium.[5)] Energy spectra of electrons were measured by an electron spectrometer with a 10 cm radius cylindrical electrostatic analyser. The resolution of the spectrometer is 21 meV FWHM for the argon $P_{3/2}$ peak. During the measurement the temperature of the instrument was maintained at 33.5°C with the aid of an electric heater; the pressure of the sample gas[6)] was about 1×10^{-2} Torr. For the calibration of the ionization energy scale known IP values of Xe are used as an internal standard.

CALCULATION

Ionization energies have been calculated by the modified CNDO/2 method which was already applied to unsaturated hydrocarbon molecules.[7)] The semi-empirical parameters are summarized as follows.

(1) One-center repulsion integral, γ_{AA}

$$\gamma_{AA}(C) = 11.144 \text{ eV}, \qquad \gamma_{AA}(H) = 12.845 \text{ eV}$$

(2) Two-center repulsion integral, γ_{AB}

$$\gamma_{AB} = e^2/\sqrt{R_{AB}^2 + G_{AB}^2} \tag{1}$$

where $G_{AB} = (e^2/2)(\gamma_{AA}^{-1} + \gamma_{BB}^{-1})$ and R_{AB} is the interatomic distance between the atoms A and B.

(3) Resonance integral, β_{AB}

$$\beta_{AB} = (1/2)(\beta_A^0 + \beta_B^0)\, S_{AB} \tag{2}$$

where S_{AB} is the overlap integral between the atomic orbitals, and β_0's are empirical parameters;

$$\beta^0(C) = -12.0 \text{ eV}, \qquad \beta^0(H) = -7.0 \text{ eV}$$ [8)]

Since the structure of dispiro[2.2.2.2]deca-4,9-diene has not yet been determined, we used the bond distances of benzene for the cyclodiene ring and those of cyclopropane for the cyclopropane rings.

RESULTS

Figure 2 shows the photoelectron spectrum of dispiro[2.2.2.2]deca-4,9-diene. There are at least nine IP bands in the spectrum. Showing the conjugation of the orbitals of the cyclopropane rings with those of the diene, the adiabatic IP of the first band, 7.2_3 eV is much lower than the corresponding value of cyclopropane, 9.8 eV.9)

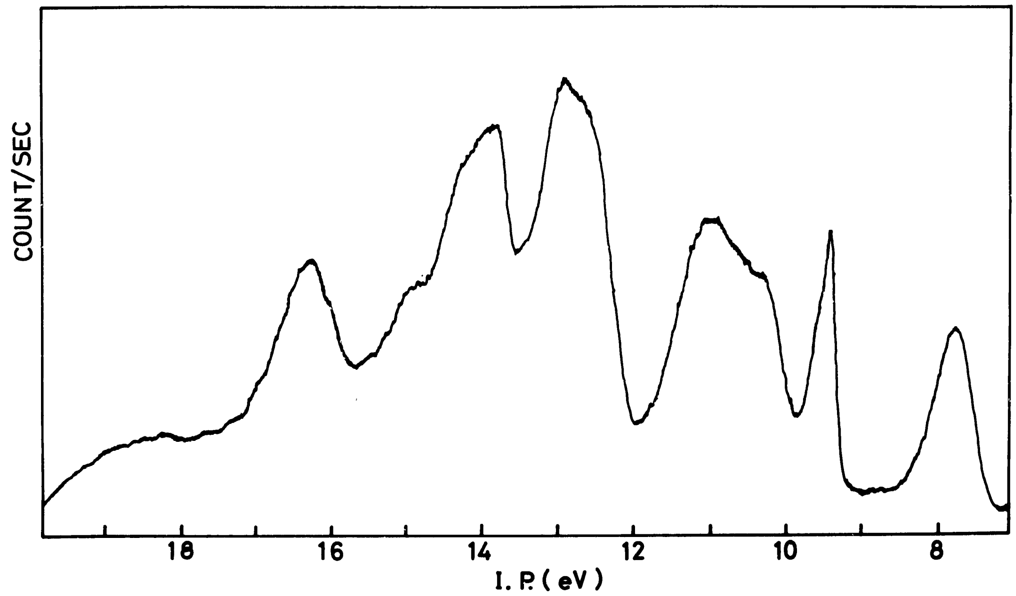


Fig. 2. Photoelectron spectrum of dispiro[2.2.2.2]deca-4,9-diene.

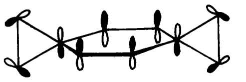
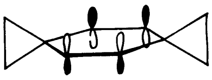
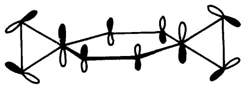
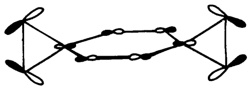
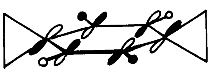
The vertical values for the lowest four IP's are listed in Table 1, together with the theoretical values based on the CNDO/2 calculation.

DISCUSSION

The first band in the PE spectrum of cyclopropane corresponds to the ionization from the highest occupied Walsh orbitals, e'.10) The double maxima (10.5 and 11.3 eV) associated with the band is a result of Jahn-Teller distortion.9) The shapes of the Walsh orbitals are shown in Figure 3. The orbital e_s' is symmetric, e_a' anti-symmetric with respect to a vertical mirror plane.

For dispirohexadiene this symmetry plane corresponds to the plane of the cyclohexadiene ring. Hence the π-orbitals of the diene ring conjugate with e_a' orbital, whereas the σ-orbitals of the ring can mix only with the e_s' orbital. The shapes of the highest three occupied π- and highest two occupied σ-orbitals

Table 1. Observed and calculated lower IP values for dispiro[2.2.2.2]deca-4,9-diene

Obs.	Calc.			
Vertical IP (eV)	IP (eV)	Symmetry	Shape of orbital	
7.75	8.16	b_{1u}		π-orbital
9.41	11.41	$b_{2g}{}^*$		
	13.24	b_{3g}		
10.3	10.62	a_g		σ-orbital
11.0	11.30	$b_{1g}{}^*$		

* Owing to the difference of local symmetry there is no mixing of the orbital of the diene ring with Walsh orbitals.

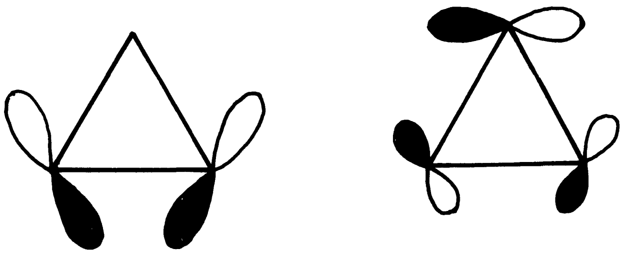


Fig. 3. Shapes of the Walsh orbitals, e'.

obtained by the calculation are shown in Table 1.

The vertical IP for the second band in the spectrum (9.41 eV) is close to that of the highest occupied π-orbitals of benzene (e_{1g}, 9.25 eV).[11,12] Accordingly, it may be reasonable to assign the second band to the b_{2g} π-orbital; the shape of the orbital is almost the same as that of one of the degenerate π-orbitals of benzene, AS (cf. Fig. 4). Furthermore the sharpness of the band suggests that it may be attributable to a π-type orbital localized in the diene ring. The calculated IP value for this orbital, 11.41 eV is somewhat higher than the observed one. The present calculation applied to benzene also gives a similar higher value, 11.18 eV for the first ionization potential.[13]

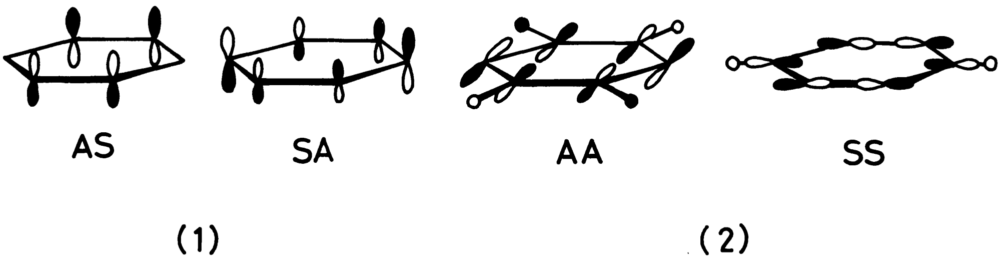


Fig. 4. Highest occupied π- and σ-orbitals of benzene;
(1) e_{1g} (IP = 9.25 eV), (2) e_{2g} (IP = 11.4 eV)

The b_{1u} π-orbital is considered to be the anti-bonding combination of two 5a" orbitals of vinyl cyclopropane (IP 9.25 eV), which are represented by the anti-bonding combination of the bonding π-orbital of ethylene and the e_a' orbital.[2,3] Accordingly, the b_{1u} π-orbital should give a considerably lower IP value than the 5a" orbital. We therefore assigned the first band to the b_{1u} π-orbital. The agreement between the observed and calculated values is reasonable.

The third band at (vertical) IP 10.3 eV probably relates to electron loss from the a_g σ-orbital which mainly consists of the e_s' orbital of cyclopropane with slight mixing of the benzene σe_{2g}, SS orbital. The reason for this assignment is that the IP value for the band should be a little less than 10.9 eV, the center of the e' band of cyclopropane.

The fourth band (vertical IP 11.0 eV) in the spectrum may be assigned to the b_{1g} σ-orbital.[14] Since the shape of this orbital is close to one of the e_{2g}

σ-orbitals of benzene, AA (cf. Fig. 4), we should expect the band due to the orbital appears near 11.4 eV, the second IP for benzene.[12)]

The good agreement between the observed and calculated IP values for the third and fourth bands supports the present assignment concerning the σ-orbitals.

ACKNOWLEDGEMENTS

We wish to thank Profs. S. Nishida and T. Tsuji for a gift of a sample of dispiro[2.2.2.2]deca-4,9-diene.

REFERENCES

1) M. Y. Lukina, Russ. Chem. Rev., 1962, 419; C. H. Heathcock, and S. R. Poulter, J. Am. Chem. Soc., 90, 3768 (1968).
2) Y. Harada, K. Seki, A. Suzuki, and H. Inokuchi, Chem. Lett., 1973, 893.
3) R. Gleiter, E. Heilbronner, and A. de Meijere, Helv. Chim. Acta, 53, 1645 (1970).
4) P. Bischof, R. Gleiter, E. Heilbronner, V. Hornung, and G. Schröder, Helv. Chim. Acta, 53, 1645 (1970); E. Heilbronner, R. Gleiter, T. Hoshi, and A. de Meijere, ibid., 56, 1594 (1973).
5) Y. Harada, Butsuri, 28, 862 (1973).
6) A sample of dispiro[2.2.2.2]deca-4,9-diene was kindly provided by Profs. S. Nishida and T. Tsuji. Its preparation has been reported in the literature [T. Tsuji, and S. Nishida, J. C. S. Chem. Comm., 284 (1972)].
7) K. Ohno, T. Hirooka, Y. Harada, and H. Inokuchi, Bull. Chem. Soc. Japan, 46, 2353 (1973).
8) In the case of planar hydrocarbons a σ-π separation factor, k was taken for carbon atoms; $\beta^0(C\pi) = k\beta^0(C)$, $\beta^0(C\sigma) = \beta^0(C)$. Using the β^0 values in the text and 0.4 for k, we obtained the calculated IP values in good agreement with the observed ones (cf. ref. 7)). In the present calculation the value of k is taken to be 1.0.
9) H. Basch, M. B. Robin, N. A. Kuebler, C. Baker, and D. W. Turner, J. Chem. Phys., 51, 52 (1969).
10) A. D. Walsh, Trans. Farad. Soc., 45, 179 (1949).
11) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy", John Wiley and Sons, London (1970).
12) B. Johnson and E. Lindholm, Chem. Phys. Lett., 1, 501 (1967).
13) Using a small σ-π separation factor (k=0.4), we obtained a resonable value, 9.77 eV for benzene (cf. ref. 7 and 8).
14) In view of the integrated intensity ratios for the 7.8, 9.4 and 10 to 12 eV peaks (ca. 1:1:3.5), another orbital may contribute the photoelectron intensity near 11 eV. Although the present calculation gives the good agreement between the observed and calculated IP values for σ orbitals, the calculated IP's for π orbitals are too high. Considering the error up to 2 eV, we might be able to expect the band due to the b_{3g} π-orbital occurs near 11 eV.

(Received July 25, 1974)