Tetrahedron Vol 33, pp 1721 to 1724 Pergamon Press 1977 Printed in Great Britain

PHOTOELECTRON SPECTRAL STUDIES ON THE INTERACTION OF THREE-MEMBERED RINGS WITH ARYL GROUPS

K. SHUDO
Faculty of Pharmaceutical Sciences, University of Tokyo, Hongo, Bunkyo-ku, Tokyo, Japan

T. KOBAYASHI
The Institute of Physical and Chemical Research, Wako-shi, Saitama, Japan

and

C. UTSUNOMIYA
The Institute for Solid State Physics, University of Tokyo, Roppongi, Minato-ku, Tokyo, Japan

(*Received in Japan 27 October 1976; Received in UK for publication 6 January 1977*)

Abstract—Photoelectron spectra of cyclopropylbenzene, 9,10-methano-9,10-dihydrophenanthrene and their related compounds have been measured and interpreted by the aid of the CNDO/IP method. The interaction between a cyclopropane ring and aryl groups is discussed.

In this paper the photoelectron spectra (PES) of 9,10-methano-9,10-dihydrophenanthrene, cyclopropylbenzene, styrene oxide and their related compounds are discussed. Recently PE spectroscopy has been proven to be useful in evaluating various kinds of electronic interaction.[1] Though it is well known that the cyclopropane ring interacts very efficiently with conjugated systems,[2] no PES study of arylcyclopropanes except for that of cyclopropylbenzene[3] has been reported so far as we know. The primary interest in this work is concerned with the interaction of a three-membered ring with aryl groups. In the interpretation of PES the recently developed CNDO/IP method[4] was used. The method has been optimized for the estimation of ionization potentials.

EXPERIMENTAL AND THEORETICAL

Samples were prepared in the same way as described in the preceding paper.[5]

The PES of the samples were recorded using the He(I) resonance line as the excitation source as described in the preceding paper.[6]

The CNDO/IP[4] calculations of the compounds treated in this paper were carried out on a FACOM 230-75 computer at the Institute of Physical and Chemical Research. The molecular dimensions of the compounds treated here were taken from, or properly assumed on the basis of Ref. 7.

RESULTS AND DISCUSSION

The PES of 9,10-methano-9,10-dihydrophenanthrene, 9,10-(dichloromethano)-9,10-dihydrophenanthrene and 9,10-dihydrophenanthrene[8] are shown in Fig. 1. The vertical ionization potentials of these compounds are also summarized in Table 1. The observed vertical ionization potentials of these dihydrophenanthrenes are plotted in Fig. 2. The calculated orbital energy diagram is shown in Fig. 3. In the case of dihydrophenanthrene, the calculations have been carried out for two dihedral angles of the biphenyl moiety, 0° and 17°52′. The latter value was estimated by using the C–C bond lengths assumed on the basis of the appropriate data given in Ref. 7. This value is quite close to the value empirically estimated formerly by Beaven and coworkers,[9] *ca.* 20°. In the case of 9,10-methano-9,10-dihydrophenanthrene the biphenyl part was assumed to be planar.

The overall pattern of the calculated orbital energy diagram resembles well that of the observed correlation diagram, and the observed ionization potentials may be

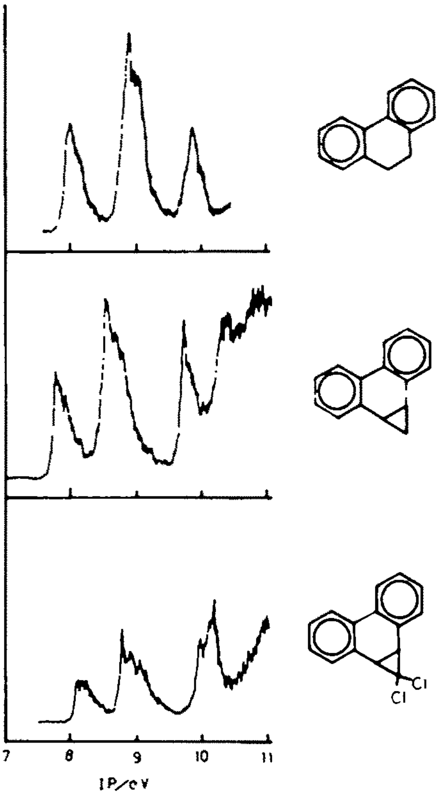

Fig. 1. Photoelectron spectra of 9,10-dihydrophenanthrene, 9,10-methano-9,10-dihydrophenanthrene and 9,10-dichloromethano-9,10-dihydrophenanthrene. The spectrum of 9,10-dihydrophenanthrene was reproduced from Ref. 8.

Table 1. Vertical ionization potentials of arylcyclopropanes and related compounds in eV

Compound	PES band 1	2	3	4	5
9,10-Dihydrophenanthrene[a]	7.96	8.80	8.95	9.80	
9,10-Methano-9,10-dihydrophenanthrene	7.77	8.53	8.70	9.76	10.36
9,10-Dichloromethano-9,10-dihydrophenanthrene	8.06	8.79	8.93	10.00	10.16
Phenanthrene[b]	7.86	8.10	9.28	9.89	10.59
Cyclopropane[c]	10.53	11.3	13.2	15.7	16.5
Ethylene[d]	10.51	12.85	14.66	15.87	19.1
Cyclopropylbenzene	8.61	9.12	10.48		
Isopropylbenzene	8.75	9.27			
Styrene oxide	9.04	9.43	10.26	11.5	
Benzyl methyl ether	9.07	9.37	9.85	11.35	
2,2-Dichlorocyclopropylbenzene	8.97	9.40	10.05	10.8	11.07
β,β-Dichloroethylbenzene	9.27	9.65			
Benzene[e]	9.23	11.67	12.32	13.97	
Ethylene oxide[c]	10.57	11.7	13.7	14.2	16.6
Dimethyl ether[f]	10.04	11.91	13.43	14.2	

[a] Ref. 8. [b] Ref. 10. [c] Ref. 13. [d] C. R. Brundle, M. B. Robin, N. A. Kuebler and H. Basch, *J. Am. Chem. Soc.* **94**, 1451 (1972). [e] T. Kobayashi and S. Nagakura, *Bull. Chem. Soc. Japan* **47**, 2563 (1974). [f] S. Cradock and R. A. Whiteford, *J. Chem. Soc. Faraday Trans. II* **68**, 281 (1972).

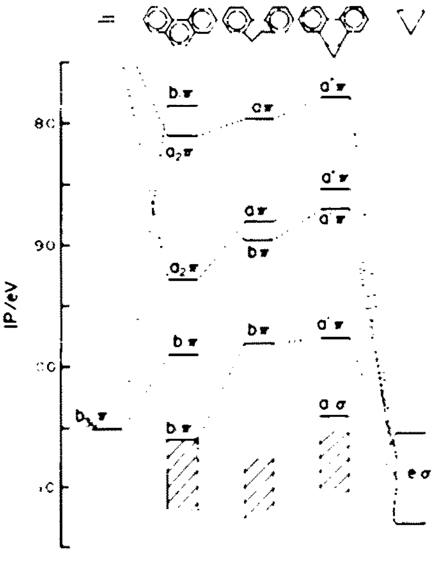

Fig. 2. Correlation diagram for the photoelectron spectral bands of dihydrophenanthrene and related compounds.

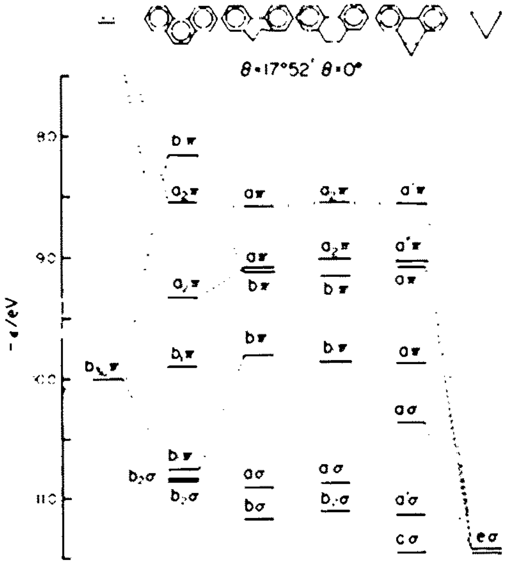

Fig. 3. Calculated orbital energy diagram of dihydrophenanthrene and related compounds. θ denotes the twist angle of the biphenyl moiety of 9,10-dihydrophenanthrene.

assigned as shown in Fig. 2, referring to the calculated diagram in Fig. 3. The PES of 9,10-dihydrophenanthrene has been discussed by Maier and Turner,[8] and their result is consistent with our calculation.

Concerning the PES of 9,10-methano-9,10-dihydrophenanthrene, the first band of dihydrophenanthrene is shifted to the lower energy side by the introduction of a cyclopropane ring. The comparison of the observed ionization potentials with the calculated molecular orbitals suggests that this shift has been caused by the decreased twisting of the biphenyl group and the interaction between the highest occupied $a_2\pi$ orbital of the biphenyl moiety and one of the highest occupied $e'\sigma$ orbitals of the cyclopropane ring. In addition to this, of course, we cannot forget the slight inductive effect of the additional methylene group also. The similar situation is found in the case of the second bands of dihydrophenanthrene and 9,10-methano-9,10-dihydrophenanthrene. According to the calculation the third band of dihydrophenanthrene is shifted to the higher energy side by making the biphenyl moiety planar, and by the introduction of a cyclopropane ring is the band shifted again to the lower energy side. This shift to the lower energy side of the third band is caused by the interaction between the third highest occupied $b_1\pi$ orbital of biphenyl moiety and one of the higher occupied cyclopropane $e'\sigma$ orbitals. The fourth vertical ionization potential of the methano derivative is quite close to that of the dihydrophenanthrene. The calculation suggests that the decreased twisting of the biphenyl moiety causes slight shift of the fourth band to the higher energy side, and that the introduction of a cyclopropane ring does not cause any additional shift. In the cases of the third and fourth bands also, the slight inductive effect of the methylene group should be considered. According to the calculations the 10.4 eV fifth band of 9,10-methano-9,10-dihydrophenanthrene should be ascribed to the $a'\sigma$ orbital localized on the cyclopropane ring. This assignment is reasonable just as in the case of the third band of cyclopropylbenzene discussed later.

The introduction of two chlorine atoms into 9,10-methano-9,10-dihydrophenanthrene causes higher energy side shifts of the lower energy bands by about 0.3 eV because of the electron withdrawing effect of chlorine atoms.

An interesting contrast to the interaction of the biphenyl moiety with the cyclopropane ring is the conjugation between the biphenyl moiety and the ethylene group in the case of phenanthrene. The first five bands of phenanthrene have already been assigned by Boschi *et al.* with the aid of HMO, PPP, EHMO and MINDO/2 calculations.[10] Our calculation also supports their assignment. Thus, the third highest occupied $b\pi$ orbital of dihydrophenanthrene is correlated with the highest occupied $b_1\pi$ orbital of phenanthrene through the quite significant conjugative interaction with the occupied π orbital of the ethylene group.

Bock and coworkers have shown that PE ionization potentials can be correlated with charge-transfer (CT) band transition energy.[11] The CT complexes of tetracyanoethylene with dihydrophenanthrenes show two CT bands.[1] The first two vertical ionization potentials of dihydrophenanthrenes were plotted in Fig. 4 against the first two electronic transition energies of the CT complexes of tetracyanoethylene with dihydrophenanthrenes. A good linear relationship between them suggests that the two CT bands are related with the electronic excitations from the two highest occupied π orbitals of dihydrophenanthrenes to the lowest vacant π orbital of tetracyanoethylene. This relationship is so good that from CT band frequencies we can estimate the ionization potentials of 9,10-epoxy-9,10-dihydrophenanthrene the PES of which we could not obtain because of thermal decomposition under the measurement conditions. Thus, the first ionization potential is estimated to be 8.24 eV and the second one 9.1 eV.

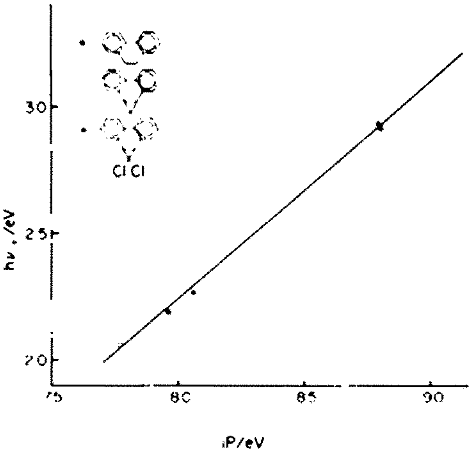

Fig. 4. Plot of the first two vertical ionization potentials of dihydrophenanthrenes against the energies of the two charge-transfer bands of dihydrophenanthrenes-tetracyanoethylene system.

The PES of cyclopropylbenzene, isopropylbenzene, styrene oxide, 2,2-dichlorocyclopropylbenzene, β,β-dichlorethylbenzene and benzyl methyl ether are shown in Fig. 5. The vertical ionization potentials of these compounds and related compounds are summarized in Table 1.

Cyclopropylbenzene and isopropylbenzene show the first two bands in the energy region from 8.6 to 9.5 eV. This energy region is also for the first PES band of benzene ascribed to the ionization from the doubly degenerate $e_{1g}\pi$ orbitals.[12] The shifts of the first bands of these compounds from the benzene $e_{1g}\pi$ band are greater than those of the second bands, and according to the first order perturbation theory the first two bands of these compounds are ascribed to the b_1-like and a_2-like π orbitals, respectively. CNDO/IP calculations also suggest that the first two PES bands of cyclopropylbenzene and isopropylbenzene are reasonably ascribed to the ionizations from the b_1-like and a_2-like π orbitals mainly localized on the benzene ring from the top, respectively. This assignment is consistent with that given by Bruckman and Klessinger.[3]

The first PES band of isopropylbenzene is vertical. On the other hand, the first PES band of cyclopropylbenzene is rather nonvertical. This fact means that there is a significant difference between the shapes of the potential curves for the neutral ground state and the cationic ground state in the case of cyclopropylbenzene. The calculations suggest that the contribution from the bonding σ orbital of the substituent group to the b_1-like π

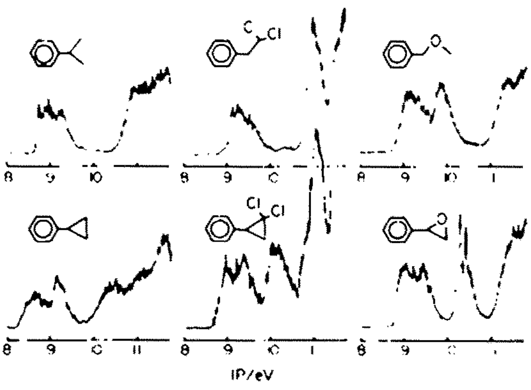

Fig. 5. Photoelectron spectra of substituted benzenes.

orbital is more significant in the case of cyclopropylbenzene, and especially that the highest occupied b_1-like π orbital of cyclopropylbenzene is more strongly antibonding at the C–C bond connecting the two groups than in the case of isopropylbenzene, and this is consistent with the present experimental result. The 10.48 eV band of cyclopropylbenzene is ascribed to the σ orbital of the cyclopropane ring according to the calculation in accordance with the assignment given by Bruckmann and Klessinger.[3]

The PES of styrene oxide and benzyl methyl ether show two bands in the energy region from 9 to 9.5 eV. These bands correspond to the first two bands of cyclopropylbenzene discussed above. Styrene oxide is an oxygen analogue of cyclopropylbenzene and the vertical ionization potentials of the first and the second bands of cyclopropylbenzene are increased by *ca.* 0.4 and 0.3 eV, respectively, by the introduction of an oxygen atom in the place of the methylene group as the constituent of the three-membered ring, because of the electron withdrawing effect of oxygen atom. Similarly, in dichlorocyclopropylbenzene, the introduction of two electronegative chlorine atoms onto cyclopropylbenzene causes increases of the first and the second ionization potentials by *ca.* 0.4 and 0.3 eV, respectively.

The third vertical ionization potential of styrene oxide, 10.26 eV, is close to the first vertical ionization potential of ethylene oxide, 10.57 eV, which is ascribed to the oxygen lone pair orbital.[13] Therefore, it is natural to assign the third band of styrene oxide as the oxygen lone pair band. The third band of benzyl methyl ether is also safely ascribed to the oxygen lone pair band.

A plot of the experimental ionization potentials against CT-absorption band energies of tetracyanoethylene complexes of the substituted benzenes shows that their correlation is poor. This may be attributed to (1) the conformational (or rotational) difference between a free molecule in a gas phase and a corresponding molecule in a complex, and (2) very different shapes of potential curves of neutral and cationic ground states of benzenes bearing three membered rings, because of the structural flexibility of these benzene derivatives.

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