

Orbital Interactions in a Dimethylbicycloalkadiene Series Studied by Photoelectron Spectroscopy: Avoided Crossing between Two HOMO Levels

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Abstract: The gas-phase He I photoelectron spectra of 2,3-dimethylbicyclo[2.2.*n*]alka-2,5-dienes (I(*n*); *n* = 1, 2, and 3) were measured. On the basis of these spectral data, it was concluded that the two *a'* HOMO levels of this series of compounds suffer an avoided crossing between *n* = 2 and 3 where the corresponding two HOMO levels of the unsubstituted bicyclo[2.2.*n*]alka-2,5-diene series just cross mutually. Simultaneously with the avoided crossing the phases of the two HOMOs of the I(*n*) series are inverted between *n* = 2 and 3, that is, the first and second HOMOs of I(1) (or I(2)) are the anti-bonding type of combination (π_-) of the two double bond group HO- π -Os and the bonding type of combination (π_+), respectively, while those of I(3) are π_+ and π_- , respectively. At the same time we can conclude that the ground and first-excited ²A' cation states of the I(*n*) series also suffer an avoided crossing between *n* = 2 and 3. This type of avoided crossing is the consequence of the overwhelming through-bond interaction over the through-space interaction at *n* = 3. This I(*n*) series provides us with an additional typical example of a new type of avoided crossing recently found by the present authors, and avoided crossings like this seem general phenomena for substituted bicyclo[2.2.*n*]alkadiene series as treated in this paper. Photoelectron spectroscopy is very powerful for studying avoided crossing phenomena as demonstrated in this work.

Photoelectron spectroscopy is simple in principle and, because of this, is very powerful for studying electronic states of atoms and molecules. Originally it gives the energy differences between the ground and cationic states of (neutral) atoms and molecules, but if we follow Koopmans' theorem² it can provide us with directly occupied orbital energy diagrams, though approximately. By taking advantage of this it is possible to analyze orbital interactions in molecules. Orbital interactions themselves are quite attractive and at the same time are nowadays becoming much more important in various fields of chemistry, particularly synthetic, reaction mechanistic, theoretical, and spectroscopic fields, and even for materials science.

In this paper the orbital interactions in 2,3-dimethylbicyclo[2.2.*n*]alka-2,5-diene series (I(*n*)) are studied by photoelectron spectroscopy. In our former papers^{3,4} we have studied the electronic structure of 2,3-dicyanobicyclo[2.2.*n*]alka-2,5-diene series (II(*n*)) and 2,3-dicyano-5,6-dimethylbicyclo[2.2.*n*]alka-2,5-diene series (III(*n*)) in detail by the combination of photoelectron spectroscopy, cyclic voltammetry, electronic absorption spectroscopy, and MO theory. One of the important findings in the work is a new type of avoided crossing; the two HOMO levels of each series of compounds have been found to avoid a mutual crossing between *n* = 2 and 3 by photoelectron spectroscopy.

In order to see if these phenomena (the avoided crossings) are general, the I(*n*) series of compounds have been designed and synthesized as model systems, and photoelectron spectra of these compounds have been measured. In the following, the unsubstituted parent compound series (IV(*n*)) is also often considered for the sake of comparison.

Results and Discussion

The gas-phase He I photoelectron spectra of the I(*n*) series of compounds are shown in Figure 2. The vertical ionization energy (VIE) values of these compounds obtained from these spectra are summarized in Table I with those of related compounds.³⁻⁸

Table I. Experimental Vertical Ionization Energies (VIE)

compd	VIE (eV)		
I(1)	8.06	9.14	10.9
I(2)	8.19	9.11	10.2
I(3)	8.14	8.81	10.2
II(1) ^a	9.60	10.40	11.90
II(2) ^a	9.81	10.34	11.33
II(3) ^a	9.74	10.04	11.41
III(1) ^b	9.00	9.98	11.74
III(2) ^b	9.03	9.93	10.94
III(3) ^b	9.00	9.73	11.11
IV(1) ^c	8.69	9.55	11.26
IV(2) ^c	8.87	9.45	10.42
IV(3) ^d	9.00	9.18	10.03
ethylene ^e	10.51	12.85	
(Z)-2-butene ^f	9.12		

^aReference 3. ^bReference 4. ^cReference 5. ^dReference 6. ^eReference 7. ^fReference 8.

In the low-energy region the compounds show two bands well separated from each other and from the following bands. The separation of the first two bands from each other in each compound of the I(*n*) series is quite clear in contrast to the case in the former series of compounds with dicyano groups.^{3,4} This situation will make the discussion clearer, and this has been the main object of the molecular design for this study. In this respect the present series of compounds is superior to the former ones for the detailed discussion of orbital interactions.

In the case of the IV(*n*) series, the two HOMOs of each compound correspond to the π MOs formed by the combination of the two ethylene-type group HO- π -Os. As the first two VIEs of the I(*n*) series are rather in the same energy region as those of the IV(*n*) series, it is natural to consider that the first and second photoelectron spectral bands of each compound of the I(*n*) series correspond to the ionization from the two HOMOs formed by the anti-bonding (out-of-phase) type and bonding (in-phase) type of combinations between the HO- π -O of the ethylene-type group

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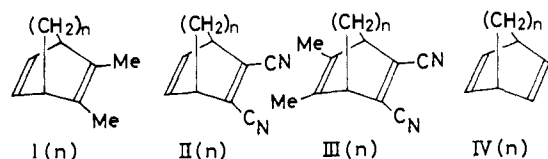
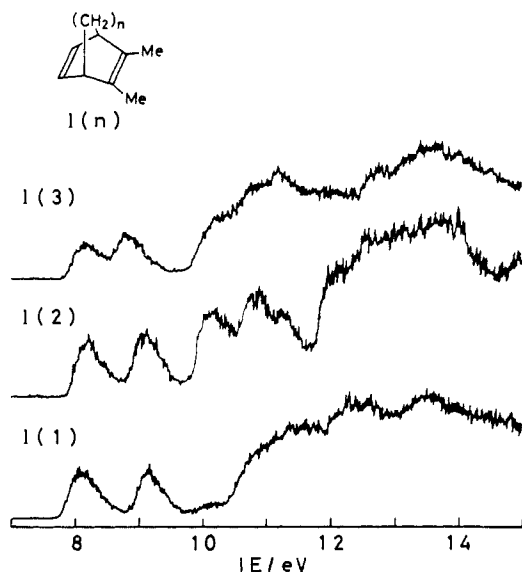


Figure 1. Molecular structural formulas.

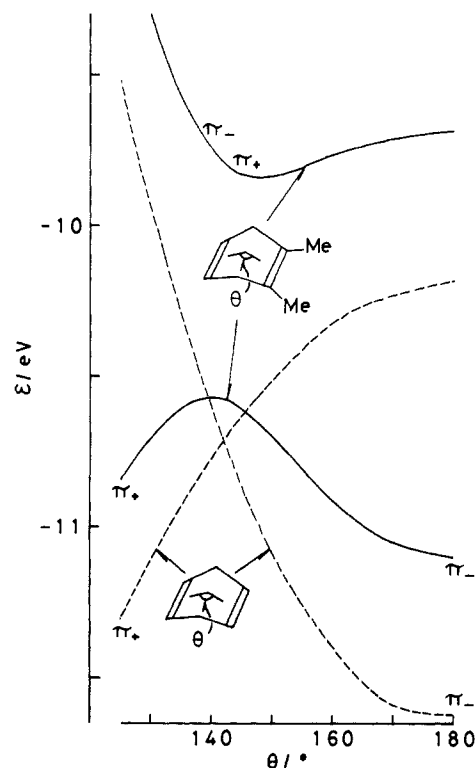
Figure 2. Photoelectron spectra of the I(*n*) series.

and that of the (*Z*)-2-butene-type group. Let us designate here these resultant MOs as π_- and π_+ for the sake of convenience. It goes without saying that in the case of the I(*n*) series the contribution of the HO- π -O of the (*Z*)-2-butene-type part to the HOMO is greater than that of the counterpart, and the reversed situation is the case for the second HOMO.

However, there still remain problems about the phases of the combinations between the two main component basis-group orbitals (BGO), that is, we cannot say a priori the π_- is the HOMO and the π_+ is the second HOMO, for example. By increasing *n* from 1 to 2 the first VIE is increased and the splitting between the first two bands is decreased. These tendencies are reasonable because by increasing *n* the dihedral angle (θ) between the ethylene-type group skeletal plane and the (*Z*)-2-butene-type group one is expected to be increased just as in the case of the IV(*n*) series,^{6,9} and the overlap integral between the two component HO- π -Os of the two olefinic groups in each molecule is decreased in absolute value. Therefore, the splitting between the two HOMOs is expected to be decreased with the increase in *n* from 1 to 2. This tendency is what has been observed. Now it is reasonable to assign the first HOMO of I(1) or I(2) to the π_- orbital and the second one to the π_+ orbital. These orbital orderings are natural.

By increasing *n* from 2 to 3, the first VIE stops increasing, and there is a tendency to decrease, though the second VIE is decreased considerably. This is peculiar so long as we take the simple overlap control model between the two BGOs (the through-space interaction¹⁰ mechanism). This apparent anomaly suggests that the splitting between the first and second bands of I(3) might be perturbed by the mixing-in of σ orbitals into the π orbitals.

In this context it should be remembered that in the case of the IV(*n*) series the first two HOMOs are known to suffer a mutual level crossing between *n* = 2 and 3. The $a_1 \pi_+$ orbital is pushed up more effectively with the increase in θ by the mixing-in of the $a_1 \sigma$ orbitals because the overlap between the a_1 type σ orbitals of the aliphatic bridge group and the $a_1 \pi_+$ orbital becomes more effective with the increase in θ .^{6,9} This through-bond interaction¹⁰

Figure 3. Dihedral angle (θ) dependence of the first and second HOMO energies (ϵ) of cyclohexa-1,4-diene and 1,2-dimethylcyclohexa-1,4-diene calculated by the modified CNDO method.

overwhelms the through-space interaction between *n* = 2 and 3 in the case of the IV(*n*) series, and the level crossing between the two HOMOs is caused between *n* = 2 and 3. As the I(*n*) series is very close structurally to this IV(*n*) series, it is natural to regard the similar σ orbital mixing into the π_+ orbital is operative in the case of the I(*n*) series also. That is, the apparent anomaly observed for the first bands of the I(*n*) series between *n* = 2 and 3 should be ascribed to the destabilization of the π_+ orbital relative to the π_- orbital at *n* = 3 because of the aliphatic bridge a' σ orbital mixing into the π_+ orbital. The fact that the above anomaly is observed between *n* = 2 and 3 just where the two HOMOs of the IV(*n*) series cross with each other supports the above discussion. Therefore, we must regard that the first and second HOMOs of I(3) should be π_+ and π_- in contrast to the case of I(1) and I(2). That is, the phase inversion between the two HOMOs occurs between *n* = 2 and 3. However, the two HOMOs belong to the same a' irreducible representation of the C_2 point group, and, therefore, these two MO levels cannot really cross but must avoid a mutual crossing because of the Neumann-Wigner noncrossing rule.¹¹

In order to get further supporting evidence we have carried out SCF-MO model calculations by a modified CNDO-type method proposed formerly,¹² 1,2-dimethylcyclohexa-1,4-diene (V) being adopted as the model compound for the I(*n*) series. The dependence of the calculated orbital energies (ϵ) on θ for V and cyclohexa-1,4-diene (VI) as the model for the IV(*n*) series reported in our previous papers^{3,4} is shown in Figure 3. The calculations suggest that the two HOMOs of V avoid a mutual crossing almost at the same θ as the two HOMOs of VI cross mutually, and this computational result supports strongly the above discussion based on the experimental data.

In our former papers^{3,4} it was concluded that the two HOMOs of the II(*n*) and III(*n*) series suffer an avoided crossing just between *n* = 2 and 3, and these series of compounds are also very close structurally to the present I(*n*) series. Therefore, these former

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results also strongly support the present results as for the avoided crossing.

The avoided crossing of the two HOMOs in the $I(n)$ series leads automatically to the conclusion that the ground and first excited $^2A'$ cation states of the $I(n)$ series suffer an avoided crossing just between $n = 2$ and 3.

Conclusion

By photoelectron spectroscopy it has been revealed that in the case of the $I(n)$ series also the two HOMOs suffer an avoided crossing just between $n = 2$ and 3 where the two HOMOs of the $IV(n)$ series cross mutually, as in the case of the $II(n)$ and $III(n)$ series; the present $I(n)$ series provides an additional typical example of a new type of avoided crossing recently found by the present authors. The first and second HOMOs of $I(3)$ are assigned as the π_+ and π_- MOs, respectively, in contrast to the case of $I(1)$ and $I(2)$. We can simultaneously conclude that the ground and first excited $^2A'$ cation states of the $I(n)$ series also suffer an avoided crossing between $n = 2$ and 3. These avoided crossings are the resultants of the overwhelming through-bond interaction over the through-space interaction between the two component basis π orbitals. It seems that avoided crossings like those discussed in this paper are general phenomena for substituted bicyclo[2.2. n]alkadiene-type series of compounds as treated here. Photoelectron spectroscopy is very powerful in detecting avoided crossings as demonstrated in our work.

Experimental Section

General Methods and Measurements. Boiling points are reported for Kugelrohr distillations. Proton NMR spectra were recorded on a JEOL FX-90Q spectrometer with TMS as internal standard. Infrared spectra were obtained with a JASCO A-102 infrared spectrometer, and only diagnostic signals are reported. Mass spectra were determined on a JEOL JMS-DX300 spectrometer.

The gas-phase He I photoelectron spectra of the $I(n)$ series were measured with the instrument described formerly.^{13,14}

Materials. 2,3-Dimethylbicyclo[2.2.1]hepta-2,5-diene ($I(1)$)¹⁵ was prepared by use of bis(phenylsulfonyl)ethylene¹⁶ as an acetylene equivalent. 2,3-Dimethylbicyclo[2.2.2]octa-2,5-diene ($I(2)$)¹⁵ and 6,7-dimethylbicyclo[3.2.2]nona-6,8-diene ($I(3)$) were synthesized by Birch

reductions of the corresponding bis exocyclic dienes as indicated by Butler.¹⁷ All the samples were purified by preparative GLC prior to analyses and measurements.

Details of Syntheses. **2,3-Dimethylbicyclo[2.2.1]hepta-2,5-diene ($I(1)$).** A mixture of 1,2-dimethylcyclopent-2-en-1-ol⁴ (2.4 g, 22 mmol) and (*Z*)-bis(phenylsulfonyl)ethylene¹⁶ (6.6 g, 22 mmol) was dissolved in 30 mL of CHCl_3 , and the solution was heated at 50 °C for 30 min. Removal of the solvent, chromatography on silica-gel/ CHCl_3 , and successive crystallization from methanol afforded a white solid of 2,3-dimethyl-5,6-bis(phenylsulfonyl)bicyclo[2.2.1]hept-2-ene (2 g, 27%). Sodium amalgam reduction of the adduct according to the procedure of Lucchi¹⁶ afforded $I(1)$ (0.35 g, 50%): bp 130 °C/760 mmHg; IR (CCl_4) 3065, 1620, 1305, 719 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 6.74 (quasi triplet, 2 H), 3.19 (m, 2 H), 1.86 (m, 2 H), 1.68 (s, 6 H); MS, m/e (rel intensity) 120 (M^+ , 80), 105 (100), 66 (95), 49 (55). Anal. Calcd for C_9H_{12} : C, 89.94; H, 10.06. Found: C, 89.89; H, 10.31.

6,7-Dimethylbicyclo[3.2.2]nona-6,8-diene ($I(3)$). A 20-mL two-necked, round-bottomed flask equipped with dry ice-acetone condenser was purged with dry nitrogen and was charged with 6 mL of liquid ammonia. To this was added a solution of 8,9-dimethylenebicyclo[3.2.2]non-6-ene¹⁸ (0.44 g, 3.0 mmol) and *tert*-butyl alcohol (0.88 g, 6.0 mmol) in 1 mL of anhydrous ether. Sodium metal (0.2 g, 8.7 mg atom) was added in small pieces, and the mixture was refluxed (-33 °C) under stirring until the blue color had disappeared. After evaporation of ammonia, the residue was extracted with pentane. The extracts were washed with water and dried over Na_2SO_4 . Cautious evaporation of the solvent and successive Kugelrohr distillation afforded colorless liquid of $I(3)$ (0.4 g, 90%): bp 60 °C/5 mmHg; IR (neat film) 3050, 1640, 1625, 705 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 6.23 (dd, $J = 3.17, 4.64$ Hz, 2 H), 2.59 (m, 2 H), 1.73 (s, 6 H), 1.68-1.16 (m, 6 H); MS, m/e (rel intensity) 148 (M^+ , 65), 133 (65), 119 (100), 105 (65). Anal. Calcd for $\text{C}_{11}\text{H}_{16}$: C, 89.12; H, 10.88. Found: C, 89.25; H, 10.79.

2,3-Dimethylbicyclo[2.2.2]octa-2,5-diene ($I(2)$). The synthetic procedure for $I(2)$ starting from 5,6-dimethylenebicyclo[2.2.2]oct-2-ene¹⁸ is similar to that for $I(3)$ described above. $I(2)$: bp 65 °C/12 mmHg; IR (neat film) 3060, 1615, 690 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 6.30 (dd, $J = 3.17, 4.39$ Hz, 2 H), 3.25 (m, 2 H), 1.70 (s, 6 H), 1.24 (m, 4 H); MS, m/e (rel intensity) 134 (M^+ , 30), 106 (100), 91 (50), 50 (20). Anal. Calcd for $\text{C}_{10}\text{H}_{14}$: C, 89.49; H, 10.51. Found: C, 89.34; H, 10.61.

Computational Details. The CNDO-type SCF-MO calculations were carried out on a FACOM M780 computer at the Institute of Physical and Chemical Research with the method described formerly.¹² The molecular structural parameters were properly assumed based on the data for 1,4-cyclohexadiene by the electron diffraction method¹⁹ and for 2,3-dicyano-1,5,6-trimethylbicyclo[2.2.1]hepta-2,5-diene by the X-ray diffraction method.²⁰

Registry No. $I(1)$, 37615-39-7; $I(2)$, 65173-34-4; $I(3)$, 115290-68-1.

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