state—appears in the ESR spectra of these dianions. When intermediate gap values are estimated, ion solvation determines the extent of singlet–triplet equilibrium via further alteration of the energy gap. In such cases the dependence of NMR line shape upon solvation factors is observed.

The present study points toward an obvious relation between NMR and ESR spectral data on the one hand and LUMO–HOMO energy separation on the other and therefore emphasizes the connection between antiaromaticity and paramagnetism. Even more so, it suggests the possibility of using the LUMO–HOMO gap, as obtained by simple $\omega\beta$ calculations, for predicting chemical and physical properties of antiaromatic species and even for preliminary estimation of the extent of antiaromatic character of $(4n)$ π conjugated systems.[9f]

Experimental Section

The benzenoid hydrocarbons were purchased from Aldrich Company and recrystallized before use from EtOH (anthracene, phenanthrene, and 9,10-diphenylanthracene) or from toluene (all other hydrocarbons).

General Procedure for the Metal Reduction Process. A wire of lithium, sodium, or potassium was introduced to the upper part of an extended tube. For NMR measurements, 5-mm tubes were used, containing 10^{-2} M (unless otherwise stated in the text) of the hydrocarbon dissolved in 0.8 mL of THF-d_8 (Aldrich reagent). For ESR measurements, 3-mm o.d. quartz tubes containing 10^{-3} M of the hydrocarbon in THF solution were used. The frozen solution of the hydrocarbon was degassed, and then the tube was sealed under vacuum. By turning the tube, the solution was brought into contact with the metal wire for controlled periods of time.

The NMR spectra were obtained on Bruker WH-300 pulsed FT spectrometer operating at 300.133 MHz and 75.46 MHz for ^{1}H and ^{13}C, respectively. The field/frequency regulations were maintained by locking to the solvent deuterium. The free induction decay signals were digitized and accumulated on an Aspect-2000 computer (32 K).

The ESR spectra were recorded on a Varian E-3 ESR spectrometer (X-band frequency) and a Varian E-257 variable-temperature unit. Long (30-min) sweep times were essential due to the narrowness of the half-field absorptions.

Registry No. 5, 56481-92-6; **5**·2Li, 39399-94-5; **5**·2Na, 11065-56-8; **5**·2K, 39399-93-4; **6**, 53571-97-4; **6**·2Li, 58054-37-8; **6**·2Na, 11067-61-1; **6**·2K, 55573-89-2; **7**, 78850-97-2; **7**·2Na, 84809-94-9; **7**·2K, 58054-36-7; **7**·2Li, 84809-96-1; **8**, 78851-99-7; **8**·2Li, 84809-98-3; **8**·2Na, 84810-00-4; **9**, 78850-93-8; **9**·2Li, 84810-02-6; **9**·2Na, 84810-04-8; **10**, 67382-15-4; **10**·2Na, 84810-06-0; **10**·2K, 84810-08-2; **10**·2Li, 54667-02-6; **11**, 78850-96-1; **11**·2Na, 83831-05-4; **11**·2Li, 83831-06-5; **12**, 78858-01-2; **12**·2Na, 84810-10-6; **12**·2Li, 84810-11-7; **13**, 78850-92-7; **13**·2Na, 84810-13-9; **13**·2Li, 84823-77-8.

Intramolecular Orbital Interactions in Triptycene Studied by Photoelectron Spectroscopy

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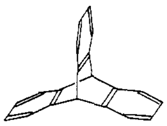
Abstract: In order to make clear the relative roles of through-space and through-bond orbital interactions in triptycene, its vapor-phase He I photoelectron spectrum was measured. A simple LCBO through-space interaction model calculation reproduced almost quantitatively the principal feature of the observed overall spectral pattern for the first two band groups. This fact suggests that the through-space interactions among the benzene ring e_{1g}-like group π orbitals are dominating as for the first six HO–π–MOs, the effect of through-bond interactions being negligibly small in contrast to the case of barrelene.

Triptycene (9,10-dihydro-9,10[1′,2′]benzenoanthracene, **1**) is



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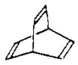

2

a molecule of high symmetry $(D_{3h})^{2-4}$ containing three benzene rings equivalent to one another as its constituents and is one of the fundamentally important systems, along with barrelene (bicyclo[2.2.2]octa-2,5,7-triene, **2**), from the standpoint of intramolecular orbital interactions. The primary interest at the present time is the relative roles of through-space and through-bond[5] interactions among the π-electron systems of the three benzene rings in **1**. In this paper, **1** is studied by photoelectron (PE) spectroscopy, which is a very powerful tool for investigating the occupied MOs, and the intramolecular interactions among the six e_{1g}-like group π orbitals of the three benzene rings in **1** are discussed on the basis of a simple LCBO model consideration.

Table I. Experimental Vertical Ionization Energies, IE_V

compound	IE_V, eV
triptycene (1)	7.98, 8.80,[a] 9.16,[a] 10.71
o-xylene[b]	8.75, 9.0, 11.25
barrelene (2)[c]	8.23, 9.65,[d] 10.02,[d] 11.25
propene[e]	9.73, 12.2
cis-2-butene[e]	9.12, 11.7

[a] Apparent band maxima in the highly overlapping region. [b] Reference 13. [c] Reference 6. [d] The Jahn–Teller split-band maxima. [e] Reference 14.

Concerning compound **2**, closely related to but much simpler than **1**, Haselbach et al.[6] discussed the interactions among the three olefinic-group occupied π orbitals based on its PE spectrum,

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(1) (a) Institute of Physical and Chemical Research and University of Tokyo. Address correspondence to Institute of Physical and Chemical Research. (b) Gifu College of Pharmacy. (c) Shionogi and Co., Ltd.

(2) Bencivenni, L.; Gigli, R.; Cesaro, S. N. *J. Mol. Struct.* **1979**, *53*, 25.

(3) Anzenhofer, K.; De Boer, J. J. *Z. Kristallogr.* **1970**, *131*, 103.

(4) Hazell, R. G.; Pawley, G. S.; Lund Petersen, C. E. *J. Cryst. Mol. Struct.* **1971**, *1*, 319.

(5) (a) Hoffmann, R.; Imamura, A.; Hehre, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 1499. (b) Hoffmann, R.; Heilbronner, E.; Gleiter, R. *Ibid.* **1970**, *92*, 706. (c) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1.

(6) Haselbach, E.; Heilbronner, E.; Schröder, G. *Helv. Chim. Acta* **1971**, *54*, 153.

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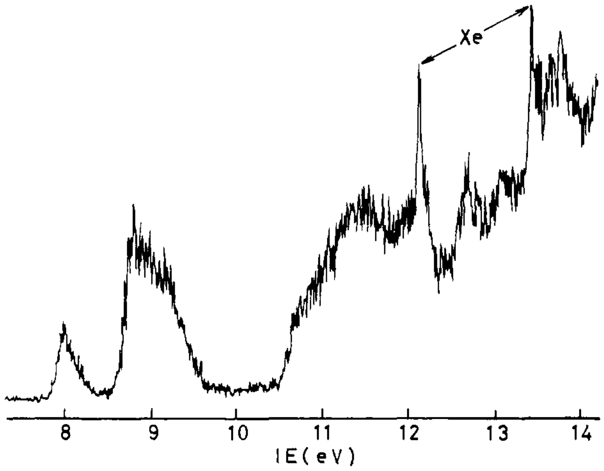

Figure 1. Vapor-phase He I PE spectrum of **1**.

concluding that through-bond interactions are far from being negligible in **2**. In this paper compound **2** is also discussed for the sake of comparison with **1**.

Experimental Section

Materials. Triptycene (**1**) purchased from the Aldrich Chemical Co. was recrystallized twice from cyclohexane just before use. Anal. ($C_{20}H_{14}$) C, H.

Measurement. The photoelectron spectrum of **1** was obtained with the He I photoelectron spectrometer described formerly.[7] An NAIG E-562 process memory (1024 channels) was used to accumulate the signals, and the accumulated spectrum was recorded on an *XY* recorder. Xe gas was used as the internal standard for the calibration of the energy scale. The sample inlet and target chamber systems were heated and kept at 127 °C during the measurement by circulating hot silicon oil.

Theoretical Methods. Theoretical methods used in this study are a simple LCBO method and two types of CNDO/S methods.[8,9] The CNDO/S methods used are those with the parameter sets suggested by Ellis et al.[8] and by Lipari and Duke.[9] For the simple LCBO treatments, overlap integrals were calculated according to Mulliken et al.[10] and the geometrical parameters of *trans*-1,3-butadiene and compound **2** were taken from ref 11 and 12, respectively. Concerning the molecular structure of **1**, Anzenhofer and De Boer[3] and Hazell et al.[4] have reported X-ray crystallographic data. In our calculations the geometrical parameter set reported by the latter group was used.

Results and Discussion

The lower energy part of the PE spectrum of **1** is shown in Figure 1, and the vertical ionization energy (IE) values of **1** obtained from Figure 1 and those of related compounds[6,13,14] are summarized in Table I. As is seen in Figure 1 the PE spectrum shows in the energy region from 7.8 to 9.8 eV two groups of bands well separated from the following bands, their integrated band intensity ratio being approximately 1:5.7. The first vertical IE is 7.98 eV, and the IEs of the apparent band maxima of the second band group are 8.80 and 9.16 eV, the relative peak-height ratio of the second band group maxima being 3:2. From the vertical IE values, these two band groups are regarded as corresponding to the ionizations from the six HO-π-MOs formed by the combinations of the six e_{1g}-like group π orbitals of the three constituent benzene rings though partly mixed with σ orbitals. From the band intensity ratio, the first band is reasonably regarded to correspond to the ionization from only one of the six π MOs mentioned above, and the following second band group to the ionizations from the other five π MOs.

As compound **1** can be regarded to be essentially of D_{3h} symmetry,[2-4] three of the six e_{1g}-like group π orbitals of the constituent three benzene rings, which are symmetric (S) against the mirror plane perpendicular to the C_3 axis, interact with one another to form an a_2' MO and doubly degenerate e' MOs. On the other hand, the remaining three e_{1g}-like group orbitals, which are antisymmetric (A) against the mirror plane mentioned above, interact with one another to form an a_1'' MO and doubly degenerate e'' MOs. Of these six MOs the a_2' and a_1'' MOs are free from through-bond interactions because of the symmetry, and these are essentially π type in nature.

In the case of compound **2**, which can also be regarded to be essentially of D_{3h} symmetry in the gas phase,[12] the three olefinic group occupied π orbitals interact mutually to form an a_2' MO and doubly degenerate e' MOs, the a_2' MO being free from through-bond interactions in this case also. The vertical IE of the first a_2' band is 8.23 eV,[6] and the second e' band is split into two components because of the Jahn–Teller effect, their band maxima being located at 9.65 and 10.02 eV.[6]

Now let us treat compounds **1** and **2** by using a simple LCBO method. The usefulness of a simple empirically parametrized LCBO method for the calculations of IEs has formerly been demonstrated for the case of *trans*-1,3,5-hexatriene by Beez et al.,[15] for example. At first we evaluate the bonding parameter value for a carbon 2p AO pair by using the first and second IEs of *trans*-1,3-butadiene, 9.03 and 11.46 eV.[15] Here we take only the π orbitals occupied in the ground states explicitly into account and regard that the two occupied π MOs of *trans*-1,3-butadiene are formed by the interactions between the two basis π-bond orbitals of the two CC double bonds equivalent to each other. Then, the interaction term energy between the two basis π-bond orbitals is evaluated to be -1.215 eV straightforwardly on the simple Hückel level. The overlap integral between the two π-bond basis orbitals in question is calculated to be 0.1377 according to ref 10, if we take all inter-AO overlap integrals into account by using the Slater-type carbon 2p AOs with the orbital exponents of 1.625. The bonding parameter value for a carbon 2p AO pair can now be evaluated to be -8.824 eV by dividing the interaction term energy value by the overlap integral value mentioned above. We use this bonding parameter β_C to predict the PE spectral patterns of **1**.

Before going to compound **1**, we briefly treat compound **2** by using the LCBO method. We regard the three π MOs occupied in the ground state of **2** be formed by the interactions among the three basis π-bond orbitals of the three component CC double bonds. As the overlap integral between two of the basis π-bond orbitals is 0.0827, the interaction term value B between the two is evaluated to be -0.730 eV by multiplying β_C by the overlap integral value. On the simple LCBO model level, the splitting between the a_2' and e' MOs is given by $|3B|$, that is, 2.190 eV, the observed splitting between them being 1.605 eV if we use the averaged IE for the Jahn–Teller-split e' bands. As the a_2' MO is free from through-bond interactions as mentioned above, the degree of the destabilizations of the e' MOs by through-bond interactions can now be estimated to be 0.59 eV. That is, in this case through-bond interactions are far from being negligible as formerly mentioned by Haselbach et al.[6] As the a_2' MO is destabilized by $|2B|$ relative to the basis π-bond orbital energy level, the latter level can be estimated to be -9.69 eV by using the a_2'-band IE free from through-bond interactions. This absolute value is very close to the first (π) IE value of propene, 9.73 eV.[14]

Now we discuss compound **1** by using the simple LCBO method. Let us estimate the basis group orbital energies for the S- and A-type group orbitals of **1** as -8.75 and -9.0 eV, respectively, using the first and second vertical IEs of *o*-xylene,[13] and

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(7) Kobayashi, T.; Yokota, K.; Nagakura, S. *J. Electron Spectrosc. Relat. Phenom.* **1973**, *2*, 449.

(8) Ellis, R. L.; Kuehnlenz, G.; Jaffé, H. H. *Theor. Chim. Acta* **1972**, *26*, 131.

(9) Lipari, N. O.; Duke, C. B. *J. Chem. Phys.* **1975**, *63*, 1748.

(10) Mulliken, R. S.; Rieke, C. A.; Orloff, D.; Orloff, H. *J. Chem. Phys.* **1949**, *17*, 1248.

(11) Almenningen, A.; Bastiansen, O.; Traetteberg, M. *Acta Chem. Scand.* **1958**, *12*, 1221.

(12) Yamamoto, S.; Nakata, M.; Fukuyama, T.; Kuchitsu, K.; Hasselmann, D.; Ermer, O. *J. Phys. Chem.* **1982**, *86*, 529.

(13) Klessinger, M. *Angew. Chem.* **1972**, *84*, 544.

(14) Bieri, G.; Burger, F.; Heilbronner, E.; Maier, J. P. *Helv. Chim. Acta* **1977**, *60*, 2213.

(15) Beez, M.; Bieri, G.; Bock, H.; Heilbronner, E. *Helv. Chim. Acta* **1973**, *56*, 1028.

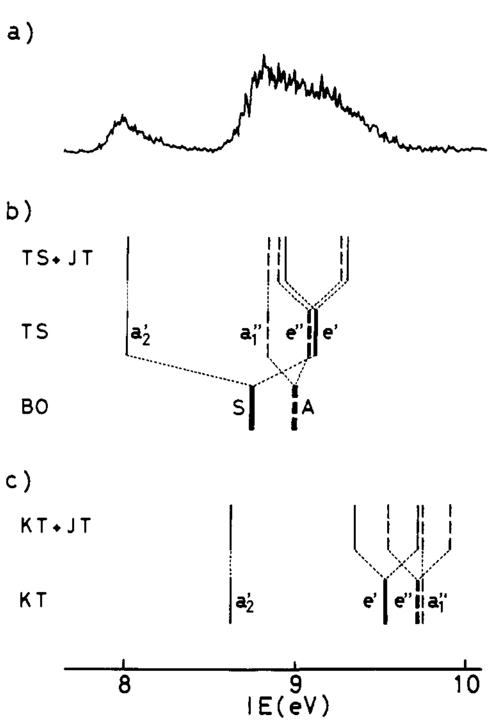

Figure 2. Calculated PE spectral patterns compared with observed spectrum of **1**: (a) the observed spectrum on an expanded scale; (b) the simple LCBO through-space interaction model calculation ((BO) the e_{1g}-like basis orbital spectrum of the benzene rings estimated on the basis of the first and second vertical IEs of *o*-xylene, (TS) the simple LCBO through-space interaction model spectral pattern, (TS + JT) the simple LCBO through-space interaction model spectral pattern taking into account the Jahn–Teller effect, approximately); (c) the CNDO/S calculation with the parameter set suggested by Ellis et al. ((KT) the spectral pattern estimated according to Koopmans' theorem, (KT + JT) the KT-level spectral pattern taking into account the Jahn–Teller effect, approximately).

estimate the interaction terms among the S- or A-type group orbitals as −0.367 or −0.081 eV using the bonding parameter β_C and the overlap integral between two component basis orbitals, 0.0416 or 0.0092. By using these values, we get the following expectation values for the IEs of **1** by the simple LCBO through-space interaction model treatment: 8.016 eV for the a_2' MO, 9.117 eV for the e' MOs, 8.838 eV for the a_1'' MO, and 9.081 eV for the e'' MOs. The expected spectral pattern with these values is drawn in Figure 2 with entry TS. This through-space interaction model spectral pattern reproduces very well the point that the first band is composed of only one component and appears around 8.0 eV well separated from the second band group.

If we include the Jahn–Teller effect in the above through-space interaction model on the assumption that the Jahn–Teller split of the e' or e'' band of **1** is comparable in magnitude to the case of the e' band of **2**, we get the expected spectral pattern as drawn in Figure 2 with entry TS + JT. In this case it is assumed that the doubly degenerate bands are split symmetrically. This finally estimated spectral pattern predicts that the first band should appear around 8.0 eV with the intensity ratio relative to the following second band group of 1:5 and that the second band group should show two band maxima around 8.8–8.9 eV and 9.2-9.3 eV with the relative intensity ratio of 3:2. These predictions are almost quantitatively correct as seen in Figure 2. This fact suggests that in the case of compound **1** the π basis bond orbitals considered here are interacting mutually, principally through space, and the effect of through-bond interactions on the e' and e'' bands may be almost negligible or less than 0.15 eV at most. On the other hand, the effect of through-bond interactions on the e' bands of **2** has been estimated to be around 0.6 eV just above. This large through-bond interaction effect in **2** in contrast to the case of **1** may be ascribed to the by far smaller number of constituent valence basis atomic orbitals in **2** than that in **1** in the minimum basis set level sense.

Finally, let us see how CNDO/S methods[8,9] work in the case of **1**. It should be pointed out that CNDO/S model calculations take into account both through-space and through-bond interactions automatically. Here we use two sets of parameters. One is the set suggested by Ellis et al.,[8] and the other one is that by Lipari and Duke.[9] The MO energies calculated with the parameter set suggested by Lipari and Duke are −9.517 eV for the a_2' MO, −9.805 eV for the e' MOs, −9.887 eV for the e'' MOs, and −9.998 eV for the a_1'' MO. These values lead obviously to a spectral pattern completely different from the observed one on the assumption of Koopmans' theorem.[16]

The CNDO/S calculation with the parameter set suggested by Ellis et al.[8] gives the orbital energies as follows: −8.621 eV for the a_2' MO, −9.533 eV for the e' MOs, −9.726 eV for the e'' MOs, and −9.747 eV for the a_1'' MO. These values do not seem to reproduce the observed overall spectral pattern for the second band group of **1** on the assumption of Koopmans' theorem (see entry KT in Figure 2) and also not even by taking into account the Jahn–Teller effect in the same manner as described above (see entry KT + JT in Figure 2). These unsatisfactory results obtained with the CNDO/S methods may have been caused by the through-bond interactions being excessively taken into account in the e' and e'' MOs in the calculations.

Conclusion

A simple LCBO model treatment of compound **1** taking into account only the through-space interactions predicts almost quantitatively the observed PE spectral pattern for the first two band groups. From this fact it is concluded that the through-space interactions are dominating in the six HO–π–MOs of **1** and the effect of through-bond interactios may be negligibly small or less than 0.15 eV at most for the e' or e'' MOs. On the other hand, the destabilizations of the e' MOs in **2** caused by through-bond interactions are estimated to amount to nearly 0.6 eV in contrast to the case in **1**.

Registry No. Triptycene, 477-75-8.

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[16] Koopmans, T. *Physica* **1934**, *1*, 104.