120. The Electronic Structure of Phenylene and Naphthylene Bicyclobutanes. Photoelectron Spectroscopy and Model Calculations

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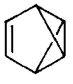
Summary

The photoelectron (PE.) spectra of 1,2,3-methenoindane (**2**), 1,2,3-metheno-2,3-dihydro-1*H*-cyclopenta[*b*]naphthalene (**3**) and 1,2,3-metheno-2,3-dihydro-1*H*-phenalene (**4**) are investigated. The PE. spectrum of 1,3-methano-2,3-dihydrophenalene (**7**) is reported and compared with that of **4**. The experimental results are analyzed in terms of empirical correlation diagrams and the results of semiempirical MINDO/3 and CNDO/S calculations. The analysis indicates that the strong impact of the bicyclobutylene group on the spectroscopic properties of the aromatic π-systems in **2**, **3** and **4** is due to hyperconjugative interactions involving bicyclobutane *Walsh* orbitals.

Introduction. - The convenient synthesis of tricyclo[3.1.0.0^{2,6}] hex-3-ene (benzvalene, **1**) and its homologues [1-4] has initiated a growing interest in the chemistry and the electronic structure of bicyclobutane derivatives. As part of our current investigation of the electronic properties of bicyclobutanes [5-8], we have presently studied the electronic structure of the phenylene and naphthylene bicyclobutanes **2**, **3** and **4** by means of photoelectron (PE.) spectroscopy and by semiempirical molecular orbital calculations. Spectroscopic data for **4** have been previously discussed [2] [6]; in view of the present results, a reassignment of the PE. spectrum is suggested.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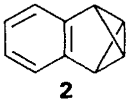
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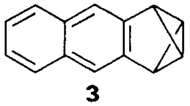
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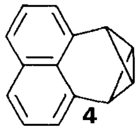
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The main objective of this undertaking is to investigate the influence of bicyclobutylene substitution on the spectroscopic properties of the aromatic π-systems in

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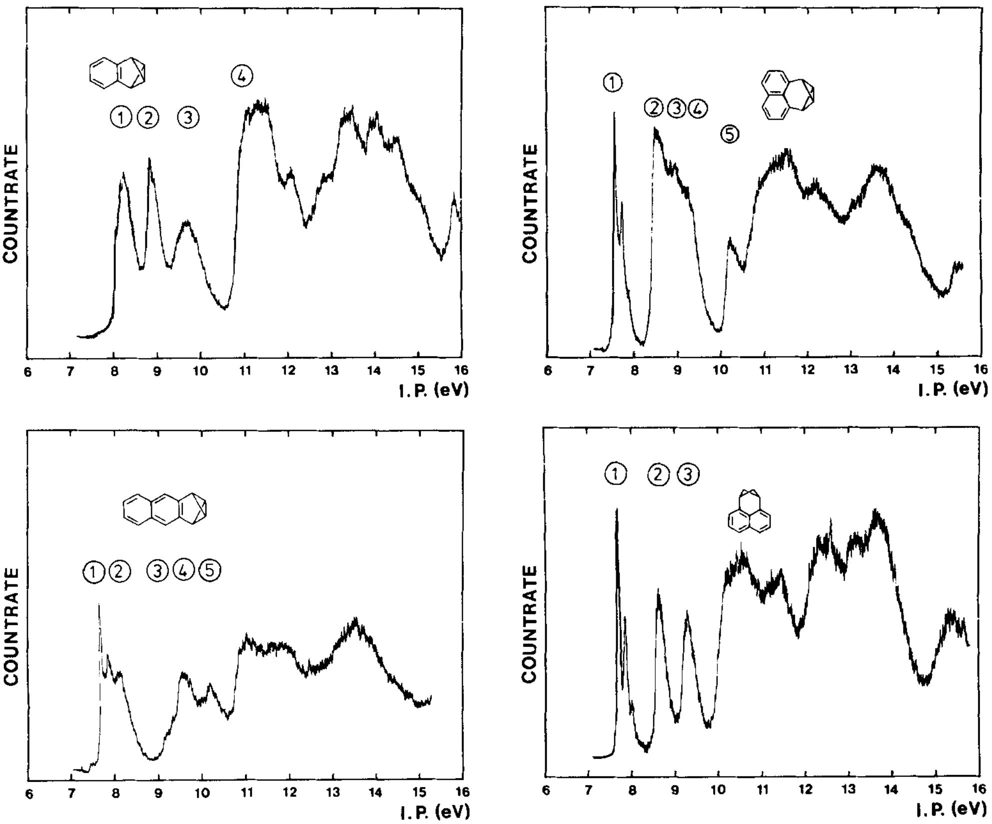


Fig. 1. *Gas phase He(I_α) photoelectron (PE.) spectra of 1,2,3-methenoindane* (**2**), *1,2,3-metheno-2,3-dihydro-1*H*-cyclopenta[b]naphthalene* (**3**), *1,2,3-metheno-2,3-dihydro-1*H*-phenalene* (**4**) *and 1,3-methano-2,3-dihydro-1*H*-phenalene* (**7**)

2, **3** and **4**. As demonstrated in this paper, the influence is profound and can be explained in terms of strong hyperconjugative interactions between π-orbitals of the aromatic fragments and high-lying occupied bicyclobutane *Walsh* orbitals.

PE. Spectroscopy. - The PE. spectrum of the parent compound **1** has been previously published and discussed in detail [5] [8] [9]. The spectra of **2**-**4** are shown in *Figure 1* and measured ionization energies are given in the *Table* together with calculational results. The lowest few ionization energies of **4** were reported recently in a brief communication [6].

For the interpretation of the PE. spectra *Koopmans'* theorem [10] was used. In this approximation the orbital energy ε_J is set equal to minus the vertical ionization energy $I_{v,J}$ ($\varepsilon_J = -I_{v,J}$). The assignment of PE. bands to orbital energy levels was based on i) application of simple band shape criteria, ii) empirical correlation of bands within series of related compounds, and iii) comparison with the results of semiempirical calculations. The resulting assignment, which is discussed below, is given in the *Table* and illustrated in the correlation diagram in *Figure 2*.

Table. *Observed vertical ionization energies $I_{v,J}$ and calculated orbital energies ε_J (eV). The PE. data for* **1** *are taken from [5].* Further experimental and calculational details are given in the text.

Compound	Band	$I_{v,J}$	Assignment	$-\varepsilon_J$(CNDO)	$-\varepsilon_J$(MINDO/3)
1	①	8.55	$3b_2(\pi)$	8.87	8.43
	②	9.8	$7a_1(\sigma)$	10.60	9.10
	③	10.8	$1a_2$	12.04	9.87
	④	12.2	$4b_1$	13.09	11.06
2	①	8.14	$4b_2(\pi)$	8.68	8.20
	②	8.79	$2a_2(\pi)$	9.56	8.69
	③	9.7	$11a_1(\sigma)$	10.53	8.98
	④	11.1	$10a_1$	11.75	9.94
3	①	7.71	$3a_2(\pi)$	8.56	7.96
	②	8.1	$5b_2(\pi)$	8.64	8.13
	③	~9.4 (sh)	$15a_1(\sigma)$	10.55	8.94
	④	9.7	$2a_2(\pi)$	10.61	9.65
	⑤	10.2	$4b_2(\pi)$	11.35	10.23
			$14a_1$	11.40	9.66
4	①	7.55	$3a_2(\pi)$	8.35	7.77
	②	8.47	$5b_2(\pi)$	9.35	8.72
	③	~8.9	$14a_1(\sigma)$	9.96	8.48
	④	~9.2	$4b_2(\pi)$	9.96	9.23
	⑤	10.2	$\{11b_1$	11.50	9.56
			$\{2a_2(\pi)$	11.93	10.42

PE. Spectrum of **2**. The low energy region of the PE. spectrum of **2** exhibits three bands with maxima at 8.1, 8.8 and 9.7 eV. Comparison with the PE. data for *o*-dialkylbenzenes and tricyclo[3.1.0.0^{2,6}]hexane (**5**) indicates that band ① and ② should be assigned to ejection of electrons from π-orbitals localized predominantly

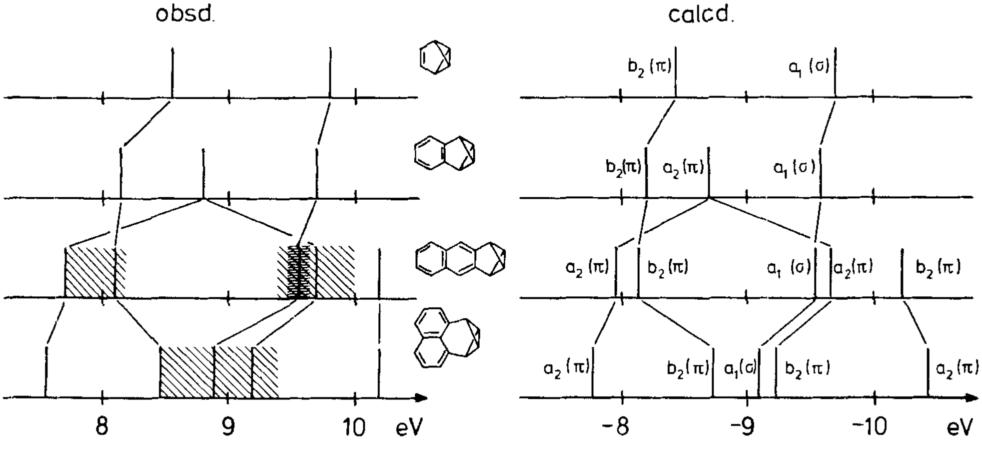


Fig. 2. *Comparison of observed ionization energies* (left) *and orbital energies* (right) *predicted by MINDO/3.* To facilitate the comparison of observed and calculated trends, the calculated energy of the $a_1(\sigma)$-level is shifted by 0.6 eV towards higher binding energies.

in the benzene fragment, while band ③ should be assigned to a σ-orbital localized in the bicyclobutane moiety. This point of view is supported by the application of qualitative band shape criteria (see, *e.g.*, [11]). The first two bands have relatively narrow peaks and steep onsets, while the third band is broad with a typical gaussian-like shape, consistent with the assignment of band ① and ② to weakly bonding π-levels and band ③ to a level with σ-bonding character.

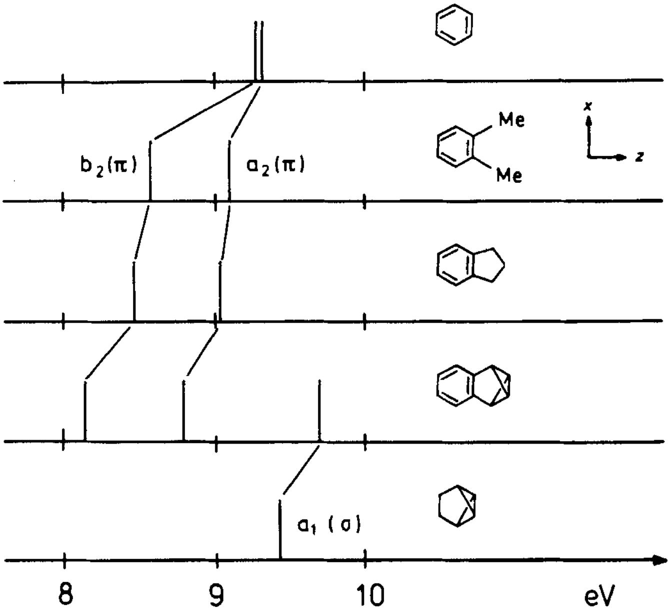


Fig. 3. *Correlation of observed ionization energies for benzene,* o-*xylene, indane [16], 1,2,3-methenoindane* (**2**)*, and tricyclo[3.1.0.0^{2,6}]hexane* (**5**) *[5].*

Band ①, which is similar in shape to the first PE. band of **1** [5] [9], shows vibrational fine structure with the third or fourth component as the most intense; this intensity distribution is somewhat atypical for a π-band and may be interpreted as indicating the admixture of significant σ-bonding character into the HOMO of **2**. The assumption of strong hyperconjugative interactions in **2** is confirmed by consideration of the large shift of the π-levels of indane observed when passing to **2** *(Fig. 3)*; this shift can hardly be explained alone by the increase of the inductive effect on substitution of a metheno group, but must be due primarily to hyperconjugative effects, involving high-lying bicyclobutane orbitals of appropriate symmetry.

The conclusions based on empirical criteria are supported by the computational results. MINDO/3 [12] [13] yields excellent numerical agreement with observed ionization energies for π-levels but underestimates the binding energy of σ-levels *(Table, Fig. 2)*. A more realistic spacing of π- and σ-levels is predicted by *Baumann*'s CNDO version [14], which according to our experience [15] is well suited for the description of alkyl substituted π-systems; the calculated interaction

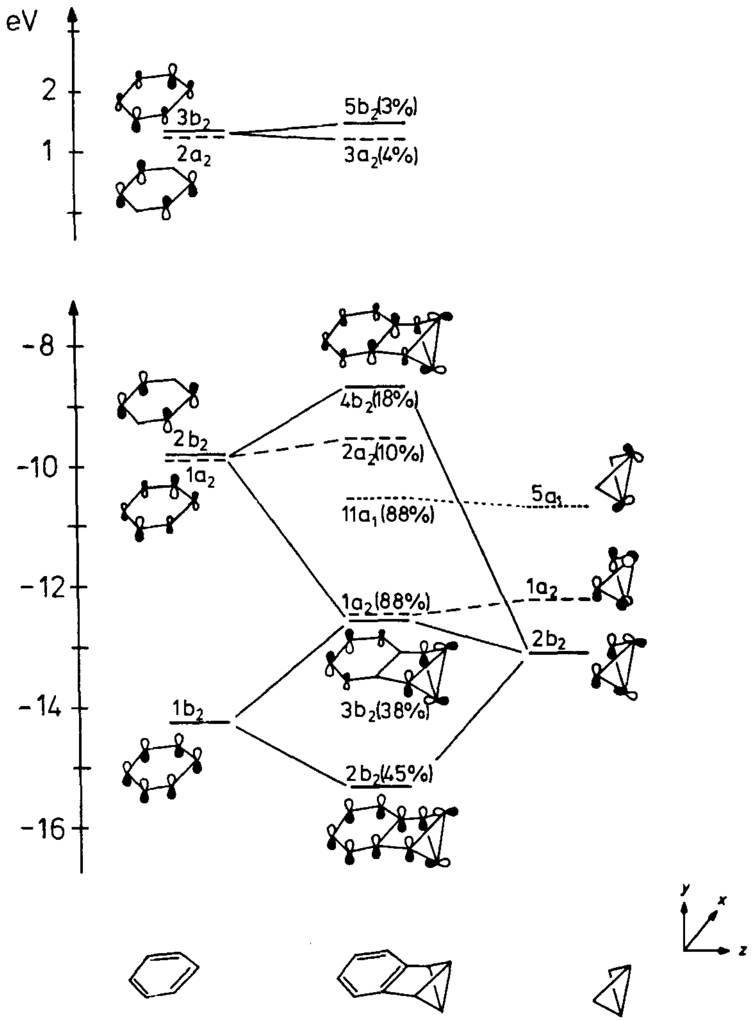


Fig. 4. *Correlation of orbital energies for benzene, 1,2,3-methenoindane* (**2**) *and bicyclobutane calculated by the CNDO method [14].* The predicted bicyclobutane character of the orbitals of **2** is indicated in brackets.

between the π-orbitals of benzene and the *Walsh*-type orbitals of bicyclobutane is indicated in *Figure 4.* The diagram correlates levels calculated for benzene (**2**) and bicyclobutane; the latter species was considered in a geometry corresponding to the bicyclobutane fragment of **2** (as predicted by MINDO/3, dihedral angle 108°). Under the assumption that inductive effects on the fragment basis orbitals can be neglected, *Figure 4* can be considered as an orbital interaction diagram in the usual sense (see also *Fig. 6*).

The most obvious feature exhibited by the diagram is the strong interaction between occupied b_2-orbitals, in contrast to the much weaker interaction between

a_2-orbitals. As a result, the degenerate π-levels of benzene are split, leading to a considerable gap between the two highest occupied levels of **2**, $4b_2(\pi)$ and $2a_2(\pi)$. This is of course easily explained by the different amplitudes of the $2b_2(\pi)$- and $1a_2(\pi)$-benzene orbitals in the substituted positions, but also indirect coupling with the $1b_2(\pi)$-benzene orbital appears to be significant. The bicyclobutane character of the $4b_2(\pi)$- and $2a_2(\pi)$-orbitals of **2** is predicted to be 18% and 10%, respectively *(Fig. 4)*. This may explain the fact that the shape of band ① is less typical for a π-band than that of band ②.

PE. Spectra of **3** *and* **4**. Inspection of *Figure 1* shows that the valence electronic structure of naphthylene bicyclobutanes is strongly dependent on the mode of linkage. This is clearly demonstrated by the striking difference between the low energy regions of the PE. spectra of **3** and **4**.

Comparison with the PE. spectra of naphthalene and alkylnaphthalenes [16] leads us to expect the presence of 4 π-bands below 11 eV, corresponding to the $1a_u(\pi)$-, $2b_{2u}(\pi)$-, $1b_{1g}(\pi)$-, and $1b_{3g}(\pi)$-levels of naphthalene *(Fig. 5)*. Also a band corresponding to band ② of **1** and band ③ of **2**, *i.e.* the low energy bicyclobutane $a_1(\sigma)$-band, must occur in this region.

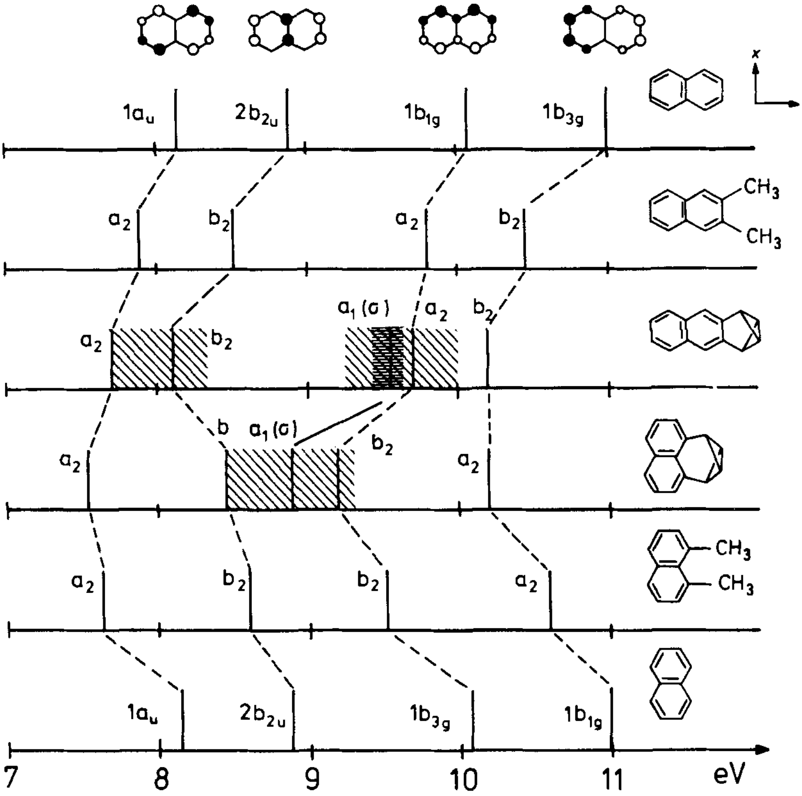
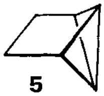


Fig. 5. *Correlation of observed ionization energies for naphthalene, 2,3- and 1,8-dimethylnaphthalene [16], and* **3** *and* **4**

The σ-band is found at 9.8 eV in **1** and at 9.7 eV in **2**; it should not be shifted strongly when passing from **2** to **3**. In the PE. spectrum of **3** two strongly overlapping bands are observed in this region, band ③ appearing only as a shoulder at 9.4 eV and band ④ with a maximum at 9.7 eV. The onset of band ③ is characteristic for a σ-band while the relatively steep rise of the peak of band ④ is consistent with the assignment of a π-band; we thus assign band ③ to the $a_1(\sigma)$ bicyclobutane-level. The peak of this band is not observed, but it does not occur below 9.4 eV; it is probably quite close to the peak of band ④ at 9.7 eV.

When passing from **3** to **4** the dihedral angle of the bicyclobutane skeleton is increased from about 108° to about 119° (MINDO/3 prediction). The energy levels of bicyclobutane are highly sensitive to variation of the dihedral angle as previously discussed in detail [5]. The first band of **5** has a maximum at 9.2 eV while the corresponding band of **6** shows a peak at 8.8 eV [8]. It is clear that this large shift towards lower energies when passing from **5** to **6** cannot be due alone to the larger inductive effect of the trimethylene bridge, but must be explained mainly as a consequence of the increase in dihedral angle. Hence, we would expect the low energy bicyclobutane σ-band to be shifted by 0.4–0.6 eV towards lower energies when going from **3** to **4**; this is consistent with the calculated shifts which are 0.6 eV (CNDO) and 0.5 eV (MINDO/3) *(Table)*. This indicates to us that one of the closely spaced bands ③ and ④ at 8.9 and 9.2 eV in the PE. spectrum of **4** should be assigned to this level. Unfortunately, the strong overlapping of bands in the 8–9.5 eV region complicates the application of band shape criteria; only the steep onset of band ② with a maximum at 8.47 eV ensures that this is a π-band. We tentatively assign band ③ as σ- and band ④ as π-band, mainly because the reverse assignment seems to be less consistent with the PE. data for the cyclobutane analogue of **4** *(vide infra)*.



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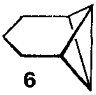

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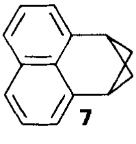
Having assigned more or less tentatively the low energy bicyclobutane σ-band in **3** and **4**, the assignment of the remaining four π-bands in the low energy region is straightforward. In both cases, band ①, ②, ④ and ⑤ are assigned to ejection of electrons from naphthalenic π-orbitals. We find that this assignment is reasonably consistent with the data for 2,3- and 1,8-dimethylnaphthalene as indicated in *Figure 5*, and it is furthermore nicely consistent with the calculated results *(Fig. 2)*.

To support the assignment in the difficult case of **4** we briefly consider the PE. spectrum of the cyclobutane analogue **7** *(Fig. 1)*. The assignment of bands in



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the low energy region is here straightforward, because of the absence of the bicyclobutane σ-band. In particular, band ② and ③ at 8.6 and 9.3 eV must be assigned to π-orbitals of b_2-symmetry, corresponding to the naphthalene $2b_{2u}$- and $1b_{3g}$-orbitals (*Fig. 5*, bottom). A brief consideration of the energy and shape of cyclobutane and bicyclobutane b_2-basis orbitals [5] [17] indicates that the $b_2(\pi)$-energy levels in **4** and **7** should be very similar, supporting our assignment of band ② and ④ of **4** at 8.5 and 9.2 eV to these levels. This assignment is slightly different from the one suggested previously [6]. A detailed analysis of the PE. spectrum of **7** will be published elsewhere [18].

Concluding remarks. - The results of our analysis are summarized in the empirical interaction diagram in *Figure 6*, which illustrates the interaction between bicyclobutane *Walsh*-orbitals and benzene and naphthalene π-orbitals to yield the

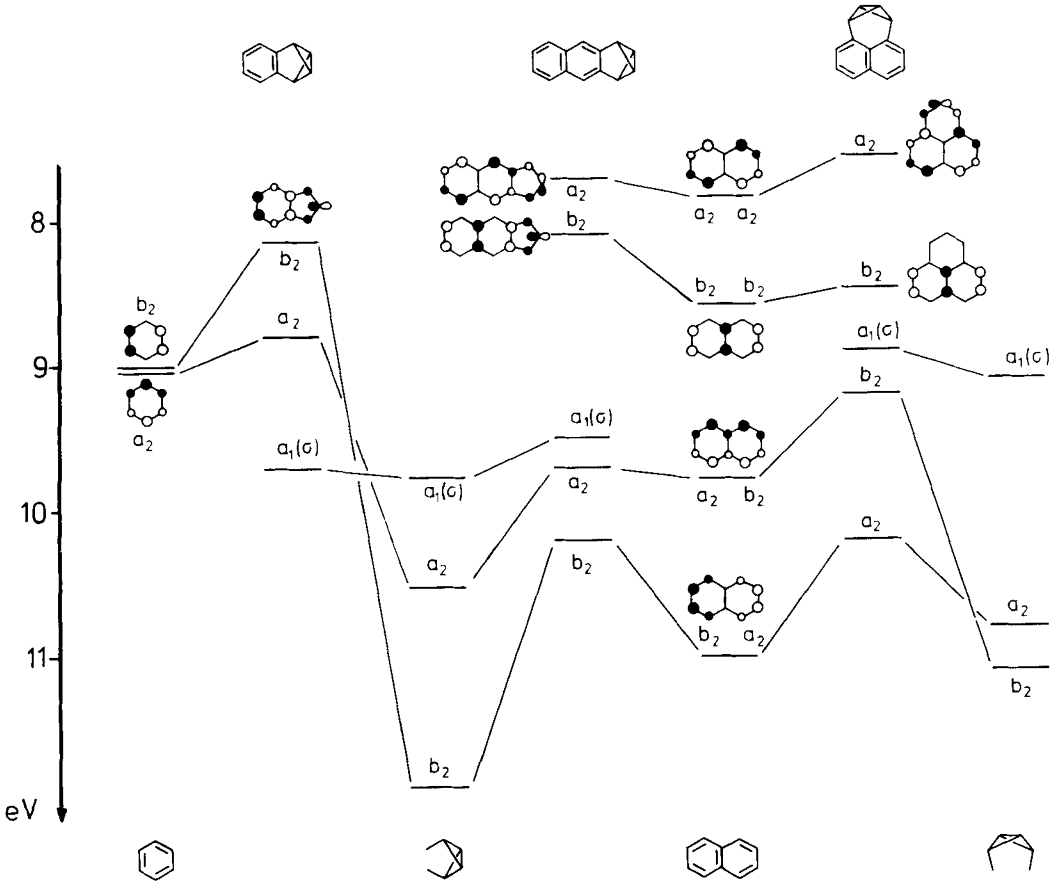

Fig. 6. *Empirical interaction diagram correlating one-electron levels of* **2**, **3**, *and* **4** *with estimated basis orbital energies for benzene, naphthalene and bicyclobutane.* Note that the effective bicyclobutane basis orbital energies differ in the case of **4** and the case of **2** and **3** (see the text).

corresponding levels of **2**, **3** and **4**. The bicyclobutane basis-orbital energies were estimated from the PE. spectrum of **5** [5] in the case of **2** and **3** and from the spectrum of **6** [5] [6] in the case of **4**; the corresponding energies for benzene and naphthalene were estimated from the spectra of the unsubstituted parent compounds [16]. Inductive effects on the effective basis-orbital energies were estimated tentatively; the trends of the diagram are not affected by minor variation of the assumptions made.

The interaction diagram can be understood by consideration of orbital shapes and application of simple perturbation theory. In the case of **2** and **3**, the b_2-orbitals of the parent compounds are much more destabilized than the a_2-orbitals, consistent with the larger amplitude of the former in the substituted positions. In the case of **4**, the a_2-levels have become more destabilized than the b_2-levels and the picture is reversed, except for the fourth π-level which has the same energy in **3** and **4**. Together with the considerable shift of the bicyclobutane $a_1(\sigma)$-level this explains the quite different level patterns of **3** and **4** in the low energy region. The fourth π-level stays constant, in spite of considerable difference in the amplitude of the corresponding naphthalene orbital in the 2,3- and 1,8-positions. This can be explained by the very large shift of the effective bicyclobutane basis-orbital energy, leading to an essentially first-order interaction in the case of **4** and thereby counteracting the trend expected on a consideration of the shape of the naphthalene π-orbital.

Calculations. - Semiempirical all-valence-electrons calculations on **1** to **4** and a number of related compounds were carried out according to the MINDO/3 method [12] [13] and the CNDO/S method by *Baumann* [14]. All geometries were taken as those predicted by MINDO/3; C_{2v}-symmetry was assumed for the bicyclobutane compounds. The standard parameters stored in the QCPE versions of the computer programs [13] [14] were employed.

Experimental Part. - The compounds **2**, **3**, **4** and **7** were synthesized according to directions in the literature.

1,2,3-Methenoindane (**2**). A mixture 2:1 of naphthalene and its valence isomer **2** was obtained according to [1]. It was separated by column chromatography at 0° on magnesia/*celite* 2:1 with pentane/dichloromethane 96:4 as eluent.

*1,2,3-Metheno-2,3-dihydro-1*H*-cyclopenta[b]naphthalene* (**3**). Compound **3** was found to be the major product of the reaction of dilithio-*s*-indacene with excess dichloromethane/butyllithium. It was isolated by column chromatography at 0° on magnesia/*celite* 2:1 (pentane) [4].

*1,2,3-Metheno-2,3-dihydro-1*H*-phenalene* (**4**). Compound **4** was obtained according to [2] and [3]. It was purified by column chromatography on magnesia/*celite* 2:1 (hexane saturated with water).

*1,3-Methano-2,3-dihydro-1*H*-phenalene* (**7**). Compound **7** was prepared according to [19] by UV. irradiation of 1,8-divinylnaphthalene [20] and purified by column chromatography on alumina (pentane).

The He(Iα) gas phase PE. spectra shown in *Figure 1* were measured on a PS 18 instrument (*Perkin Elmer Ltd.*, England) equipped with a heated probe. The spectra were calibrated with argon; a resolution of *ca.* 20 meV on the Ar-line was obtained. The inlet temperature was 25°, 50°, 68° and 31° in the case of **2**, **3**, **4** and **7**, respectively. The small peak at 7.4 eV in the PE. spectrum of **3** (*Fig. 1*) gained intensity when the sample temperature was increased. The vertical ionization energies listed in the *Table* were generally estimated from the maximum of the PE. band.

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REFERENCES

[1] *T.J. Katz, E.J. Wang & N. Acton*, J. Am. Chem. Soc. *93*, 3782 (1971).
[2] *I. Murata & K. Nakasuji*, Tetrahedron Lett. *1973*, 47.
[3] *R.M. Pagni & C.R. Watson*, Tetrahedron Lett. *1973*, 59.
[4] *G. Gandillon, B. Bianco & U. Burger*, Tetrahedron Lett. *1981*, 51.
[5] *P. Bischof, R. Gleiter & E. Müller*, Tetrahedron *32*, 2769 (1976).
[6] *R. Gleiter, R. Haider, I. Murata & R.M. Pagni*, J. Chem. Res. (S) *1979*, 72.
[7] *P. Bischof, R. Gleiter, R.T. Taylor, A.R. Browne & L.A. Paquette*, J. Org. Chem. *43*, 2391 (1978).
[8] *R. Gleiter*, Topics in Current Chemistry 86, 197 (1979), and literature cited therein.
[9] *P.J. Harman, J.E. Kent, T.H. Gan, J.B. Peel & G.D. Willet*, J. Am. Chem. Soc. *99*, 943 (1977).
[10] *T. Koopmans*, Physica *1*, 104 (1934).
[11] *C.R. Brundle & M.B. Robin*, in 'Determination of Organic Structures by Physical Methods', F. Nachod & G. Zuckerman, Eds., Academic Press, New York 1971, Vol. 3, p. 1.
[12] *R.C. Bingham, M.J.S. Dewar & D.H. Lo*, J. Am. Chem. Soc. *97*, 1285 (1975).
[13] *P. Bischof*, J. Am. Chem. Soc. *98*, 6844 (1976); QCPE *12*, 383 (1979).
[14] *H. Baumann*, QCPE *10*, 333 (1977).
[15] *J. Spanget-Larsen & R. Gleiter*, Helv. Chim. Acta *61*, 2999 (1978).
[16] *E. Heilbronner, T. Hoshi, J.L. von Rosenberg & K. Hafner*, Nouv. J. Chim. *1*, 106 (1977); *E. Heilbronner*, private communication.
[17] *R. Gleiter, P. Bischof, W.E. Volz & L.A. Paquette*, J. Am. Chem. Soc. *99*, 8 (1977).
[18] *R. Gleiter & K. Gubernator*, to be published.
[19] *J. Meinwald & J. W. Young*, J. Am. Chem. Soc. *93*, 725 (1971).
[20] *R. H. Mitchell & F. Sondheimer*, Tetrahedron *24*, 1397 (1968).