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19. Near Cancellation of Through Space and Through Bond Interaction in Bicyclo[3.2.2]nona-6,8-diene[1]

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(17. XI. 72)

Summary. The photoelectron spectra of bicyclo[3.2.2]nonane and its five dehydrogenated analogues are reported. Analysis of the π-bands reveals that the unsymmetrical diene **5** retains the 'natural order' of the π-orbitals present in the lower homologues, i.e. the in-phase below

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[1] Part 45 of 'Applications of Photoelectron Spectroscopy'. Part 44: [1].

the out-of-phase combination of the basis π-orbitals π_a and π_c. The isomeric diene **4** is the first member of the symmetrical homologous series (*I*), which inverts this order, so that $\mathbf{a}_1(\pi)$ (in phase!) lies above $\mathbf{b}_2(\pi)$ (out-of-phase!).

Introduction. – In previous papers of this series [1], [2], the heuristically useful distinction between 'through space' and 'through bond' interactions [3] has served to rationalize the unusual pattern of first and second ionization potentials of the bridged bicyclic dienes $I(n)$ (Fig. 1).

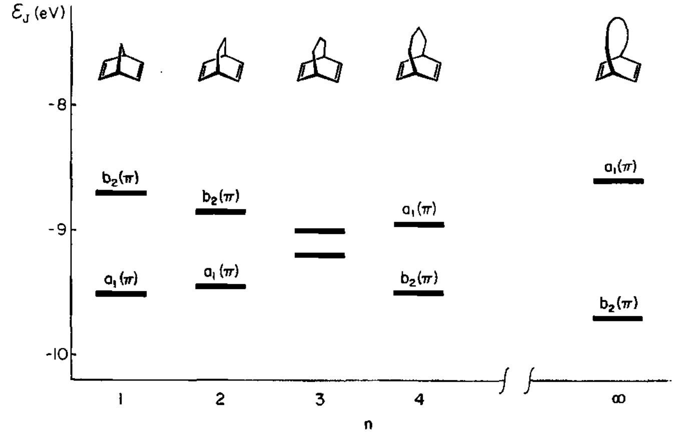
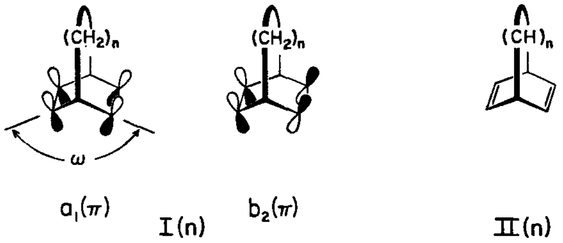


Fig. 1. *Inversion of level ordering in the bicyclic dienes, I(n), with increasing homologation*

'Through space' interaction of the two diene bridges is understood to decrease as n, and therefore ω, increase. As a result, the orbital energy of the through space bonding combination, ε ($\mathbf{a}_1(\pi)$), increases while that of the antibonding one, ε ($\mathbf{b}_2(\pi)$),



decreases. This latter orbital is also the critical one for stabilizing the closely related longicyclic cations ($II(n)$, n is odd) [4]. The known or anticipated thermodynamic stability of such ions has been attributed to first order stabilization of $\mathbf{b}_2(\pi)$ by the vacant nonbonding molecular orbital of the polymethine bridge. This latter orbital belongs to the same irreducible representation (within idealized C_{2v} symmetry) whenever $n = 1, 5, 9 \ldots$ As a result, stabilization of $II(n)$ should also fall off, to this extent, with increasing n. A correspondingly anticipated decrease in anionic stabilization ($II(n)$, $n = 3, 7, 11 \ldots$) will also depend upon the degree to which the pairing principle applies to such hydrocarbons.

Much better understood, at present, is the inversion in the 'natural order', *i.e.* $\mathbf{a}_1(\pi)$ below $\mathbf{b}_2(\pi)$ [5], that is apparent for I $(n > 4)$; $\mathbf{a}_1(\pi)$ is now the crucial orbital. As n and ω increase, $\mathbf{a}_1(\pi)$ mixes increasingly with an occupied high lying σ level, localized largely in the polymethylene bridge. Such increased 'through bond' interaction thus raises $\mathbf{a}_1(\pi)$.

In this paper, we show that the observed ionization potentials of the most ambiguous member of this series, (I $(n = 3) \equiv$ **4**), is more simply understood by assigning $\mathbf{a}_1(\pi)$ above $\mathbf{b}_2(\pi)$. The crossover point thus appears between $n = 2$ and $n = 3$. Our approach includes a detailed comparison of the photoelectron spectra of hydrocarbons **1–6**, illustrated in Fig. 2 and 3 and listed in Table 1. Vertical ionization potentials are equated with negative orbital energies within the framework of *Koopmans'* theorem [6].

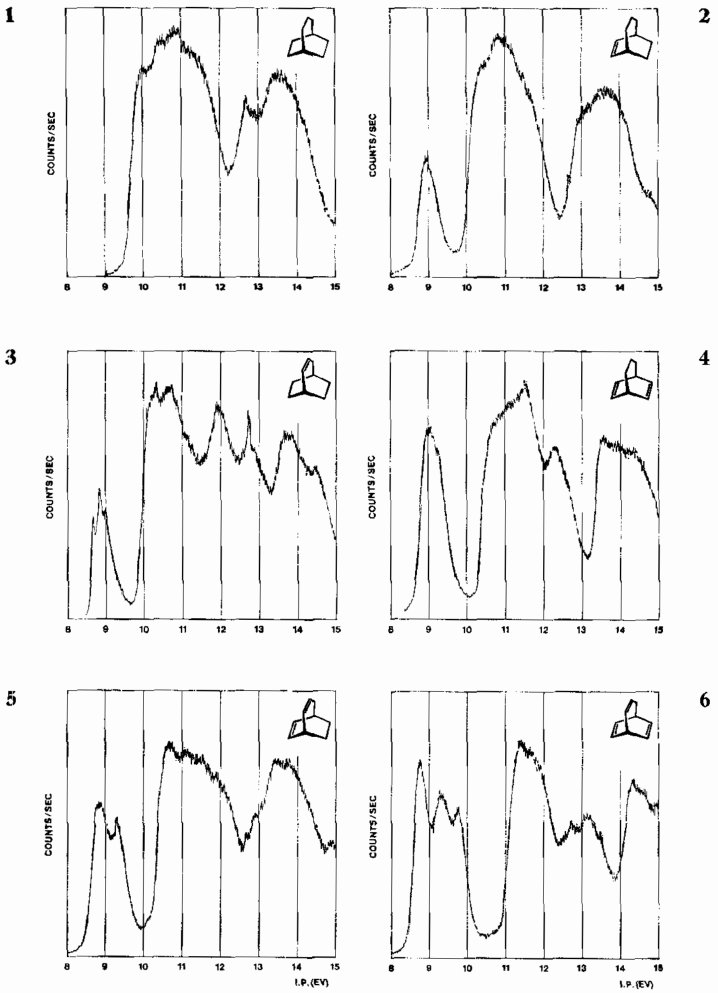


Fig. 2. *Experimental photoelectron spectra of* **1–6**

We begin by assigning basis π-orbital energies (A_i) for subsequent use within the context of a linear combination of bonding orbitals approach. In this way, symmetry assignments of diene levels can be achieved by correlation with those of the triene **6**. A subsequent correlation with the less equivocal bicyclo[2.2.2]octyl series [7] permits orbital assignment to the unsymmetrical bicyclo[3.2.2]nona-2,6-diene, **5**. It also confirms the previously deduced assignments of the symmetrical isomer **4**.

Table 1. *Vertical Ionization Potentials (eV) of the Hydrocarbons* **1–6**
The vertical ionization potentials are taken as the positions of the maxima of the corresponding bands.

Hydrocarbon	$I_{v,1}$	$I_{v,2}$	$I_{v,3}$	σ-Onset
1				9.6
2	8.95			9.9
3	8.84			9.8
4	9.00	9.18		10.3
5	8.84	9.29		10.3
6	8.72	9.24	9.74	10.9

Basis Orbitals and Their Interaction. – Fig. 2 and 3 illustrate the now general observation [8] that successive incorporation of double bonds into a saturated hydrocarbon leads to a lowering of σ-orbital energies; the onset of σ-bands shifts towards higher ionization potentials. As in the bicyclooctyl system [7], this shift is greater in going from diene to triene (0.60 to 0.85 eV) than from monoene to diene (0.20 to 0.40 eV).

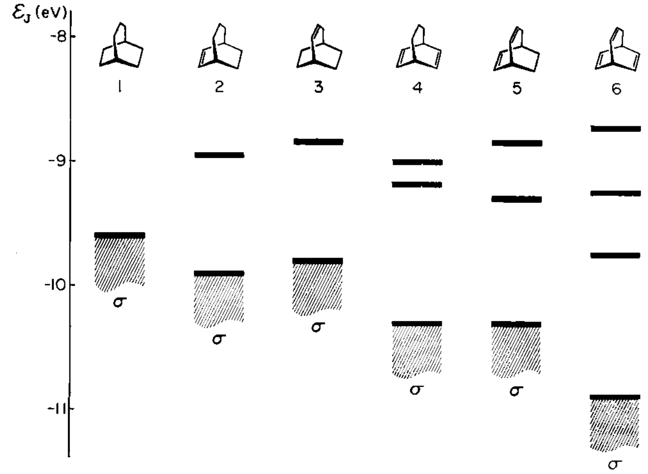


Fig. 3. *π and σ levels of* **1–6**

The mean ionization potentials of the π-bands also shift in the same direction, if to a lesser degree. Following past custom [5], we shall denote the basis π-orbital energy of the unsaturated two-carbon bridge of the dienes **4** and **5** and of the triene **6** as A'_a ($\equiv A'_b$ in **4** and **6**). The corresponding energy of the three-carbon bridge π-orbital in **5** and **6** is called A'_c.

These differ so little from those (A_a^o and A_c^o) of the corresponding monoenes, that it becomes simplest to assume $A'_a - A_a^o = A'_c - A_c^o = \delta$. If so, the diene and triene basis energies can be evaluated by using equation (1). The magnitude of δ is selected (equation (2)) as the mean discrepancy between the observed π-ionization potential of the appropriate monoene model ($I_{v,j}^o$) and that ($I'_{v,j}$) of the diene ($m = 2$) or triene ($m = 3$). The alternative (3) is

$$A'_i = A_i^o + \delta \tag{1}$$

$$\delta = -(1/m) \sum_{j=1,m} (I'_{v,j} - I_{v,j}^o); \qquad m = 2, 3 \tag{2}$$

$$\delta = k\delta_\beta; \quad \delta_\beta = -0.17_5 \text{ eV} \tag{3}$$

to assume a constant increment (δ_β) for each bishomoconjugated double bond and to multiply this by the number of such interactions (k = 1 for the two dienes; k = 2 for triene **6**). The value of δ_β (-0.17_5 eV) is one that was previously evaluated from the P.E. – spectra of monocyclic polyenes [1]. As Table 2 demonstrates, the results differ negligibly. We shall henceforth employ those values obtained via (1) and (2).

It is then possible to calculate the interaction terms, $|B_{ab}|$ of the symmetrical diene **4** and $|B_{ac}|$ of the unsymmetrical one **5**, by using formula (4) and thus to obtain 0.09 eV for **4** and 0.22 eV for **5**. This does not, however, provide the sign of B_{ai} – negative if 'through space' interaction is dominant and positive if 'through bond' interaction prevails.

Table 2. *Estimated Basis Orbital Energies* (*eV*)

The basis orbital energies A'_a and A'_c have been calculated according to (1) using the approximations (2) or (3) for the evaluation of δ.

Hydrocarbon	A'_a (2)	(3)	A'_c (2)	(3)
4	−9.09	-9.12_5		
5	−9.12	-9.12_5	−9.01	-9.01_5
6	−9.27	−9.30	−9.16	−9.19

$$B_{ai}^2 = \left(\frac{I_{v,1} - I_{v,2}}{2}\right)^2 - \left(\frac{A'_a - A'_i}{2}\right)^2 \tag{4}$$

Orbital Assignments of **4** *and* **6**. – As in previous studies [2b, 9], such a distinction is achieved by interposition of a third olefinic bridge. This can interact only with $\mathbf{b}_2(\pi)$ of the diene component to generate linear combinations that must account for two of the three π-bands in the photoelectron spectrum of triene **6**. The $\mathbf{a}_1(\pi)$ orbital of diene **4** is that one whose energy (after appropriate basis correction) remains unchanged in the triene. Such correction is obtained by depressing the observed mean π-orbital energy of **4** (−9.09 eV) to that of the triene basis ($A'_a = -9.27$ eV) which is then split by $B_{ab} = \pm 0.09$ eV.

It is apparent from Fig. 4 that $-I_{v,2}$ of triene **6** (−9.24 eV) matches the energy of the upper combination (−9.18 eV) significantly better than it does the energy of the lower one (−9.36 eV). Indeed, the alternative approach (3) to the selection of orbital basis energies would have improved the agreement still more (ε ($\mathbf{a}_1(\pi)$) = −9.21 eV; ε ($\mathbf{b}_2(\pi)$) = −9.39 eV). In view of the unusually small gap, the experimental uncertainities, and the approximations used in this analysis, no more convincing evidence can be expected.

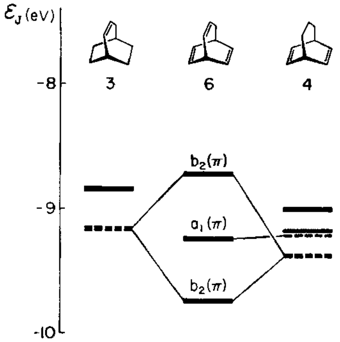


Fig. 4. *Correlation of the π levels of* **3**, **4** *and* **6**. Solid lines are the negative ionization potentials. Dashed lines are corrected to the triene basis. See text.

Correlation with the Bicyclo[2.2.2]octyl Assigments. – Although 'through bond' interactions raise $\mathbf{a}_1(\pi)$ above $\mathbf{b}_2(\pi)$ in the symmetrical diene **4**, this need not be true for the unsymmetrical **5**. Indeed, the greater energy gap observed for the latter suggests that it cannot be. As demonstration, we first correlate the π-orbital of triene **6** with those [7] of barrelene, **7**. The latter (5) are graphically displayed, end on, in Fig. 5.

$$\begin{aligned}\mathbf{a}_2'(\pi) &= \frac{1}{\sqrt{3}}\,(\pi_a - \pi_b - \pi_c)\\ \mathbf{e}'(\mathrm{S}) &= \frac{1}{\sqrt{2}}\,(\pi_a + \pi_b)\\ \mathbf{e}'(\mathrm{A}) &= \frac{1}{\sqrt{6}}\,(\pi_a - \pi_b + 2\pi_c)\end{aligned} \tag{5}$$

Homologation of barrelene to bicyclo[3.2.2]nonatriene is expected to have two principal 'through space' effects apart from a minor inductive contribution.

a) It should reduce the interaction of π_c with π_a and π_b. This lowers $\mathbf{a}_2'(\pi)$ and raises $\mathbf{e}'$(A) by an amount crudely indicated by the open arrows of Fig. 5; $\mathbf{e}'$(S) remains unaffected.

b) The increasing dihedral angle (ω) should reduce the interaction between π_a and π_b. As indicated by the dotted arrows of Fig. 5, $\mathbf{a}_2'(\pi)$ and $\mathbf{e}'$(A) are now both lowered, the latter to a lesser degree; $\mathbf{e}'$(S) is raised.

The resultant of the two effects, indicated by the solid arrows, adequately reproduces the assigned correlation of orbital energies with those of triene **6**. Such support for the previously deduced assignments of **6** (and, therefore, of the symmetrical diene **4**) is helpful in yet another way. The correlation, **7** → **6**, provides an estimate of δB_{ac} which can directly be carried over to the correlation, **8** → **5**.

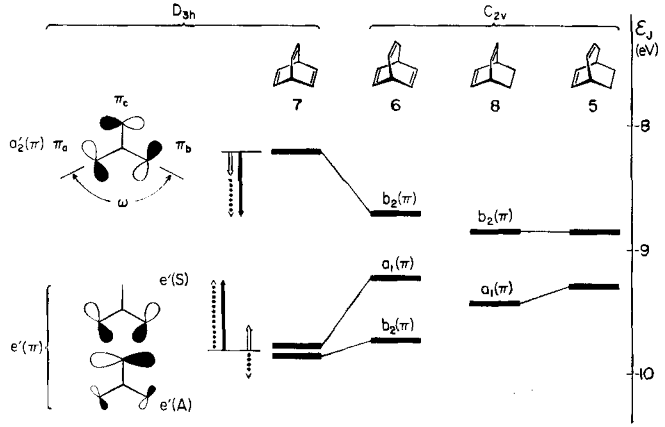


Fig. 5. *Correlation of bicyclo[2.2.2]octyl and bicyclo[3.2.2]nonyl trienes and dienes.* The orbitals representations are those of **7**. See text.

In detail, equation (5) requires that the near cancellation of effects, (a) and (b) operating on **e'**(A), be interpreted as $2(2/\sqrt{6})(1/\sqrt{6})\ \delta B_{ac} \approx (1/\sqrt{6})(1/\sqrt{6})\ \delta B_{ab}$ or $\delta B_{ac} \approx (1/4)\ \delta B_{ab}$. δB_{ab} is then evaluated as *ca.* 0.4 eV whereupon $\delta B_{ac} \approx 0.1$ eV. This small increment is consistent with the rather minor decrease in the $\mathbf{b}_2(\pi) - \mathbf{a}_1(\pi)$ gap upon homologating bicyclo[2.2.2]octadiene to the unsymmetrical bicyclo[3.2.2]nonadiene **5**. An inversion of levels is unequivocally excluded.

We conclude that **5** retains the 'natural order' of the π-orbitals, insofar as the in-phase linear combination $\pi_a + \pi_c$, corresponding to $\mathbf{a}_1(\pi)$ in the dienes $I(n)$, lies below the out-of-phase linear combination $\pi_a - \pi_c$, which corresponds to $\mathbf{b}_2(\pi)$ in $I(n)$. The isomeric symmetrical diene **4** is thus the first homologue which permits 'through bond' interaction to invert this order.

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Experimental – PE.-spectra were recorded on a modified *Perkin-Elmer Ltd:* PS-16 spectrometer which corresponds essentially to one described by *Turner* [10]: an open He discharge lamp (584 Å, 21.21 eV), electrostatic analyzer (radius 10 cm, sector angle $\pi/\sqrt{2}$, resolution 0.02 eV at 5.46 eV photoelectron kinetic energy). Spectra were calibrated relative to the signals of an Ar/Xe mixture, used as an internal standard.

All hydrocarbons were purified by gas chromatography through a 450 × 0.95 cm column packed with FFAP on 60/80 A/W DMCS Chromasorb G (*Varian Aerograph* Co.) using a He flow rate of 200 ml/min. Melting points were obtained in sealed capillaries and are uncorrected. Elemental analyses were performed by *Galbraith Laboratories*, Inc., Knoxville, Tennessee 37921, U.S.A.

Bicyclo[3.2.2]non-2-ene (**3**), *bicyclo[3.2.2]nona-2,6-diene* (**5**), and *bicyclo[3.2.2]nona-2,6,8-triene* (**6**) were prepared by methods to be described elsewhere [11]. Their IR. and PMR. spectra were wholly consistent with the assigned structures. The results of elemental analysis agreed with expectation to within ±0.3%.

Bicyclo[3.2.2]nona-6,8-diene (**4**). The maleic anhydride adduct of cyclohepta-1,3-diene [12] could only partly be hydrolyzed by conventional aqueous treatment. As a result, 4.00 g of the acid, contaminated with *ca.* 26% anhydride (*via* IR. analysis), was heated at 60–65° with 12.5 g 96% lead tetraacetate (27.1 mmol) in 70 ml dry pyridine under nitrogen for 8–10 min whereupon further gas evolution ceased. The cooled contents were then diluted with 125 ml pentane, treated with 135 ml 8 M nitric acid, and the pentane extracts successively washed with 4 M nitric acid, water, and aqueous sodium bicarbonate. After drying over magnesium sulfate, the pentane solution was concentrated to *ca.* 5 ml by distillation through a 1 × 30 cm glass helix-packed column and the product was collected by gas chromatography at 150°; 464 mg (20%); m.p. 84° (lit. [13] 84°); PMR. (CCl_4) $\tau = 3.82$ (*d*×*t*, $J = 7.5$, 4.5 Hz, 3.99 ± 0.02), 7.15 (*qi*, $J = 3.5$ Hz, 1.97, ±0.01), 8.24 (*m*, 2.02 ± 0.01), and 8.69 (*m*, 4.01 ± 0.02) ppm.

C_9H_{12} Calc. C 89,94 H 10,06% Found C 89,88 H 9,92%

Bicyclo[3.2.2]non-6-ene (**2**). 6.3 g of the mixed acid-anhydride, described above, in 75 ml acetic acid was hydrogenated at 3 atm using 320 mg 10% Pd/C. The corresponding crude acid could be obtained in the conventional manner, free of anhydride (IR.) or olefinic contaminants (PMR.), m.p. 140° (dec.) (ref. [12] 147°). 3.00 g (14.2 mmol) of this material were subsequently treated with 9.37 g (20.3 mmol) of 96% lead tetraacetate and the product isolated, in the same manner as was described for **4** above, to provide 930 mg (54%); m.p. 118° (ref. [14] 118°); PMR. (CCl_4) $\tau = 3.90$ (*d*×*t*; $J = 8.0$, 6.0; 1.98 ± 0.05), 7.62 (broad *m*; 2.02 ± 0.03), 8.30 and 8.47 (*d*, $J = 2.0$ Hz, and *m*; 9.99 ± 0.02) ppm.

C_9H_{14} Calc. C 88,45 H 11,55% Found C 88,25 H 11,74%

Bicyclo[3.2.2]nonane (**1**). 0.304 g (2.58 mmol) of **6** in 15 ml methanol consumed 3.04 molar equivalents of hydrogen at atmospheric pressure using 56 mg pre-reduced PtO_2. Partitioning between pentane and water was followed by drying of the pentane, concentration and gas chromatographic isolation of the product, as described for **4**, to provide 261 mg (81%); m.p. 161° (ref. [15] 159°, [16] 161°, [14] 162°); PMR. (CCl_4) reveals two broad overlapping bands centered at $\tau = 8.12$ and 8.39 in the approximate ratio 2:14.

C_9H_{16} Calc. C 87,02 H 12,98% Found C 86,72 H 13,08%

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