Photoelectron Spectrum of 5-Methylenenorborn-2-ene and Through-space Interactions (Homobutadiene Conjugation)

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Summary The photoelectron spectra of 5-methylenenorborn-2-ene (I), 2-methylenenorbornane (III), and norbornene show that the π-orbitals in the diene (I) interact strongly but the interaction leads to little or no stabilization of the π-system; simple HMO arguments and consideration of the photoelectron spectrum of norbornadiene (II) suggest that the interaction is mostly π-bonding through-space.

Recently, there has been considerable theoretical interest in through-space and through-bond interactions of formally isolated functional groups.[1] Photoelectron spectroscopy provides an excellent means of examining these interactions and a number of compounds have been investigated in this way.[1,2]

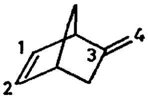
We have measured the photoelectron spectrum of 5-methylenenorborn-2-ene (I), which has two double bonds in a 'homobutadiene' system, and compared the observed π-orbital interaction with that reported for norbornadiene (II), which has two double bonds in a 'homocyclobutadiene' arrangement. The vertical ionization potentials of the π-orbitals in compound (I) and in 2-methylenenorbornane (III) were obtained from their photoelectron spectra by using the 21·21 eV helium line, and are given in the Table.

Vertical ionization potentials (eV)

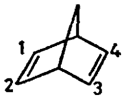
Compound	π-Orbital energy
(I)	8·93, 9·31
(II)	8·69, 9·55[3]
(III)	9·02

The through-space interaction between carbon atoms 1, 2, 3, and 4 in the diene (II) can be described by a modified Hückel molecular orbital treatment with $<\phi_m|\mathrm{H}|\phi_m>$ (m = 1, 2, 3, or 4) $= \alpha$, $<\phi_1|\mathrm{H}|\phi_2> = <\phi_3|\mathrm{H}|\phi_4> = \beta$, $<\phi_1|\mathrm{H}|\phi_4> = <\phi_2|\mathrm{H}|\phi_3> = \mathrm{k}\beta$, and all other $<\phi_m|\mathrm{H}|\phi_n> = 0$. Evaluation of the secular determinant yields occupied π-orbital energies, $\alpha + (1 \pm \mathrm{k})\beta$, and there is therefore a predicted splitting of the π-orbital levels of $2\mathrm{k}\beta$ in norbornadiene. This may be compared with the 'bond treatment' used by Heilbronner.[3,4] The observed splitting of the π-levels in norbornadiene is 0·86 eV and so $2\mathrm{k}\beta = 0{\cdot}86$ eV. Similarly, for the methylenenorbornene (I) [$<\phi_m|\mathrm{H}|\phi_m> = \alpha$, $<\phi_1|\mathrm{H}|\phi_2> = <\phi_3|\mathrm{H}|\phi_4> = \beta$, $<\phi_2|\mathrm{H}|\phi_3> = \mathrm{k}\beta$, and all other $<\phi_m|\mathrm{H}|\phi_n> = 0$] the secular determinant gives two occupied π-levels at $\alpha + \beta\{(2 + \mathrm{k}^2) \pm (4\mathrm{k}^2 + \mathrm{k}^4)^{\frac{1}{2}}\}^{\frac{1}{2}}/2^{\frac{1}{2}}$. Insertion of the value of 0·86 eV for $2\mathrm{k}\beta$ into these levels predicts a splitting of the π-levels in 5-methylenenorborn-2-ene (I) of 0·43 eV (*i.e.* $\mathrm{k}\beta$ as expected), which may be compared with the observed value of 0·38 ± 0·05 eV (Table). Thus, the through-space π-interaction in the diene (I) is adequately predicted from parameters obtained from the diene (II). The interaction leads to one π-orbital moving to higher energy and one to lower energy. If these movements of the π-orbitals are equal and opposite there is no net stabilization of the π-system by homoconjugation.

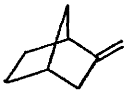
Heilbronner has estimated a stabilization energy, δA, for norbornadiene from the equation, $\delta A = I_1 - (I_2 + I_3)/2 = -0{\cdot}15$ eV, where I_1 is the ionization potential of the π-orbital in norbornene (8·97 eV) and I_2 and I_3 those of the π-orbitals in norbornadiene (Table). We define a similar stabilization, $\delta A'$, for 5-methylenenorborn-2-ene (I) by the equation, $\delta A' = (I_1 + I_4)/2 - (I_2 + I_3)/2 = -0{\cdot}13$ eV, where I_1 is the ionization potential of the π-orbital in norbornene, I_4 that in 2-methylenebornane (III), and I_2 and I_3 those in the diene (I) (Table). The net stabilization is approximately the same for both the dienes (I) and (II) and is close to zero. The change in delocalisation energy (δE) between butadiene and the homoconjugated butadiene (I) may be estimated by application of the equation, $\delta E = 2p_{23}\delta\beta_{23} + \pi_{23,23}\delta\beta^2{}_{23}$ where p_{23} is the bond order, $\pi_{23,23}$ the bond polarisability, and $\delta\beta_{23}$ the change in the resonance integral between atoms 2 and 3.[5] With $\mathrm{k}\beta = 0{\cdot}43$ eV and assuming $\beta \simeq 2{\cdot}5$ eV, the change in delocalisation energy, δE, is approximately $-0{\cdot}5\beta$. As the predicted delocalisation energy for butadiene is about $+0{\cdot}5\beta$ greater than that of two isolated double bonds, the predicted net π-stabilization of the homobutadiene (I) is about zero, in agreement with the photoelectron spectrum.



(I)



(II)



(III)

We conclude from these experiments that π-orbital through-space interaction (homobutadiene conjugation) in 5-methylenenorborn-2-ene will change the reactivities of the double bonds as compared with the fully isolated ones, but will lead to little change in the total stability of the π-system.

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[2] For some examples, see E. Haselbach, E. Heilbronner, and G. Schröder, *Helv. Chim. Acta*, 1971, **54**, 153; D. Chadwick, D. C. Frost, and L. Weiler, *J. Amer. Chem. Soc.*, 1971, **93**, 4962; P. Bruckmann and M. Klessinger, *Angew. Chem. Internat. Edn.*, 1972, **11**, 524.

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[4] P. Bischof, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Tetrahedron Letters*, 1970, 1033; P. Bischof, R. Gleiter, and E. Heilbronner, *Helv. Chim. Acta*, 1970, **53**, 1425.

[5] C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.* (*A*), 1948, **193**, 447.