[3]-, [4]-, and [5]-Pericyclyne: Through-bond *vs.* Through-space Interactions

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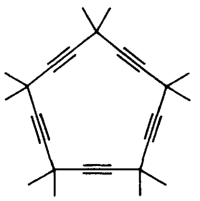
MNDO calculations for [3]-, [4]-, and [5]-pericyclyne indicate that interactions between triple bonds are hyperconjugative in the π system and homoconjugative in the σ system and that [3]pericyclyne may be interconverted with a valence tautomer, tricyclopropabenzene.

Recently, Scott *et al.* reported[1] the synthesis and photoelectron spectrum of decamethyl[5]pericyclyne (**1**), the permethylated derivative of (**2**). A number of low energy ionizations were observed, implying interactions between the π MOs of the acetylene groups. These interactions were assumed to be of the homoconjugative (through-space) type and similar homoconjugation was suggested for the lower pericyclynes, (**3**) and (**4**), which have yet to be synthesized.

We have performed MNDO[2] RHF calculations on (**2**), (**3**), and (**4**) at D_{5h}, D_{4h}, and D_{3h} geometries, respectively. These were shown to be minima by calculating force constants.[3] Their calculated heats of formation and geometries are shown



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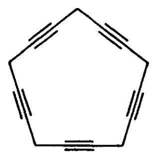

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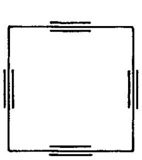

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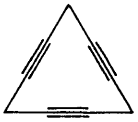

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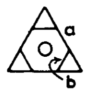
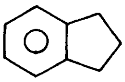


(5)

(6)

(7)



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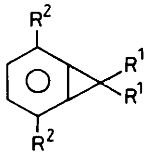

(9a) $R^1 = Cl, R^2 = Ph$
(9b) $R^1 = CO_2Me, R^2 = Ph$

Table 1. MNDO RHF heats of formation (kcal/mol) and geometries of (**2**), (**3**), and (**4**) (bond lengths in Å, angles in degrees).

Compound	ΔH_f	C≡C	C–C	C–H	C–C–C	C–C≡C	H–C–C	H–C–C≡C
(**2**)	204.6	1.198	1.456	1.12	108.0	180.0	110.5	±121
(**3**)	173.1	1.200	1.458	1.12	106.7	171.6	110.9	±121
(**4**)	165.9	1.210	1.468	1.11	100.0	160.0	119.2	±119

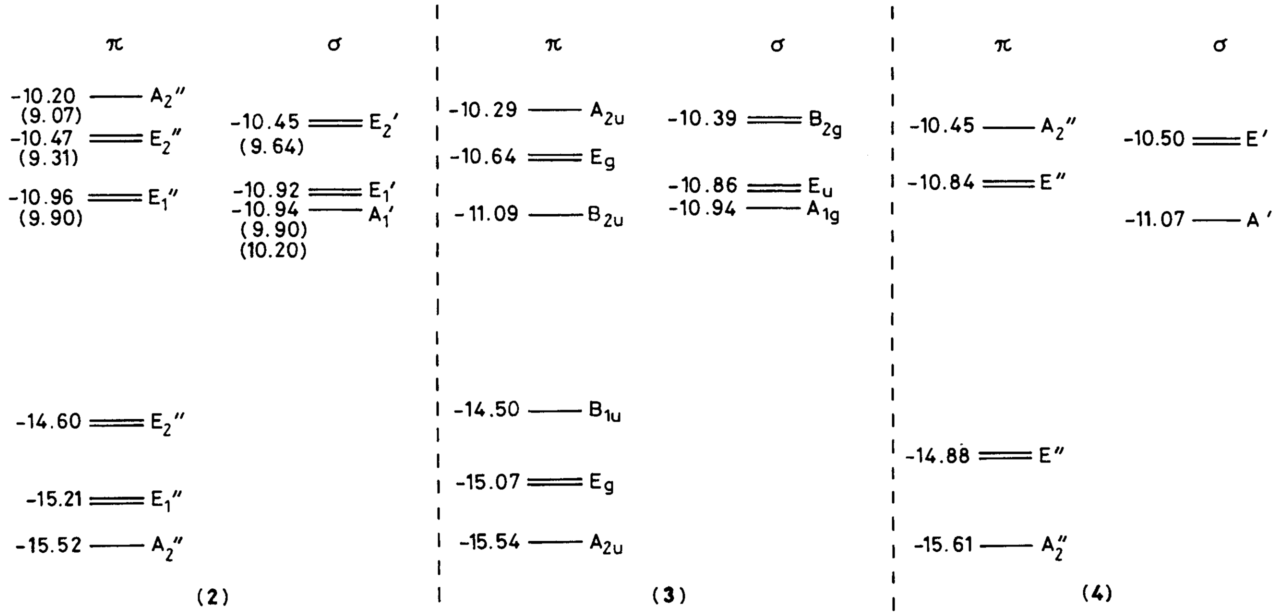

Figure 1. Calculated π orbitals (eV) for (**2**), (**3**) and (**4**). The upper half contains the acetylenic π and σ type orbitals while the lower half contains the methylenic π type orbitals.

in Table 1; the π-orbital energies and symmetries in each are depicted in Figure 1.

Since the internal angles of a five-membered ring are a relatively unstrained 108°, the acetylene units in (**2**) are, not unexpectedly, calculated to be linear. However, (**3**) and (**4**) have C–C≡C bond angles of 172 and 160°, respectively, thereby relieving the angle strain at the methylene groups.

The ten highest occupied MOs of (**2**) are acetylenic π MOs, five being of π type and five of σ type, with two degenerate pairs of MOs in each set. Their energies (see the upper half of Figure 1) correspond quite well to the ionization potentials (I.P.s) reported for (**1**) (9.07, 9.31, 9.64, 9.90, and 10.20 eV) apart from being greater by *ca.* 1 eV.† This difference can be attributed to the inductive field effects of the methyl groups which should uniformly raise the energies of all the π MOs. The assignments of the observed I.P.s for (**1**) are indicated in parentheses in Figure 1.

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† MNDO is expected to underestimate long-range through-space interactions owing to the use of Slater AOs to calculate overlap integrals and hence resonance integrals. Thus, while the splittings of the π-type MOs in (**2**) are likely to be reproduced reasonably well, those of the σ-type MOs are probably underestimated.

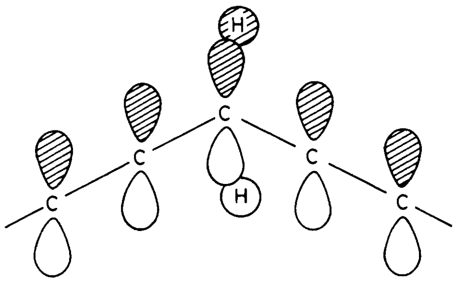

Figure 2. A depiction of the contribution of CH bond MOs to the π system of a pericyclyne.

If the interactions between the acetylenic π MOs were of the homoconjugative (through-space) type, their order in increasing energy would be $A < E_1 < E_2$. As Figure 1 shows, the order of MOs in the σ set conforms to this. However, the order of the π MOs is exactly the opposite. Here, the acetylenic MOs must interact in some other way.

Hoffmann *et al.*[4] have pointed out that inversion of the order of the MOs can occur in analogous situations if the coupling between π units is by a hyperconjugative (through-bond) interaction involving a single intervening carbon atom. In the case of (**2**), each methylene group will contribute a single orbital to the π system, this being an antisymmetric combination (ψ_{1-5}) of CH bond MOs, as depicted in Figure 2. The occupied π MOs are then derived from these five orbitals and five acetylenic π MOs (ϕ_{1-5}). The resulting set of cyclic π MOs follows the same pattern as the π MOs in an analogous polymethine, with A-type MOs at the top and bottom and degenerate E-type MOs in between. Since the CH orbitals (ψ) are lower in energy than the acetylenic orbitals (ϕ), the lower five MOs are composed mainly of CH orbitals and the upper five of acetylenic ones. The inversion in the order of the low-energy π MOs in (**2**) is thus seen to be due to the fact that they represent the upper five MOs of a ten-orbital set rather than a single five-orbital set.

As there are no σ MOs that can interact effectively with the five σ type acetylene MOs, they appear in a 'normal' order, with the interactions between them being strictly of the through-space type.

The order of the π MOs in (**3**) and (**4**) is again inverted, implying that the through-bond interactions still dominate. The difference in energy between CH orbitals and acetylenic π MOs in (**3**) leads to the removal of the degeneracy of the fourth and fifth MOs. The pattern of the four higher MOs consequently seems deceptively normal. The order is, however, inverted: the MO in which all the acetylenic orbitals have similar signs is the highest in energy instead of the lowest.

The coupling between acetylene units in the σ-type MOs of (**3**) and (**4**) is again of the through-space type, as in (**2**).

A geometry for (**4**) with linear acetylene units and internal angles of 60° was also found to be a minimum on the MNDO RHF potential surface, corresponding to tricyclopropabenzene‡ (**5**), a valence tautomer of (**4**) which has also yet to be synthesized. The geometry and heat of formation of (**5**) are shown in Figure 3(a). Since the formerly acetylenic bonds (a) are still much shorter than the shared ring bonds (b) this structure could be considered as a bond-localized benzene ring in which Kekulé structure (**6**) is favoured over (**7**). The idea of bond localization in small-ring fused benzenes was first proposed by Mills and Nixon[5] for benzocyclopentene (**8**). Although *X*-ray studies[6] of benzocyclopropene derivatives (**9**) showed no evidence for bond fixation beyond a shortening of the bond common to both rings, the effect of three small-ring fusions could be much greater.

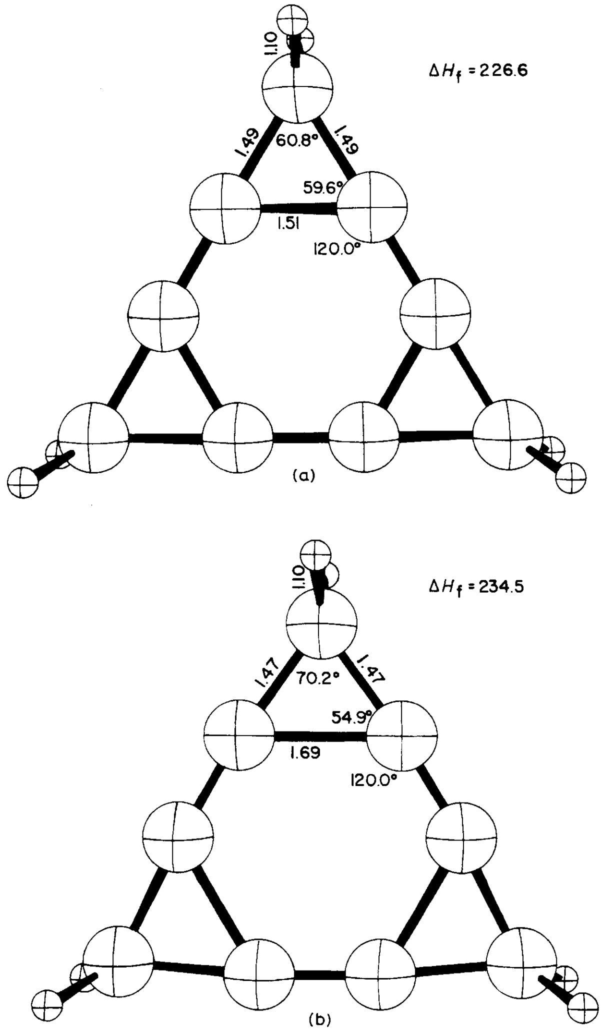

Figure 3. Calculated geometries (bond lengths in Å and angles in degrees) and heats of formation (kcal/mol)¶ for (a) (**5**) and (b) the transition state for interconversion of (**4**) and (**5**).

Since (**5**) might be formed from (**4**) *via* an allowed $[_{\pi}2_s + {}_{\pi}2_s + {}_{\pi}2_s]$ cycloaddition process,[7] we were interested in examining this portion of the C_9H_6 potential surface, particularly as a synchronous concerted reaction path seemed likely. This was found to be the case: the highly symmetrical transition state§ geometry and its heat of formation are shown in Figure 3(b). The calculated activation barrier for conversion of (**4**) into (**5**) is 68.6 kcal/mol,¶ while that for the opposite reaction is 7.9 kcal/mol. The transition state geometry is very like (**5**), as might be expected based on the Hammond postulate.[8]

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‡ Tetracyclo[6.1.0.0^{2,4}.0^{5,7}]nona-1,4,7-triene.

§ The transition state was shown to have one, and only one, negative eigenvalue by calculating force constants (ref. 3).

¶ 1 kcal = 4.184 kJ.

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