Geometry and Electronic Structure of the Transition State for the Cope Rearrangement of *endo*-Tricyclo[5,2,1,$0^{2,6}$]deca-4,8-diene

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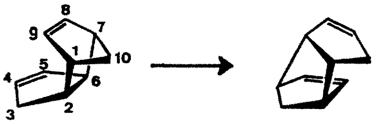
Summary Calculations by the CNDO/2 method favour a six-centre transition state for the Cope rearrangement of the title compound.

IN recent years, the mechanism of the Cope rearrangement of compounds containing the nucleus of *endo*-tricyclo-[5,2,1,$0^{2,6}$]deca-4,8-diene (cyclopentadiene dimer) has been investigated.[1,2] The relative ease by which these compounds undergo the rearrangement has been explained in terms of a favourable pre-orientation of the two allylic groups[3] and of a relief of steric strain in the transition state.[1] For a better understanding of the reaction (I) → (II) the geometry and the electronic structure of the corresponding transition state have been calculated by the CNDO/2 method.[4]



(I) (II)

Since the reaction is concerted and symmetrical, it seemed reasonable to assume a transition state at half-way along the reaction path, and with C_2 symmetry (the C_2 axis is the y axis in the Figure). To limit computing time, the number of variables has been reduced, assuming a rigid geometry for the cyclopentene fragment and a length of 1·54 Å for the C-1–C-2 bond. The relevant bond lengths and angles were deduced from X-ray results,[1] following criteria to be described in the full paper. Energy has been minimised with respect to the remaining degrees of freedom, *i.e.*, the variables θ, ϕ, and α shown in the Figure. A single minimum was found, for $\theta = 90·5°$, $\phi = 6·5°$, and $\alpha = 79°$.

For this geometry, the following interatomic distances were calculated: C-6–C-7 = C-4–C-9 = 1·61 Å; C-5–C-8 = 1·59 Å. Energy-partitioning[5] calculations have been performed in order to classify the different kinds of CC bonds. Results are shown in the Table.

The resonance energy terms, which correlate well with the bond strength,[5] indicate the presence of a bonding interaction between atoms C-5 and C-8, although it is weaker than that between the end positions of the two allylic systems. The significance of the C-5–C-8 interaction is clear when the corresponding value of E^{R}_{CC} is compared with those for non-bonded atom pairs (see C-5–C-7 in the Table). Such partial bonding, although allowed by orbital symmetry rules,[6] is not predicted by qualitative quantum mechanical arguments.[7]

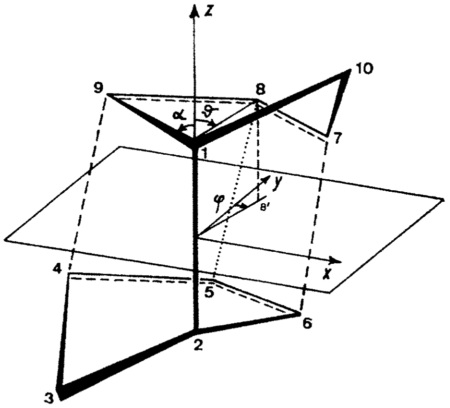


FIGURE. *Model of transition state, showing angles* θ, ϕ, *and* α, *used as variables for the computations. Point* 8' *is the projection, of atom* C-8 *on the* xy *plane.*

Resonance energy terms (E^{R}_{CC}) *for* CC *interactions*

	Length (Å)	$-E^{R}_{CC}$ (a.u.)
C-7–C-8, C-4–C-5	1·40	1·146
C-8–C-9, C-5–C-6	1·43	1·101
C-7–C-10, C-3–C-4	1·52	1·060
C-1–C-2	1·54	1·001
C-1–C-10, C-2–C-3	1·55	1·014
C-1–C-9, C-2–C-6	1·555	1·022
C-5–C-8	1·59	0·780
C-6–C-7, C-4–C-9	1·61	0·886
C-5–C-7, C-4–C-8	2·11	0·102

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