Diazabullvalene; a "Nonclassical" Molecule?

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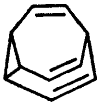
Summary MINDO/2 calculations for 3,7-diazasemibullvalene (3,7-diazatricyclo[3,3,$0^{2,8}$]octa-3,6-diene) indicate that it should exist as a "nonclassical" bishomopyrazine, the classical structure being unstable.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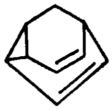
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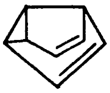
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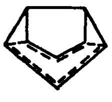
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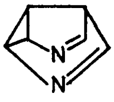
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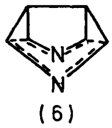
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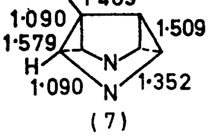

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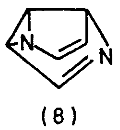

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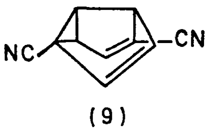

(9)

THE MINDO/2 semiempirical SCF MO all-valence-electron approximation[1] has been applied successfully to the study of several Cope rearrangements. It accounts for the fact[2] that hexa-1,5-diene rearranges *via* a "chair" transition state in preference to a "boat" conformer and correctly predicted the difference in energy between them, it correctly predicted[3] the difference in energy of chair transition states for the rearrangement of hepta-1,5-diene with the methyl group in axial and equatorial positions, and it correctly accounted[4] for the low activation energies for rearrangement in bullvalene (**1**), barbaralane (**2**), and semibullvalene (**3**) and for the progressive decrease in activation energy along the series (**1**, calc. 11·3, obs. 11·5,[5] 12·8[6] kcal mol^{-1}; **2**, calc. 6·5, obs [7] 8·2 kcal mol^{-1}; **3**, 2·3 kcal mol^{-1}). In the case of

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(**3**), the rearrangement is fast[8] on the n.m.r. time scale of the lowest attainable temperatures; indeed it was even suggested[8] that here the intermediate structure (**4**), which would normally be the transition state for rearrangement of (**3**), might be the stable form of the system, this existing as a bishomobenzene. While the available evidence[8] and our calculations[4] indicate that this is not the case, it is clear that the difference in energy between (**3**) and (**4**) is so small that it might be reversed by suitable substituents *etc.*

An analysis[9] of our MINDO/2 wave functions by the method of energy partitioning[10] indicated that the low activation energy for (**1**) is due, as might have been expected, to relief of strain on passing to the transition state. This analysis indicated, however, that the further increase in rate along the series (**1**) $<$ (**2**) $<$ (**3**) is *not* due to the undoubted increase in ring strain along the series but to contributions by one-centre terms. On passing to the transition state, there is a transfer of negative charge from the rest of the molecule into the delocalized "aromatic" ring arising from the biallyl system in the reactant. This implies that an increase in electrophilicity of the biallyl moiety should favour conversion of the reactant into the transition state.

We therefore studied the diazasemibullvalene (**5**) by MINDO/2, minimizing its energy, and that of the corresponding bishomopyrazine (**6**), by our iterative SIMPLEX procedure.[3] The calculations for (**6**) proceeded normally, leading to the predicted structure shown in (**7**). When, however, we tried to calculate the geometry of (**5**), the bond lengths and angles changed progressively with each iteration until they, and the total energy, were virtually identical with those calculated for (**6**). Therefore according to the MINDO/2 method, this should prove the first example of a Cope-like system whose ground state has a "nonclassical" bishomoaromatic structure, the "classical" isomer (**5**) not ever being a stable species but rearranging to (**6**) without activation.

Since changes in electronegativity at the terminal allylic carbon atoms in (**6**) are predicted[10] to have a greater effect than at the central one, our calculations imply *a fortiori* that (**8**) should also be "nonclassical". One would also expect the same to be true for (**9**) where the nonclassical structure should be favoured further by conjugation between the CN groups and the aromatic ring in the transition state. Calculations for these are in progress and also for analogous derivatives of barbaralane in case such changes in structure are enough to favour the nonclassical structure there also.

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