ORBITAL INTERACTIONS IN MOLECULES CONTAINING UNSATURATIVELY

BRIDGED CYCLOBUTANE AND BICYCLOBUTANE RINGS

William L. Jorgensen

Department of Chemistry, Harvard University, Cambridge, Mass.   02138

and

Weston Thatcher Borden

Department of Chemistry, University of Washington, Seattle, Wash.   98195
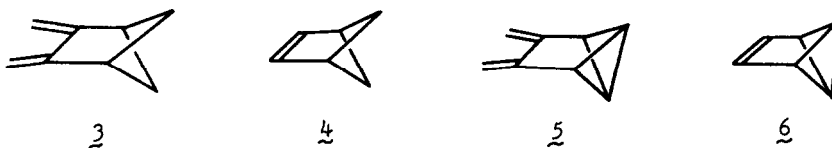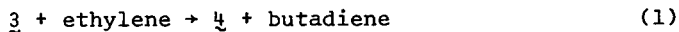
Hogeveen has found the Diels-Alder reactivities of 1 and 2 to be surprisingly different, considering the apparent structural similarity of these two molecules.[1] The former, like another molecule containing a butadiene bridged cyclobutane ring that has previously been studied,[2] reacts only sluggishly with TCNE, the reaction requiring 20 hr at 55° for completion.[1a] In contrast, the reaction of 2 with TCNE is complete at room temperature in less than a minute.[1b]

1   2
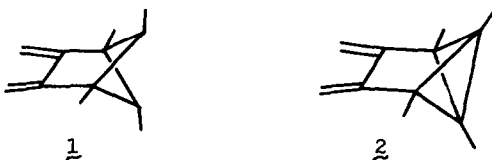
We have previously[3] rationalized the lack of Diels-Alder reactivity of molecules that, like 1, contain a butadiene bridged cyclobutane ring, in terms of the interactions of the orbitals of the ring with those of the unsaturated bridge in reactant and product. Specifically, the net π interactions between the orbitals of the ring and the bridge are found to be stabilizing in

$\underset{\sim}{3}$ and destabilizing in $\underset{\sim}{4}$. The π bond order between ring and bridge is calcula-

ted to be 0.078 in $\underset{\sim}{3}$ and -0.007 in $\underset{\sim}{4}$.[3] Thus, in molecules like $\underset{\sim}{1}$ and $\underset{\sim}{3}$ the

Diels-Alder reaction, which replaces the butadiene bridge by ethylene, is

energetically impeded by the exchange of net stabilizing for net destabilizing

orbital interactions between the ring and bridge. This is revealed by the

large endothermic heat of reaction (+17 kcal/mol) calculated[3] for the iso-

desmic[4] process

$$\underset{\sim}{3} + \text{ethylene} \rightarrow \underset{\sim}{4} + \text{butadiene} \qquad\qquad (1)$$

$$\underset{\sim}{3} \qquad\qquad \underset{\sim}{4} \qquad\qquad \underset{\sim}{5} \qquad\qquad \underset{\sim}{6}$$

The net π antibonding between bridge and ring in $\underset{\sim}{4}$ can be traced to the

interaction between the filled π orbital and the high-lying filled cyclo-

butane orbital of the same symmetry.[3] In the D_{2d} symmetry of a puckered

cyclobutane ring, the highest occupied orbitals, in order of increasing energy,

may be labelled a_2, e_s, and e_a.[3,5] The e_a orbital does not have the proper

symmetry to interact with the π orbitals of an unsaturated bridge across atoms

1 and 3 of the ring. The four-electron destabilizing interaction (overlap

repulsion)[3] between e_s and the filled π orbital of the bridge in $\underset{\sim}{4}$ dominates

the stabilizing mixing between a_2 and the empty π^* bridge orbital.[3] It is

important to note that there are in $\underset{\sim}{4}$ no low-lying unfilled orbitals of the same

symmetry as e_s and π to mitigate the overlap repulsion between these two filled

orbitals. Butadiene, however, is a more accommodating bridging group than

ethylene;[3,6] since it not only has an empty orbital that can mix with the filled

a_2 orbital of the ring, but also its lowest unoccupied MO (LUMO) can mix with

e_s, the highest occupied MO (HOMO) of the ring.
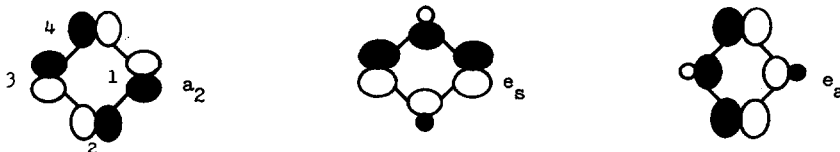
If the much higher Diels-Alder reactivity of $\underset{\sim}{2}$ compared to $\underset{\sim}{1}$ is due to a disparity between bicyclobutane and cyclobutane in the orbital interactions each undergoes with unsaturated bridges, then the difference between the calculated ring-bridge π bond orders in $\underset{\sim}{5}$ and $\underset{\sim}{6}$ should be considerably smaller than the difference of 0.085 between those in $\underset{\sim}{3}$ and $\underset{\sim}{4}$. In addition, the reaction

$$\underset{\sim}{5} + \text{ethylene} \rightarrow \underset{\sim}{6} + \text{butadiene} \qquad\qquad (2)$$
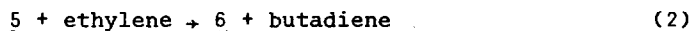
should be computed to be much less endothermic than that in eq. 1. In fact, Extended Hückel calculations[7] find the π bond order between ring and bridge to be 0.121 in $\underset{\sim}{5}$ and 0.093 in $\underset{\sim}{6}$, which differ by only a third as much as those in $\underset{\sim}{3}$ and $\underset{\sim}{4}$. Moreover, the heat of the reaction in eq. 2 is computed to be +8 kcal/mol, less than half the value found for the reaction in eq. 1. Indeed, the difference in π bond order between $\underset{\sim}{5}$ and $\underset{\sim}{6}$ and the heat of the reaction in eq. 2 are very similar to the corresponding quantities calculated for unsaturatively bridged cyclopentane.[3] Since 2,3-dimethylenenorbornane undergoes a Diels-Alder reaction with maleic anhydride,[8] the Diels-Alder reactivity of $\underset{\sim}{2}$[1b] is not surprising.

The results of these calculations indicate that the difference in the Diels-Alder reactivity of $\underset{\sim}{1}$ and $\underset{\sim}{2}$ can be traced to differences in the orbital interactions that the two types of four-membered rings in these molecules undergo with unsaturated bridges. In particular, the difference in the ring-bridge π bond order between $\underset{\sim}{4}$ (-0.007) and $\underset{\sim}{6}$ (0.093) is striking. The significantly stabilizing interactions in $\underset{\sim}{6}$ may be analyzed in a fashion similar to that used to explain the net destabilizing interactions in $\underset{\sim}{4}$. The three highest filled orbitals of bicyclobutane are, in order of increasing energy, b_2, a_2, and a_1.[9] The HOMO is prohibited by symmetry from interacting with the π orbitals of an unsaturated bridge. The a_2 and b_2 orbitals of bicyclobutane are very similar to a_2 and e_s of cyclobutane; however, their ordering is reversed. The smaller energy separation between a_2 of the ring and π^* of the bridge in $\underset{\sim}{6}$ than in $\underset{\sim}{4}$ permits their interaction to be significantly more stabilizing in the molecule containing the bicyclobutane ring. In addition to the reversal of the orbital ordering from that in cyclobutane, bicyclobutane has a particularly low-lying unoccupied orbital, b_2^*,[9] that can mix with the filled π orbital

of the bridge in $\underline{6}$. The interaction of $b_2{}^*$ with π mitigates the overlap repulsion between the π and b_2 orbitals, in the same way that the unoccupied orbitals of the butadiene bridge in $\underline{3}$ and in $\underline{5}$ alleviate the repulsions that arise from overlap between filled orbitals of the same symmetry in these molecules.

The calculations and qualitative arguments presented here rationalize the apparent anomaly in the Diels-Alder reactivities of $\underline{1}$ and $\underline{2}$ and provide further evidence of the importance of orbital interactions in the chemistry of unsaturatively bridged small rings.[3,6]

Acknowledgment

References

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