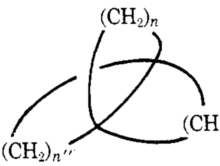
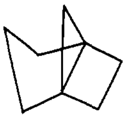
Electronic Structure of [2.2.2]Propellane

Sir:

The [*n*.*n*′.*n*′′]propellanes[1] of general structure I are a



I



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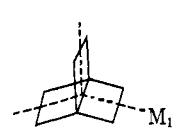

III

family of tricyclics whose three rings are fused to a common carbon–carbon bond and which therefore exhibit a number of new bonding possibilities. For example, tricyclo[3.2.1.0^{1,5}]octane or [3.2.1]propellane (II) is thermally unreactive, although it may well have its four bridgehead carbon–carbon bonds within a hemisphere.[2] In a recent theoretical study we have shown[3] that (hypothetical) tricyclo[1.1.1.0^{1,3}]pentane or [1.1.1]propellane would contain bridgehead carbons separated by only 1.60 Å, although by all traditional electronic criteria for bonding these atoms should be considered slightly antibonding. The closely related system, [1.1.0]bicyclobutane, has been shown[4,5] to contain a central carbon–carbon bond formed from almost pure p hybrids (sp^{24}). It was, in fact, this latter result which led us to anticipate[4] a similar bonding scheme in [2.2.2]propellane (III), a system which has now been studied and is reported on here.

That [2.2.2]propellane is an important molecule in its own right follows from the fact that the bridgehead carbon atoms, when separated by a normal CC single bond distance, would be characterized by nominal trigonal-pyramidal geometry, thus providing possible models for the geometries attending SN1 transition states. If, in addition, one of the external lobes behind the central bond in III were capable of supporting a fifth ligand (*e.g.*, a Lewis acid), the resulting pentavalent carbon might be a viable model for the SN2 transition state. A final point of interest is the suggestion by Stohrer and Hoffmann[6] that [2.2.2]propellane should exhibit, by dint of interplay between through-bond coupling and direct bridgehead interactions, a double-well potential along the C_1–C_4 or *R* coordinate. The present study[7] validates this conjecture and estimates both the positions of the minima and the position and height of the intervening barrier.

Assumption of a D_{3h} framework,[8] with CC side-bond lengths and HCH angles taken from cyclobutane[9] and bicyclooctane,[10] led to a minimum SCF energy for a C_1–C_4 separation of 1.52 Å. At this geometry, the highest occupied SCF orbital is symmetric (hereafter denoted ϕ_S) with respect to the mirror plane M_1 (III). Thus to a good approximation, III is the formal fusion of three planar[8] cyclobutane rings, which in turn suggests a total strain energy of $3(25 \pm {\sim}4) = 87$ kcal/mol (25 kcal is the cyclobutane strain energy, and the distortion effect attending fusion is estimated to contribute ~4 kcal per ring). Alternatively, from the calculated ΔH of the hypothetical reaction, III + 2 ethanes = 3 cyclobutanes, and the known heats of formation of ethane and cyclobutane, we estimate a strain energy of 90 kcal/mol (at 298 °K).

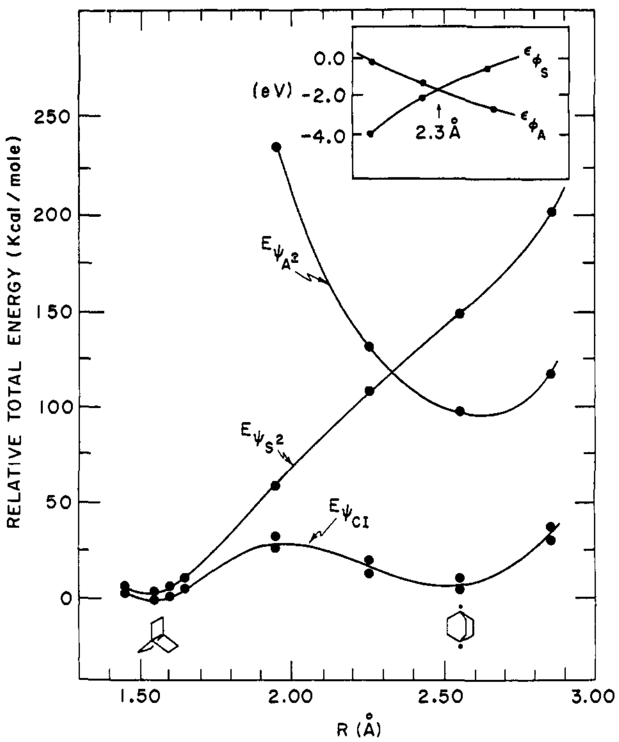

Figure 1. Total SCF energies ($E_{\psi_{S2}}$ and $E_{\psi_{A2}}$) and CI energies ($E_{\psi_{CI}}$) are plotted as a function of the central CC bond length (*R*) of III, with other bond lengths frozen. Energies on the ordinate are given in kilocalories per mole relative to the minimum CI energy.

Near its inner equilibrium *R* value, III, unlike [1.1.1]propellane, has a relatively strong central bond whose overlap population (0.64 e) is comparable with those in the C_1–C_2 (0.68 e) and C_2–C_3 (0.70 e) side bonds. The relatively high p character in the bridgehead hybrids forming the central bond can be seen from the INDO[11] localized molecular orbitals, which give sp^9 (90% p character) hybrids for III [*cf.* the sp^{18} hybrids (95% p character) in bicyclobutane].

Further interest in III stems from its behavior upon stretching of the C_1–C_4 bond (maintaining D_{3h} symmetry and fixed side bond lengths). Figure 1 reveals that the energy of the SCF configuration (ψ_{S^2}) with ϕ_S doubly occupied rises monotonically beyond 1.52 Å and is crossed at ~2.30 Å by the energy of the SCF configuration (ψ_{A^2}) whose highest doubly filled MO is antisymmetric (ϕ_A) with respect to the mirror plane M_1 and whose energy has a minimum at ~2.60 Å. It is interesting to note that the ψ_{S^2} and ψ_{A^2} total SCF energies cross almost precisely at the point where the

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[7] Energies were calculated with *ab initio* SCF and CI wave functions, using the STO-3G minimal contracted-Gaussian basis of W. J. Hehre, R. J. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

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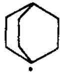
[11] J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).

corresponding one-electron energies of their highest filled orbitals intersect (inset, Figure 1).

Since ψ_{S^2} and ψ_{A^2} are both overall totally symmetric, the noncrossing rule dictates that they mix in a manner represented by the configuration interaction function $\bar{\psi} = c_{S^2}\psi_{S^2} + c_{A^2}\psi_{A^2}$. Denoting the bonding hybrids on carbons C_1 and C_4 by h_1 and h_4, respectively, we have $\phi_S = h_1^S + h_4^S + \ldots$ and $\phi_A = h_1^A - h_4^A + \ldots$, which are analogous to the g and u combinations of $1s_A$ and $1s_B$ in H_2. The dotted terms indicate the smaller contributions to ϕ_S and ϕ_A from other centers in the molecule. We recall that variations in the CI coefficients as a function of R serve to alter the relative amounts of covalent and ionic character. In the limiting case where hybrids in ϕ_S and ϕ_A are identical and their overlap is neglected, the ratio of covalent and ionic contributions is given explicitly by $(C_{S^2} - C_{A^2})/(C_{S^2} + C_{A^2})$, and we shall employ this quantity as a rough measure of bonding character in the discussion of actual cases which follows.

Ideally, one could simultaneously obtain the orbitals for ψ_{S^2} and ψ_{A^2}, as well as the coefficients C_{S^2} and C_{A^2}, in a unified self-consistent procedure (multiconfiguration SCF). We have, however, taken the following, simpler approach. For small values of R (≤ 1.648 Å) where the SCF energies are well separated, ψ_{S^2} is taken as the SCF solution, and ψ_{A^2} is constructed from the 58-electron core of ψ_{S^2} and its virtual ϕ_A. At larger R values (≥ 1.948 Å), where the ψ_{S^2} and ψ_{A^2} SCF energies become closer, we have carried out two alternative CI calculations: first with ψ_{S^2} (SCF) and ψ_{A^2} (virtual) and then with ψ_{A^2} (SCF) and ψ_{S^2} (virtual). The validity of this essentially two-electron approach is indicated by the fact that similar CI energies (constant to within $\pm\sim 3$ kcal; see Figure 1) and coefficients are obtained from either choice for ψ_{S^2} and ψ_{A^2}.[12]

Figure 1 plots the CI energy as a function of R and clearly shows the persistence of an inner (1.54 Å) and outer minimum (2.51 Å) of similar depth, with a separating barrier at $\sim$1.95 Å, whose height is $\sim$29 kcal/mol above the inner minimum. The inner well corresponds to the valence-bond structure III, in which there is 57:43 covalent to ionic bonding. The outer minimum at 2.54 Å corresponds to 97% covalent character and is best represented in valence bond terms as the diradical



i.e., analogous to the case of H_2 at large separation, we find that CI gives proper dissociation into two weakly interacting electrons, insofar as a two particle description is valid.

The sizable barrier between roughly symmetric wells of $\sim$29 kcal/mol suggests that III could be expected to have a lifetime of several hours at room temperature within the inner well.[13] Since our calculated barrier must be considered uncertain by at least a few kilocalories per mole, a precise estimate of the lifetime is not possible. At any rate, the barrier seems rather low for a process which is symmetry forbidden in the orbital sense,[6] thus demonstrating how useful quantitative calculations can be in complementing predictions based on orbital symmetry. The stability of the inner minimum species is important, since the interconversion of the outer minimum diradical to dimethylenecyclohexane symmetry is symmetry-allowed, and, though the barrier for this process is of unknown magnitude, most synthetic attempts at [2.2.2]-propellane do, in fact, give this latter Grob fragmentation product.[2]

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[12] CI calculations using orbitals from triplet SCF calculations yield a singlet CI energy curve roughly parallel to that in Figure 1 for $R \geq 1.9$ Å and a few kilocalories lower in energy. We feel, however, that at the level of approximation adopted, the singlet SCF orbitals provide the best overall basis for studying the bridgehead–bridgehead interaction in III.

[13] The least-energy path must cross the singlet barrier, since the triplet energy is >1 eV above the singlet at $R \sim 1.95$ Å. At the crossing point, which occurs for a substantially greater value of R ($\sim$2.3 Å), the triplet must lie below the singlet, in the level of approximation used here.[14]

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A Flexible and Directed Synthesis of Azoxyalkanes[1]

Sir:

Azoxyalkanes are currently of great interest. Four naturally occurring examples, macrozamin,[2] cycasin,[3] elaiomycin,[4] and LL-BH872α,[5] exhibit potent biological properties; the initial three are carcinogenic,[6] the latter possesses antifungal qualities.[5,7] Recently, studies of the photolytic closure of azoxyalkanes to oxadiaziridines have appeared,[8,9] and photoisomerization now makes acyclic *cis*-azoxyalkanes available.[9,10]

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[10] Oxidation of *cis*-azoalkanes can also be used.[9a] Previous reports of *ciz*-azoxyalkanes are discussed by Woodward and Wintner.[11] Cyclic