

ORIGIN OF STRAIN IN BICYCLO[1.1.1]PENTANE

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Abstract The 1,3-nonbonded distance in bicyclo[1.1.1]pentane has been calculated to be rather sensitive to substituents at the 1 and 3 carbons. Electron withdrawing groups lead to a shorter distance, suggesting that the 1,3-nonbonded repulsion is an important factor in destabilizing bicyclopentane. The repulsion is relieved when a bond is created between the carbons forming [1.1.1]propellane.

The unusual stability of [1.1.1]propellane (1)¹ is at least in part related to the high strain energy of bicyclo[1.1.1]pentane² (2). As a result, processes which cleave the central bond of 1 are much less exothermic than would be found with [2.1.1]- or [2.2.1]propellanes.¹ It was therefore of interest to inquire as to why 2 has such a high strain energy.



Cyclobutanes generally have longer than normal C-C bond lengths,³ and this has been attributed to a repulsive 1,3-nonbonded repulsion between the carbons.³ The 1,3-distance is only 2.14 Å,³ which is significantly shorter than that in unstrained alkanes (2.57 Å).⁷ It is possible that much of the strain energy of cyclobutane results from such an interaction.¹⁰ Unfortunately, it has not proven possible to test this hypothesis experimentally since the introduction of substituents may lead to changes in structure resulting from other interactions.

If the above interaction is important in determining the energies of cyclobutanes, the short bridgehead-bridgehead distance in 2 may be the source of much of its strain. The formation of a bond between the 1 and 3 carbons, as in the closure to 1, will relieve the interaction, and then lead to only a modest increase in energy resulting from the increased

angle strain at the three methylene groups.

The 1,3-distance has been found to be 1.845 \AA in $\underline{2}$ via electron diffraction,⁴ and 1.89 \AA by X-ray crystallography in a derivative of $\underline{2}$ with substituents at the 2 carbon.¹¹ The strong interaction between the backsides of the bridgehead CH bond orbitals is presumably the factor responsible for the very large long-range nmr proton-proton coupling constant (18 Hz) found for $\underline{2}$.¹² It then remains to be determined whether or not this is an important interaction as far as the energy and structure are concerned.

If the 1,3-interaction is important, removal of some of the electron density in the bridgehead orbital should decrease the repulsion, and lead to a shorter distance. A chlorine should be effective in decreasing the electron density in the relevant orbital, but although the structure of 1-chlorobicyclo[1.1.1]pentane has been determined by microwave spectroscopy ($r(C_1 \dots C_3) = 1.85 \text{ \AA}$),¹³ the precisions of all the structural studies are inadequate to determine whether or not there is a change in this distance.

In order to examine this question further, and to determine which compounds might be profitably examined experimentally, we have carried out calculations of the equilibrium geometries of a series of 1,3-disubstituted bicyclo[1.1.1]pentanes using the 3-21G basis set.¹⁴ These compounds were chosen since substituents at both centers should amplify any effect which might be present. The results are shown in Table I. A fluorine would be expected to be particularly effective at removing electron density from the carbon bridgehead orbital, and should lead to a shorter 1,3 distance. The calculations suggest that this will be the case. A chlorine is predicted to have essentially the same effect. In both cases, the decrease in the calculated 1,3-distance is quite remarkable ($0.07\text{--}0.08 \text{ \AA}$). On the other hand, cyano groups are far less effective, leading to only a small change in structure. Although cyano often appears to be a better electron withdrawing group than halo, it has this effect because it is electron withdrawing via both σ and π interactions whereas halo is electron withdrawing via σ interactions but electron releasing via π . The σ effect should be the only important one in the present case.

Similarly, electron releasing groups such as SiH_3 and CH_3 should increase the electron density in the orbitals, and should increase the non-bonded distance. This is found in the calculated structures, and again a significant change in distance is predicted (0.02 \AA).

The striking geometry changes which are predicted has led us to begin an experimental study of the compounds in Table I. The bicyclo[1.1.1]pentane-1,3-dicarboxylic acid reported by Applequist, Renken and Wheeler^{1,5} provides a convenient starting point for the preparation of the compounds. The preparations and structural parameters will be reported subsequently.

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Table I
Structural Parameters for 1,3-Disubstituted Bicyclo[1.1.1]pentanes (Å)

X	$r(C_1 \dots C_3)$	$r(C_1-C_2)$	$r(C_2 \dots C_4)$	$r(C-H)$
H	1.916	1.574	2.163	1.081
F	1.849	1.561	2.178	1.077
Cl	1.832	1.558	2.182	1.076
CN	1.903	1.572	2.168	1.078
CH ₃	1.939	1.578	2.156	1.082
SiH ₃	1.938	1.581	2.163	1.080

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2. The heat of formation of bicyclo[1.1.1]pentane has not been determined experimentally, but using group equivalents (Wiberg, K. B. *J. Comput. Chem.*, 1984, 5, 197) which correctly predict heats of formation from 6-31G* energies, the ΔH_f is estimated to be 50.4 kcal/mol, leading to a strain energy of 67 kcal/mol.
3. For a summary of C-C bond lengths in cyclobutanes, see ref 4. Cyclobutane has $r(C-C) = 1.548 \pm 0.003$ Å (ref. 5) whereas ethane has $r(C-C) = 1.532 \pm 0.003$ Å (ref. 6), *n*-butane has $r(C-C) = 1.531 \pm 0.002$ Å (ref. 7) and cyclohexane has $r(C-C) = 1.536 \pm 0.002$ Å (ref. 8).
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