

SOME THEORETICAL OBSERVATIONS ON CYCLOPROPANE

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The peculiarities of the electronic structure of cyclopropanes have often been noted. In a previous communication (1) extended Hückel calculations were used to obtain a molecular orbital representation of cyclopropane in essence very similar to the Walsh picture of bonding in this molecule (2). Also studied was the preferred edge-on protonation of the molecule and the favored "bisected" (I) conformation of a classical cyclopropyl carbanyl cation (3). Some further results of a predictive nature obtained by the same method



are presented below.

1. The relative conjugating ability of cyclopropane. The potential energy for twisting around the single bond in R-CHO was computed for R = cyclopropyl, vinyl, phenyl, isopropyl and cyclobutyl, and is illustrated in fig. 1. The carboxaldehyde grouping was chosen since it presents minor secondary steric difficulties and also because most quantitative measurements are available for this group. It is immediately noted that cyclopropyl, vinyl and phenyl fall into one class, characterized by two potential minima 180° apart, corresponding to positions of maximum overlap of the π systems, or in the case of cyclopropane

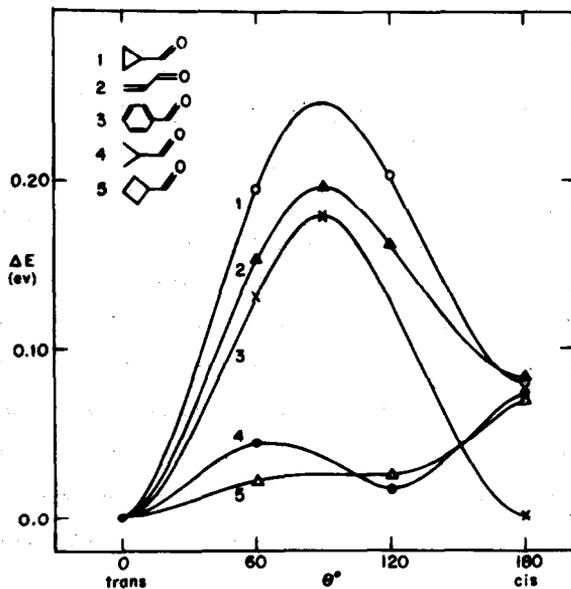


Fig. 1. Potential energy curves for rotation in R-CHO, arbitrarily referred to the same energy zero for the conformation in which the carbon chain in R is trans to the carbonyl group.

of the quasi- π orbitals located in the plane of the three-membered ring, and perhaps appropriately denoted as Δ orbitals. On the other hand isopropyl and cyclobutyl possess lesser potential minima $\approx 120^\circ$ apart, corresponding to eclipsing C=O with CH_3 or H. The calculations are not to be trusted quantitatively for the heights of barriers between rotamers, but the following experimental points of reference are available. The nmr energy of activation to interconversion of benzaldehyde conformers has been estimated as 7.9 kcal. (4), and the twofold barrier has been assigned by direct observation of the torsional frequency as 4.66 kcal. in the gas phase and 6.7 kcal. in the liquid (5). The maximum in the propenal torsion has been placed 4.96 kcal. above the cis conformation, which in turn is 2.06 kcal. less stable than the trans (6).

The potential minima in acetaldehyde correspond to H eclipsing C=O and the barrier to rotation is 1.17 kcal. (7). Electron diffraction studies agree with the shape of the computed energy curves for cyclopropyl and isopropyl carboxaldehyde (8). The calculations are thus in reasonable agreement with the known facts and predict that cyclobutyl should resemble isopropyl rather than cyclopropyl in its conjugative ability, and that the conformational preference of cyclopropyl is at least as strong as that of vinyl or phenyl.*

2. The relative ability of cyclopropane to interact with cation centers.

In connection with a theoretical study of nonclassical cations in the norbornadiene system (9), a potential energy curve was calculated for a symmetrical distortion of a classical 4-cyclopentenyl cation in which C_4 was moved in the plane bisecting $C_1=C_2$ and passing through C_4 , while keeping C_3-C_4 and C_4-C_5 bond distances fixed. To complete the series, calculations were also done on the hydrindenyl and 3-bicyclo (3.1.0) hexyl cations and are all compared in fig. 2. The cyclopentenyl curve shows a small "nonclassical minimum" for a highly bent molecule, superimposed on a steeply rising strain energy. As expected, benzene is intermediate between a single and double bond; thus hydrindenyl shows only an inflection in the potential energy surface. Cyclopropane actually has the deepest nonclassical minimum in the series and further calculations on the hypothetical cation (II) indicate the presence of an unsymmetrical double minimum resembling that calculated for 7-norbornadienyl, and with the deeper well for bending toward the cyclopropane.†

* In the previous work (1) it was similarly computed that cyclopropyl carbonyl is conformationally more stable than benzyl. Tricyclopropyl carbonium ion is more stable than triphenyl carbonium (3a).

† In the case of bicyclohexyl another minimum is obtained for a cation with a shallow boat-like conformation. Symmetrization of the chair form to a trihomocyclopropenyl structure (S. Winstein, J. Am. Chem. Soc., 81, 6524 (1959) is definitely favored in these calculations.

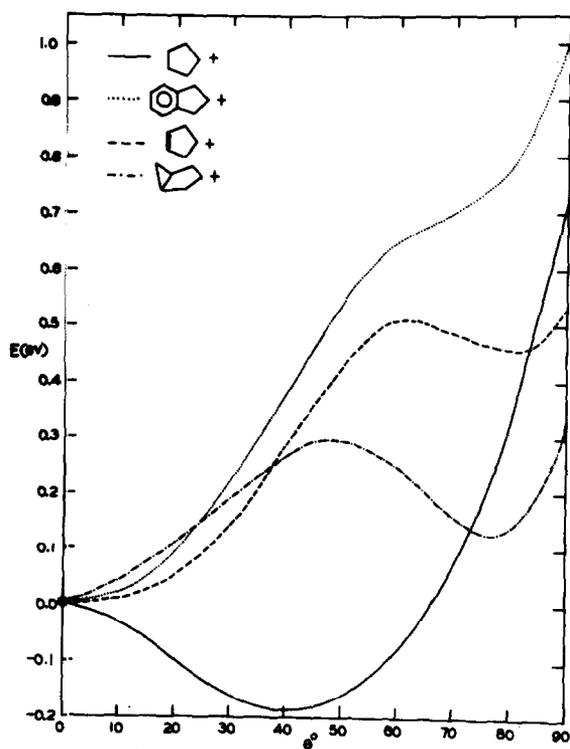


Fig. 2. Potential energy surfaces for the interaction of a single bond, double bond, a benzene and cyclopropane ring with a secondary carbonium ion center. The angle θ is the dihedral angle by which C^+ is lifted above the arbitrary zero of energy, a planar five ring. For bicyclohexyl the bending is toward a chair-like form.

3. Excited states of cyclopropanes and spiropentane. The degenerate pair of highest occupied molecular orbitals (Δ) of cyclopropane, in these calculations or from simple overlap considerations lie higher in energy than the σ orbitals of normal saturated hydrocarbons and approach the energies of π and "lone pair" n orbitals. If this is so one might, in highly strained systems containing a cyclopropyl structure and, say, a carbonyl group near each other, expect low lying excited states arising from $\Delta \rightarrow \pi^*$ excitations, at energies comparative to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ states. Such transitions should

1. be weak because of small spatial overlap of the orbitals involved.
2. possess considerable charge transfer character.
3. weaken cyclopropane bonding in the excited state.

These hypothetical transitions should have considerable significance in organic photochemistry and a search for them has been undertaken.

The absorption spectra of saturated hydrocarbons in the vacuum ultraviolet have not been analyzed but it appears reasonable that they are primarily Rydberg transitions. Cyclopropane, once again standing between normal saturated hydrocarbons and olefins, absorbs strongly at lower energies than any other saturated hydrocarbon. The location of the lowest triplet state of cyclopropane is not known. If the absorption of cyclopropanes is properly described as a $\sigma \rightarrow \sigma^*$ excitation (and not a Rydberg transition) one may inquire if any significant geometry change ensues. Extended Hückel calculations on spiro-pentane quite clearly predict that in its lowest $\sigma \rightarrow \sigma^*$ excited state all five carbon atoms prefer to lie in one plane; and thus excitation should lead to relative rotation of the two three-membered rings.

This work was carried out at Harvard University, while the author was a Junior Fellow in the Society of Fellows.

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