

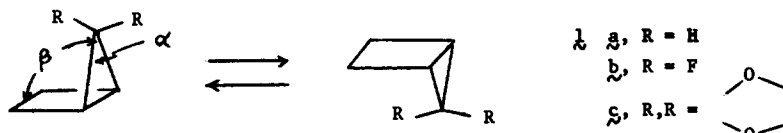
SUBSTITUENT EFFECTS IN BICYCLOPENTANE ISOMERIZATIONS

By D. B. Chesnut, S. Ferguson, L. D. Smith and N. A. Porter*

Paul M. Gross Chemical Laboratory, Duke University,
Durham, North Carolina 27706

(Received in USA 12 June 1972; received in UK for publication 31 July 1972)

1,3-Biradicals have been claimed as intermediates in the thermal ring flip isomerization of bicyclopentane;¹ and recently a dramatic lowering of this isomerization barrier has been reported for bicyclopentanes with π -donor substituents.² These observations prompted us to report here the results of extended Hückel calculations carried out on the bicyclopentanes **1a-c**. The purpose of our calculations was to determine a likely geometric pathway for bicyclopentane isomerizations and also to examine the effect of substituents on this process.



In Figures 1 and 2 are presented the extended Hückel energies³ for bicyclopentanes **1a** and **1c** as a function of the geometric parameters α and β . Only α (the C-C-C angle) and β (the bicyclopentane envelope angle) were allowed to vary in our calculations, the other independent bond lengths and independent angles being held fixed at their standard values. Note that the 1,3 CC bond length and the internal CCC angles are all determined by specifying α and β .⁴

Substitution by oxygen and fluorine on the one-carbon bridge of the bicyclopentane changes the energy surface in two important ways. First, for **1a**, two local energy minima are found, the bicyclopentane ($\alpha = 63^\circ$, $\beta = 110^\circ$) and the planar "biradical" species ($\alpha = 105^\circ$, $\beta = 180^\circ$). According to our calculations, bicyclopentane must cross an energy barrier of some 1.25 ev. to get to the planar species (The experimental value reported is 1.7 ev.). Only one minimum is found however, on the energy surface for **1b** or **1c**, no barrier separating the bent and planar forms when electronegative substituents are present.

Analysis of the symmetry of the occupied biradical orbitals for **1a** and **1c** leads to a credible explanation of the differences in behavior for the two systems. The filled biradical orbital for **1a** has A-type symmetry (see drawing) whereas **1b** and **1c** have HOMO's of S symmetry. Bicyclopentane is geometrically constrained to open to the planar species by a disrotatory motion.

Fig. 1

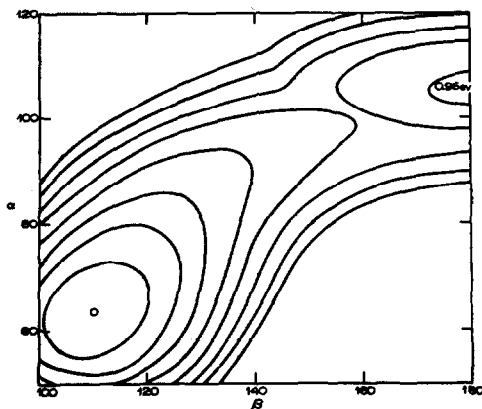


Fig. 1 Extended Hückel Energies for $1a$ in increments of 0.25 eV.

Fig. 2

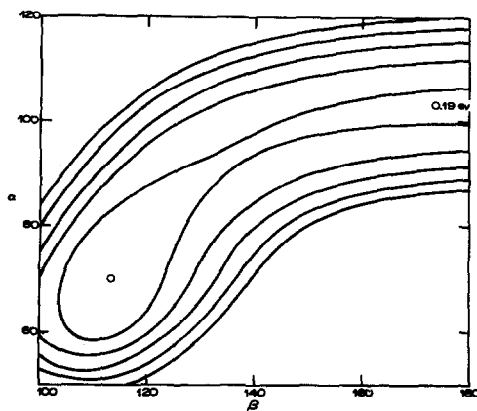
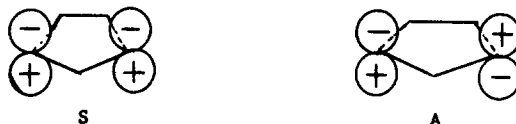


Fig. 2 Extended Hückel Energies for $1c$ in increments of 0.25 eV.

Thus in $1b$ and $1c$ where the biradical orbital is symmetric (as is the σ bridge bond which is broken) this disrotatory opening is symmetry allowed. On the other hand, $1a$ must open to an antisymmetric biradical species and thus a symmetry imposed energy barrier exists between the bent and planar forms.



The explanation⁵ for the existence of an A-type HOMO biradical orbital in trimethylenes analogous to $1a$ is that the S orbital is raised in energy by a destabilizing interaction with the $-\text{CH}_2-$ group between the radical centers. With electronegative substituents, this interaction is decreased since (1) the energy difference between the interacting orbitals is now quite large and (2) the orbitals on the electronegative substituents are compact and overlap with the S orbital is reduced.⁶ The decrease in this destabilizing interaction results in allowing the S orbital to remain below the A orbital both in substituted cyclopentadiyls and trimethylenes.

A second difference in the energy surfaces of $1a$ and $1c$ is that the planar form lies much closer in energy to the bent bicyclopentane when π -donor substituents are present. For $1c$, the planar species lies .19 ev. above the bicyclopentane (cf. .96 ev. for $1a$) and for $1b$ our calculations suggest that bicyclopentane is unstable with respect to the planar species. Analysis of the molecular orbitals for this system shows that π -donor substituents at C-5 of bicyclopentane interact with the carbon framework in much the same way that π -donors interact with cyclopropane Walsh orbitals.⁷ Antibonding character is thus mixed into the bridge C-C bond resulting in destabilization of the bent form of bicyclopentane relative to the planar species.

In summary, oxygen and fluorine substituents on the one-carbon bridge should reduce the barrier for bicyclopentane isomerization in two ways. The substituents (1) destabilize the strained ring system⁷ and (2) they eliminate a symmetry imposed barrier since conversion to the planar species is now an "allowed" process.

We thank the Research Corporation and the National Science Foundation for financial support.

REFERENCES

1. J. Chesick, J. Am. Chem. Soc., 84, 3250 (1962).
2. a) K. Fallenberger, U. Scholkopf, C. A. Bahn and P.V.R. Schleyer, Tetrahedron Letters, 359 (1972).
b) J. J. Tufariello, A. C. Bayer and J. J. Spadaro, ibid., 363 (1972).
c) J. J. Tufariello, and A. C. Bayer, ibid., in press. We thank Professor Tufariello for informing us of this work before publication.
d) Our calculations on mono-methoxy substituted bicyclopentanes places the isomerization barrier at about .75 ev. for this system (cf. 1.2 ev. experimental).
3. CNDO calculations appeared to underestimate strain but the symmetry of the biradical orbitals were the same in the CNDO and extended Hückel calculations. Our CNDO results will appear elsewhere.
4. The bridgehead protons were placed on a vector defined by the bridgehead carbon atom and the center of mass of the molecule.
5. R. Hoffmann, J. Amer. Chem. Soc., 90, 1475 (1968).
6. At large values of α the A-type MO is slightly raised in $1b$ and $1c$ relative to that of $1a$. This is apparently due to a spiro-conjugation interaction in $1b$ and $1c$. H. E. Simmons and T. Fukunaga, J. Amer. Chem. Soc., 89, 5208 (1967).
7. a) R. Hoffmann, Tet. Letters, 2907 (1970).
b) H. Gunther, ibid., 5173 (1970).
c) R. Hoffmann and W. Strohrer, J. Amer. Chem. Soc., 93, 6941 (1971).