Tetrahedron Letters,Vol.22,No.48,pp 4799-4802,1981 0040-4039/81/484799-04$02.00/0
Printed in Great Britain

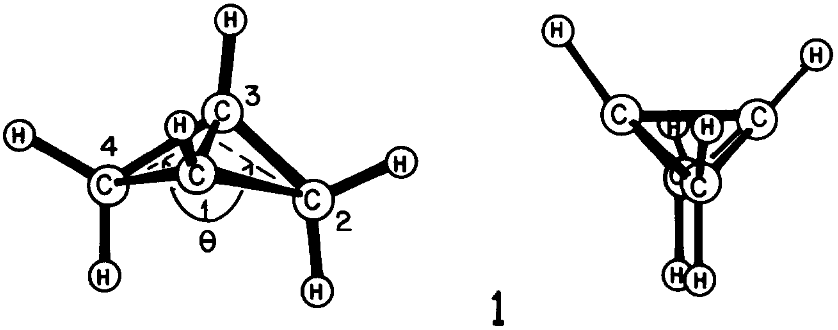
SYNCHRONIZED DISTORTIONS OF BICYCLOBUTANES

Michael N. Paddon-Row,*[1] K. N. Houk,* Paul Dowd*
Philip Garner and Raymond Schappert

Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15260, U.S.A.

Summary: The linear relationship between flap angle, θ, and bridging bond length, r_{13}, in bicyclobutanes, found empirically by Irngartinger through x-ray analysis, is reproduced by ab initio STO-3G calculations. Additional distortions of the bicyclobutane geometry which are synchronized with flap angle variations are predicted.

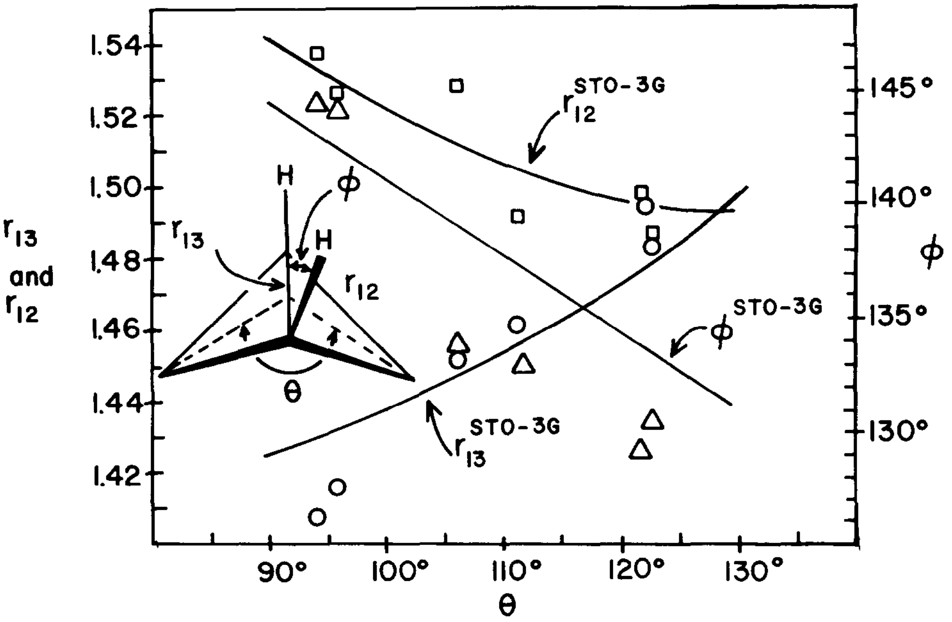
The extraordinary C_1C_3 bond of bicyclobutane, **1**, has stimulated fascinating experimental[2] and theoretical[3] studies. Calculations[3b,3c] indicate that the C_1C_3 bond is formed of nearly pure p orbitals.[3] The negative C_1-C_3 coupling constant observed in derivatives of bicyclobutane **1**[4] supports this conclusion. The experimental geometry[2d] of **1**, shown above,[5] reveals that C_1 and C_3 are inverted; the four internuclear bond vectors from C_1 and C_3 lie in a single hemisphere.[2d]



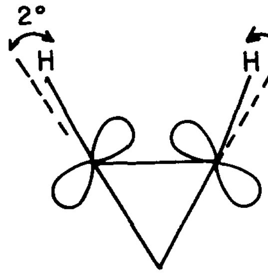
1

Irngartinger and Lukas recently discovered a linear relationship between the flap angle, θ, and the C_1C_3 bond-length, r_{13},[6] in which r_{13} decreases as θ decreases. This result seems counterintuitive; increasing strain in **1** might have been expected to weaken the C_1-C_3 bond and increase r_{13}. Ab initio calculations we have performed on distorted bicyclobutanes and various tricyclic derivatives using the STO-3G basis set,[7,8] indicate the origin of this relationship and predict other geometrical variations that will be synchronized with variations in the flap angle.

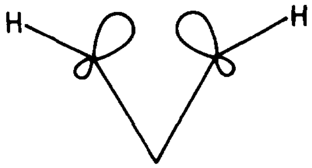
Shown below is a plot of the calculated CC bond lengths, r_{13} and r_{12} and the C_1C_3H angles, ∅, obtained when the flap angle, θ, is fixed at different values and all other parameters are optimized.[9] A 30° decrease in θ is accompanied by a 0.06 Å decrease of r_{13}, identical to the experimentally observed change.[5] At the same time each peripheral CC bond length (r_{12}) increases by about half this amount, and ∅ increases by 10°. As θ increases beyond the equilibrium value, the opposite trends are observed. For comparison, experimental values of these geometrical parameters for bicyclobutane and five derivatives are shown on the same graph (○ = r_{13}, □ = r_{12}, and △ = ∅).[10]



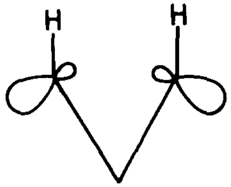
These changes may be understood if we consider the C_1-C_3 bond to result from the overlap of the p orbitals of two radicals centered at C_1 and C_3. At the equilibrium bicyclobutane geometry, where θ = 118°, the angles $C_2C_1C_4$ = $C_2C_3C_4$ are 96°. The formal radical carbons, C_1 and C_3, have only a slight tendency to pyramidalize at this geometry, and the C_1-C_3 bonding may be represented as in 2a, below. Outward bending of the CH bonds (as in 2b) increases C_1-C_3 bonding due to admixture of s character, but only at the expense of destabilization due to increased pyramidalization. Inward bending (2c) is unfavorable since the resulting C_1 and C_3 orbitals overlap poorly. Upon a decrease in θ, there is a strong tendency for the formal radical centers to be come pyramidal, as there



2a



2b



2c

is for the methyl radical when one HCH angle is contracted.[11] The direction of pyramidalization (2b rather than 2c) maximizes C_1-C_3 bonding, by increasing the s character of the hybrids pointing toward each other. The result is a strengthening of the C_1-C_3 bond and a concomitant contraction of r_{13}. Decreasing ϕ as in 2c, should lead to a weakening of the C_1-C_3 bond. Calculations indicate that a decrease of ϕ is accompanied by a lengthening of r_{13} and vice versa. An extreme example of the effect of decreasing ϕ is provided by calculations on [1.1.1]propellane which predict the central bond to be very long (1.600 Å).[3c]

The lengthening of the peripheral CC side bonds (r_{12}, etc.) in 1 upon decreasing θ is a result of increasing p character of C_1 and C_3 in these bonds. We find that the methine CH bonds are also slightly shortened as θ decreases, as calculated by Jemmis et al.[10] for one CH bond in the methyl radical when the angle between the other two CH bonds is contracted.

Opening the flap angle, θ, to 130° will not, in itself, cause pyramidalization at C_1 and C_2, since when θ is 130°, the angle $C_2C_1C_4$ is 103°; the methyl radical remains nearly planar at an analogous geometry.[10] As θ is increased above 130°, bicyclobutane begins to undergo a ground state orbital symmetry forbidden reaction, the conversion of 1 into cyclobutane-1,3-diyl, for which θ is near 180°. The forbiddenness of this reaction arises from the overlap of the methylene "π_{CH_2}" orbitals with the developing radical p lobes, which ultimately causes the A^2 (1-3 antibonding) configuration to be lower in energy than the S^2 (1-3 bonding). For $\theta > 115°$, the bridgehead CH bonds rotate inward (ϕ decreases), in order to reduce the antibonding overlap between developing radical orbitals and π_{CH_2} orbitals. This motion leads to a weakening of the C_1-C_3 bond, and an increase in r_{13}.

Additional synchronized distortions and structures of tricyclic derivatives of bicyclobutane will be discussed in a forthcoming paper.

Acknowledgment: We are grateful to the National Science Foundation for financial support of this research, to Professor Irngartinger for providing unpublished crystallographic data, and to Professor John A. Pople for use of GAUSSIAN 80 and the CMU VAX.

References

(1) On leave from the New South Wales Institute of Technology, Sydney, Australia, 1980. Address correspondence to the Australian address.

(2) *Inter alia*: (a) K. B. Wiberg, G. M. Lampman, R. P. Cuila, D. S. Conner, P. Schertler, and J. Lavanish, *Tetrahedron*, **21**, 2749 (1965); (b) E. P. Blanchard, Jr., and A. Cairncross, *J. Am. Chem. Soc.*, **88**, 487 (1966); (c) S. Masamune, *Tetrahedron Letters*, 945 (1965); (d) K. W. Cox, M. D. Harmony, G. Nelson, and K. B. Wiberg, *J. Chem. Phys.*, **50**, 1976 (1969); (e) M. Horner and S. Hunig, *J. Am. Chem. Soc.*, **99**, 6122 (1977).

(3) (a) M. Pomerantz and E. W. Abrahamson, *J. Am. Chem. Soc.*, **88**, 3970 (1966); (b) J. M. Schulman and G. J. Fisanick, *ibid.*, **92**, 6653 (1970); (c) M. D. Newton and J. M. Schulman, *ibid.*, **94**, 767, 773 (1972).

(4) H. Finkelmeier and W. Lüttke, *J. Am. Chem. Soc.*, **100**, 6261 (1978).

(5) Drawings were prepared on the PROPHET computer system, sponsored by the Division of Research Resources, National Institutes of Health.

(6) (a) H. Irngartinger and K. L. Lukas, *Angew. Chemie, Int. Ed. Engl.*, **18**, 694 (1979); (b) H. Irngartinger, K. L. Lukas, and A. Goldmann, *Fresenius Z. Anal. Chem.*, **304**, 269 (1980).

(7) Calculations were performed using the STO-3G basis set and the GAUSSIAN 80 program.[8] All geometries were completely optimized using gradient procedures with a C_{2v} symmetry constraint.

(8) J. S. Binkley, R. A. Whiteside, R. Krishnan, R. Seeger, D. S. DeFrees, H. B. Schlegel, S. Topiol, L. R. Kahn, and J. A. Pople; GAUSSIAN 80; Carnegie-Mellon University; 1980.

(9) W. H. Hehre and J. A. Pople, *J. Am. Chem. Soc.*, **97**, 6941 (1975), previously reported the full STO-3G optimization of bicyclobutane.

(10) These experimental values are for the five compounds included on the Irngartinger-Lukas graph,[6a] and for a 1,3-*bis*-acetoxymethyl derivative of bicyclobutane bridged by a carbonyl connecting C-2 and C-4; H. Irngartinger, A. Goldman, R. Schappert, P. Garner, and P. Dowd, *J. Chem. Soc., Chem. Comm.*, (1981).

(11) E. E. Jemmis, V. Buss, P. v. R. Schleyer and L. C. Allen, *J. Am. Chem. Soc.*, **98**, 6483 (1976).

(Received in USA 3 August 1981)