compared to the emission lifetime. Spin–orbit coupling appears to be large between the radical-like singlets and triplets based on the short lifetime of the phosphorescence as well as its relatively high intensity and the apparent absence of a radical-like fluorescence. We believe an important source of the spin–orbit interaction is from first-order coupling (one-center terms).

The presence of the unusually low-energy radical-like triplet appears to be important in the triplet-triplet sensitized cis–trans isomerization of 1,2-diphenylcyclopropane with low energy sensitizers. In addition either or both of the radical-like triplet and singlet states are the important excited states leading to direct photoisomerization and/or cycloelimination.

Acknowledgment. This work was supported by the Robert A. Welch Foundation. We wish to thank Professor R. Shimada, Kyushu University, for helpful suggestions regarding certain aspects of this work.

Vinylcyclopropane and Vinylcyclobutane

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Abstract: We have applied single determinant *ab initio* molecular orbital theory to the description of internal rotation in vinylcyclopropane and vinylcyclobutane. Using the minimal STO-3G basis we find the two molecules to be most stable in their s-trans forms but also predict both to possess flat secondary s-cis and gauche minima. Further investigation on vinylcyclopropane with the extended 4-31G basis set confirms the gauche minimum but places doubt on the stability of the s-cis structure. Substitution on the vinyl group in vinylcyclopropane by π-electron donors at the 2 carbon deepens the gauche minimum, while equivalent substitution one position removed has the opposite effect. Substitution by π-electron acceptors reverses the trend. These effects are readily accounted for by a simple one-electron model and are consistent with available experimental information on related systems. Small, but significant substituent effects are found on the relative energies of the vinylcyclobutane conformers. Here 2 substitution by either π acceptors or π donors destabilizes the gauche structure relative to the other two. The 1 substitution has little effect.

Compounds involving small rings have long held a special place in chemistry, in that they exhibit properties intermediate between systems which are formally saturated and those which contain some degree of unsaturation. Perhaps on account of their pecularity they have received constant and thorough attention from experimentalists and theorists alike but still in all several important questions remain unambiguously answered. Most of these stem from our present lack of knowledge as to the exact extent to which the formally saturated small ring compounds behave as if they were unsaturated. Such quantitative information should, in principle, be accessible by thermochemical and structural measurements, but up till now these experiments have either been impossible to perform or have led to ambiguous findings.[2] Our aim in this paper is to consider the first two members of the vinylcycloalkane family and to investigate theoretically both the conformational preferences of these molecules and the degree of interaction between the vinyl and cycloalkyl groups. We shall accomplish this by a straightforward application of *ab initio* molecular orbital theory, using our previously developed STO-3G[3a] and 4-31G[3b] basis sets. These have already met with considerable success in problems of potentials to internal rotation for a number of simple polyatomics.[4–6]

Methods

Standard single determinant molecular orbital theory is used throughout. We employ two different sets of basis functions in this study. The first closely simulates a minimal set of Slater-type orbitals (STO's) in that each STO is least-squares fitted to a sum of three Gaussians. The resulting functions, termed STO-3G,[3a] have been uniformly rescaled to be adequate for use in molecular calculations. In addition, we have recalculated several points on the potential surface of vinylcyclopropane using the extended 4-31G basis.[3b] Here atomic inner shells are each described by a single function written in terms of four Gaussians, while the valence shell is split into inner (three Gaussian) and outer (one Gaussian) parts. The Gaussian expansions, originally determined as energy optimum for the atom, have been rescaled. All calculations have been made with the GAUSSIAN 70 series of programs.[7]

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[1] (a) National Science Foundation Postdoctoral Fellow, 1971–1972. (b) The laboratoire de Chimie Théorique is also part of the Laboratoire de Physico-Chimie des Rayonnements, associated with the CNRS.

[2] For a good example of the uncertainty in the experimental spectroscopic interpretation of molecules containing small rings, see G. J. Karabatsos and D. J. Fenoglio, *Top. Stereochem.*, 5, 167 (1970).

[3] (a) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, 51, 2657 (1969); (b) R. Ditchfield, W. J. Hehre, and J. A. Pople, *ibid.*, 54, 724 (1971).

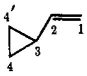
[4] L. Radom and J. A. Pople, *J. Amer. Chem. Soc.*, 92, 4786 (1970).

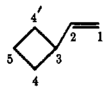
[5] L. Radom, W. J. Hehre, and J. A. Pople, *ibid.*, 94, 2371 (1972).

[6] L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *Aust. J. Chem.*, in press.

[7] GAUSSIAN 70, a series of programs designed to perform *ab initio* molecular orbital calculations on organic molecules: W. J. Hehre, W. A. Lathan, and J. A. Pople, to be submitted to the Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Ind. Typical times for a single calculation on the molecules discussed in this paper are as follows (Univac 1108 computer): vinylcyclopropane,

Geometries for vinylcyclopropane and vinylcyclobutane have been chosen by the use of optimum STO-3G structures for cyclopropane,[8] planar (D_{4h}) cyclobutane,[9] and ethylene,[10] linked together with a bond length of 1.52 Å.[11] Using the following numbering system

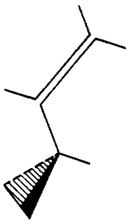




we define the CCC angles $\alpha = \angle C_2C_3C_{44}'$[12] and $\beta = \angle C_1C_2C_3$. For each choice of twist angle $\omega = \angle C_1C_2C_3H$ these two angles will be treated as parameters to be optimized. Such a model is similar to the flexible rotor scheme used successfully by Radom and Pople[4] in their treatment of internal rotation in the C_3 and C_4 acyclic hydrocarbons. The vinyl-substituted molecules (fluoro and cyano substituents have been considered as typical π-electron acceptors and donors, respectively[13]) are constructed simply by replacing a single hydrogen of the optimum STO-3G structures retaining the original angles of attachment.[14]

Results and Discussion

The Parent Molecules. Nuclear magnetic resonance studies on vinylcyclopropane have been interpreted in terms of either a twofold or threefold barrier to rotation of the ring about the vinyl group. The former instance corresponds to a potential curve for rotation with energy minima for s-trans I and s-cis II structures, while a threefold barrier would imply a single minimum for either s-trans I or s-cis II forms and a second minimum for a gauche structure III. Lüttke and de Meijere[15] have concluded that their data are best interpretable in terms of a twofold barrier to rotation, the s-trans structure I being 1.1 ± 0.2 kcal/mol the more stable. However, two independent studies by Günther and Wendisch[16] and by De Mare and Martin[17] have decided upon a threefold rotational potential, the s-trans form I having a lower energy (by 0.65 ± 0.05 and 0.80 ± 0.15 kcal/mol, respectively) than the gauche conformer III.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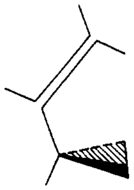
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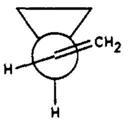

III

More pertinent to direct comparison with theoretical calculations are structural measurements on the gas phase. A microwave study on vinylcyclopropane by Schwendeman and Codding[18] has resolved only the s-trans conformer I so no conclusions as to the nature of the rotational potential may be drawn from it at this time. de Meijere and Lüttke[19] have reported an electron diffraction analysis which favors a threefold rotational potential with an energy difference between the (lower energy) s-trans form and the gauche conformer of 1.1 ± 0.2 kcal/mol.

It would appear that no structural measurements have been performed to date on vinylcyclobutane. However, an nmr study on a closely related molecule, cyclobutylaldehyde, indicates it to possess a threefold barrier to rotation, the s-trans form being the lower in energy.[20] Also noteworthy is an electron diffraction study of cyclobutanecarboxylic acid chloride,[21] interpretable in terms of a gauche structure.

Theoretical results for internal rotation in vinylcyclopropane and vinylcyclobutane are presented in Figures 1 and 2. Consistent with available experimental information, we find vinylcyclopropane to possess an s-trans ground-state conformation but also predict the existence of two additional minima, one corresponding to a gauche structure ($\omega \simeq 120°$) and the other to an s-cis form ($\omega = 180°$). The gauche minimum is found to be very shallow (with a barrier to rotation to the s-cis form of <0.1 kcal/mol) and higher in energy than the s-cis form by 0.4 kcal/mol. Application of the 4-31G basis at several points along the potential curve[22] (Figure 1) confirms our assignment of an s-trans ground state and strengthens the case for a secondary gauche minimum. At the same time, however, these calculations shed doubt upon the prediction of the STO-3G basis of yet a third s-cis minimum.[23] Theoretical values for the angles α and β in the s-trans form of vinylcyclopropane (124.2 and 123.8°, respectively) are in good agreement with the corresponding electron diffraction results of 123.7 and 123.8° obtained by de Meijere and Lüttke.[19,24] Another interesting comparison of the theoretical and experimental electron diffraction results is in the prediction of the twist angle ω in the gauche form. Referring to Figure 1 de Meijere

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STO-3G, 33 atomic orbitals, 99 Gaussians, 5 min; cyanovinylcyclobutane, 49 atomic orbitals, 147 Gaussians, 40 min; vinylcyclopropane, 4-31G, 61 atomic orbitals, 132 Gaussians, 80 min.

(8) L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 5339 (1971); $r_{CC} = 1.502$ Å, $r_{CH} = 1.081$ Å, $\angle HCH = 113.8°$.

(9) W. J. Hehre and J. A. Pople, *ibid.*, manuscript to be submitted; $r_{CC} = 1.553$ Å, $r_{CH} = 1.087$ Å, $\angle HCH = 108.7°$. We have used a "planar" D_{4h} structure for cyclobutane rather than the "puckered" D_{2d} form. This simplification is not expected to seriously effect any of our conclusions.

(10) W. A. Lathan, W. J. Hehre, and J. A. Pople, *ibid.*, **93**, 808 (1971); $r_{CC} = 1.305$ Å, $r_{CH} = 1.079$ Å, $\angle HCH = 115.4°$.

(11) This has been selected on the basis of preliminary optimization studies on vinylcyclopropane.

(12) C_{44}' refers to the bisector of the C_3C_4 and C_3C_4' bonds.

(13) See, for example, W. J. Hehre and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 2191 (1970); W. J. Hehre, L. Radom, and J. A. Pople, *ibid.*, **94**, 1496 (1972).

(14) Standard model bond lengths have been assumed: C–F = 1.33 Å, C–CN = 1.45 Å, C≡N = 1.16 Å [J. A. Pople and M. Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967)].

(15) W. Lüttke and A. de Meijere, *Angew. Chem., Int. Ed. Engl.*, **5**, 512 (1966).

(16) H. Günther and D. Wendisch, *ibid.*, **5**, 251 (1966).

(17) G. R. De Mare and J. S. Martin, *J. Amer. Chem. Soc.*, **88**, 5033 (1966).

(18) R. M. Schwendeman and E. G. Codding, "Symposium on Molecular Structure and Spectroscopy," Columbus, Ohio, Sept 1968; quoted in ref 2.

(19) A. de Meijere and W. Lüttke, *Tetrahedron*, **25**, 2047 (1969).

(20) G. J. Karabatsos and M. Hsi, *J. Amer. Chem. Soc.*, **87**, 2864 (1965).

(21) W. J. Adams and L. S. Bartell, *J. Mol. Struct.*, **8**, 199 (1971).

(22) The optimum STO-3G values for α and β were used for each choice of ω.

(23) This result is in line with an earlier noted trend of the STO-3G basis to slightly overestimate the stability of compact ring structures. See, for example, ref 8.

(24) de Meijere and Lüttke (see ref 19) present two alternative schemes for the interpretation of their electron diffraction data. Our theoretical results are in good agreement with the first of these two with regard to the angles α and β and also the bond length connecting the vinyl and cyclopropyl groups.

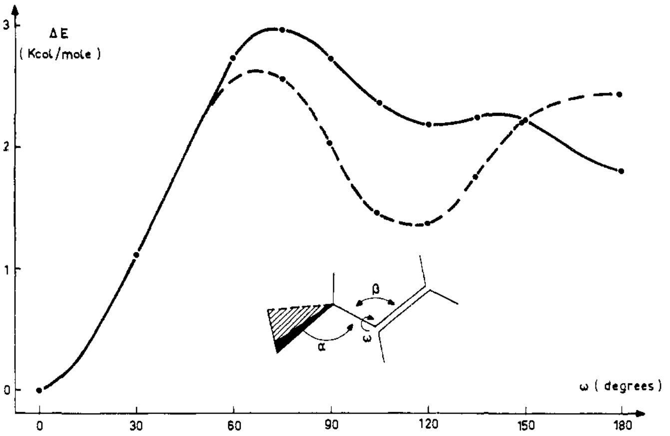


Figure 1. Potential for internal rotation in vinylcyclopropane. ω (0 shown) is the angle of twist of the ring relative to the vinyl group. (———) STO-3G, $E(0) = -191.60520$ hartrees; (- - - -) 4-31G, $E(0) = -193.65341$ hartrees.

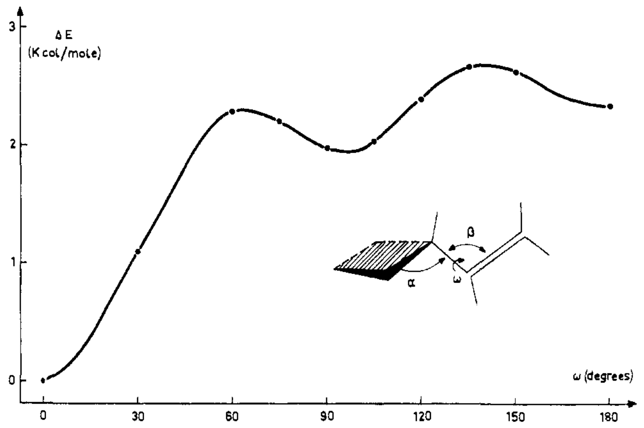


Figure 2. Potential for internal rotation in vinylcyclobutane. ω (0 shown) is the angle of twist of the ring relative to the vinyl group. $E(0) = -230.21001$ hartrees.

and Lüttke favor angles ω between 110 and 120°. Both STO-3G and 4-31G calculations are in good agreement.

The STO-3G method similarly predicts three rotational minima for vinylcyclobutane (Figure 2). Again an s-trans ground state is found, but this time the gauche structure (2.0 kcal/mol above the s-trans form) is favored by 0.3 kcal/mol over the s-cis form with a considerable (0.7 kcal/mol) barrier between the two. Unfortunately, the molecule is too large to be considered at the 4-31G level at this time, but based on our experiences with vinylcyclopropane one might expect a deepening of the gauche well at the expense of the s-cis minimum.

Substituent Effects on the Potential to Internal Rotation

Vinylcyclopropane. Figures 3 and 4 summarize the predicted effects of "typical" π-acceptor (F) and π-donor (CN) substituents, upon the potential to internal rotation in vinylcyclopropane. Both 2-fluoro and 1-cyano substitution, which polarize the vinyl π system in the manner[13] seen in A, lead to a flattening of the gauche minimum and hence a tendency for the molecules to adapt a twofold rotational barrier. When the positioning of the substituents is reversed and an opposite polarization noted (B), the gauche minimum is deepened at the expense of the other two, especially the s-cis structure. In both cases the cyano substituent is the more influential.[25] Although no experimental barrier determinations exist for substituted vinylcyclopropanes the observed trends are not at all unexpected. Thus cyclopropanecarboxyaldehyde (C) possesses a significant

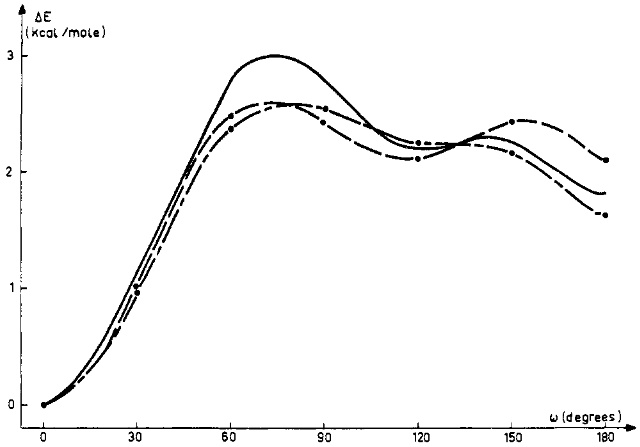


Figure 3. Potential for internal rotation in fluoro-substituted vinylcyclopropanes: (———) vinylcyclopropane; (- - - -) 1-fluorovinylcyclopropane, $E(0) = -289.06199$ hartrees; (— — —) 2-fluorovinylcyclopropane, $E(0) = -289.06561$ hartrees.

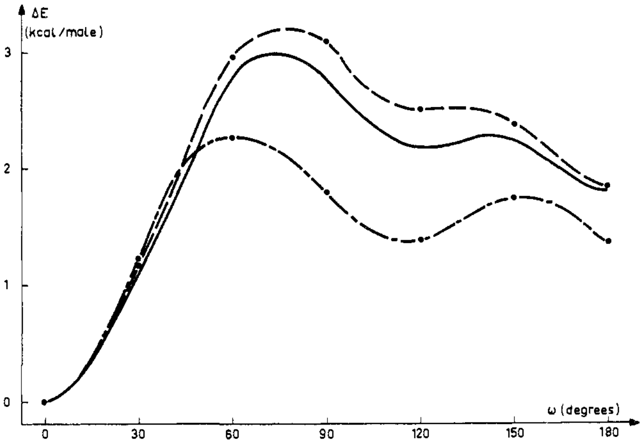
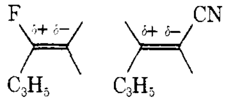
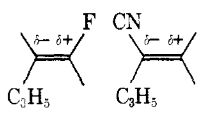


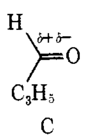
Figure 4. Potential for internal rotation in cyano-substituted vinylcyclopropanes: (———) vinylcyclopropane; (- - - -) 1-cyanovinylcyclopropane, $E(0) = -282.16008$ hartrees; (— — —) 2-cyanovinylcyclopropane, $E(0) = -282.15623$ hartrees.



A



B



C

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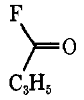
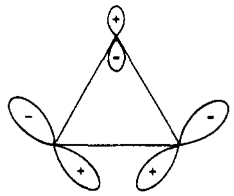
[25] This trend is opposite that noted in theoretical studies on a variety of alkyl cations: L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 92, 6987 (1970); L. Radom, J. A. Pople, and P. v. R. Schleyer, *ibid.*, in press.

twofold rotational barrier (4.4 kcal/mol),[26] while the corresponding barrier in cyclopropanecarboxylic acid fluoride (D), in which the charge polarization in the

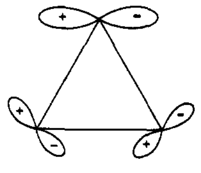


D

π system would be expected to be greater still, has increased to 5.2 kcal/mol.[27] The observed effects may easily be rationalized with the aid of a model recently proposed by Hoffmann and Davidson.[28] Following their argument we consider the interaction of a p orbital of unspecified occupation with the highest occupied e′ orbitals of cyclopropane structures IV and V.



IV



V

In the bisected conformation[29] (left-hand side of Figure 5) the antisymmetric component of the cyclopropane e′ orbital, structure V, interacts strongly with the p function leading to a significant energy splitting. The symmetric component, structure IV, remains unaffected. The situation is reversed but considerably subdued when the methylene group is twisted 90° into an eclipsed conformation (right-hand side of Figure 5). Here the antisymmetric e′ component of structure V is unaffected while the symmetric function of structure IV overlaps and interacts only slightly with the p orbital. In the case of a zero (or nearly zero) p occupation this argument leads to a clear preference for a bisected conformation. Experimental[30,31] and theoretical[32] studies on cyclopropylcarbinyl-like systems are in strong agreement. As the electron population of the p orbital increases the model predicts increasing destabilization of the bisected conformation relative to the eclipsed form. Thus, cyclopropylcarbinyl[33,34] and related[35] free radicals might be expected to exhibit little conformational preference while cyclopropylcarbanion (where the p orbital is now formally doubly occupied) probably exists in an eclipsed geometry.[36]

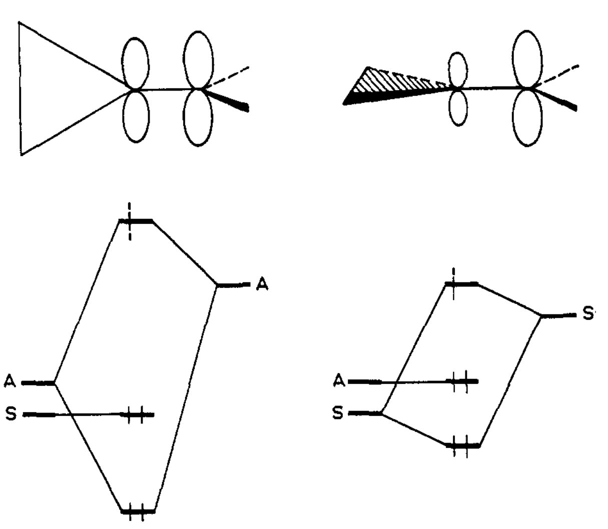


Figure 5. Interaction of the e′ orbitals of cyclopropane with an external p orbital in the bisected (left) and perpendicular (right) conformations. Symmetry labels S and A refer to the plane perpendicular to the cyclopropane ring (following Hoffmann and Davidson, ref 28).

Vinylcyclobutane. Theoretical energy data for the fluoro- and cyano-substituted vinylcyclobutanes are presented in Figures 6 and 7. The behavior noted here is markedly different from that found in the substituted vinylcyclopropanes and is seemingly in conflict with the notions recently put forth by Hoffmann and Davidson.[28] The substitution by fluorine preferentially (but only very slightly) lowers the energy of the gauche conformer, while equivalent substitution by cyano has the opposite effect. It should be noted that, although these substitution patterns are exactly opposite to those found for vinylcyclopropane, they are too small to allow us to draw any firm conclusions. Perhaps more important are the interesting effects of 2 substitution. Indeed, substitution here either by the π-accepting fluorine atom or the donating cyano group produces the same effect, that of destabilizing the gauche conformer relative to the other two and accordingly an increased tendency for a twofold rotational potential. Closely paralleling the studies of Hoffmann and Davidson we consider the interaction between the valence

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(26) H. N. Volltrauer and R. H. Schwendeman, *J. Chem. Phys.*, **54**, 260 (1971). Note that an electron diffraction study of methylcyclopropanecarboxyaldehyde assigns 20% of the molecules to *gauche* conformers: L. S. Bartell, J. P. Guillory, and A. T. Parks, *J. Phys. Chem.*, **69**, 3043 (1965). Analysis of the microwave spectrum fails, however, to turn up any evidence for this structure: P. J. Lee and R. H. Schwendeman, *J. Mol. Spectrosc.*, **41**, 84 (1972).

(27) H. N. Volltrauer and R. H. Schwendeman, *J. Chem. Phys.*, **54**, 268 (1971).

(28) R. Hoffmann and R. B. Davidson, *J. Amer. Chem. Soc.*, **93**, 5699 (1971).

(29) We employ the terms bisected and eclipsed to represent the geometrical relationship of the methylene and cycloalkane. The relationships between the p function and the ring are the opposite.

(30) For a summary of the structural data on cyclopropylcarbinyl and its mono- and dimethyl derivatives, see G. A. Olah, C. L. Jeuell, D. P. Kelly, and R. D. Porter, *J. Amer. Chem. Soc.*, **94**, 146 (1972). Although mono- and dimethylcyclopropylcarbinyl have been established to exist in bisected conformations, this paper questions the assignment of a cyclopropylcarbinyl-like structure to the parent $C_4H_7^+$ system.

(31) The barrier to rotation of dimethylcyclopropylcarbinyl has been directly determined by nmr to be 13.7 kcal/mol: D. S. Kabakoff and E. Namanworth, *J. Amer. Chem. Soc.*, **92**, 3134 (1970).

(32) A complete list of references is given in ref 28. The barrier to rotation in cyclopropylcarbinyl calculated using the STO-3G wave function and molecular geometries optimized for both bisected and eclipsed forms is 26.3 kcal/mol.

(33) Experimentally parent cyclopropylcarbinyl free radical has been shown to exist in a bisected conformation with a barrier to rotation to the eclipsed form of <3 kcal/mol: J. K. Kochi, P. J. Krusic, and D. R. Eaton, *J. Amer. Chem. Soc.*, **91**, 1877, 1879 (1969); P. Krusic, P. Meakin, and J. Jesson, *J. Phys. Chem.*, **75**, 3438 (1971).

(34) STO-3G calculations with partial optimization of molecular geometry predict the bisected form of the cyclopropylcarbinyl free radical to be 1.4 kcal/mol favored over the eclipsed conformation. Unrestricted wave functions were used in these calculations: J. A. Pople and R. K. Nesbet, *J. Chem. Phys.*, **22**, 591 (1954).

(35) N. L. Bauld, J. D. McDermed, C. E. Hudson, Y. S. Rim, J. Zoeller, Jr., R. D. Gordon, and J. S. Hyde, *J. Amer. Chem. Soc.*, **91**, 6666 (1969).

(36) No direct experimental evidence appears to exist. See, however, ref 31. STO-3G calculations with partial optimization of molecular geometry predict a threefold rotational potential for the cyclopropyl carbanion, the most stable form being eclipsed. The CH_2^- group is significantly puckered in all conformations.

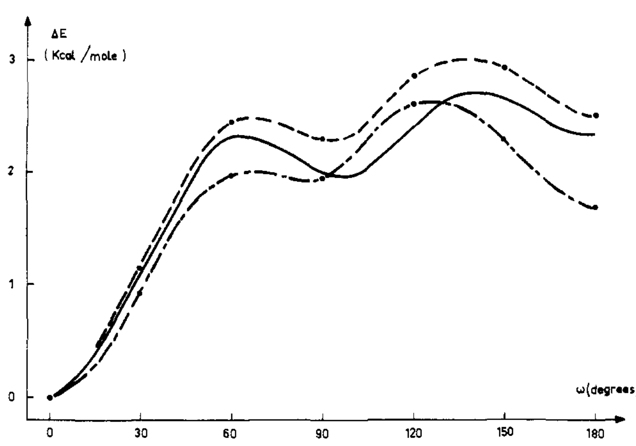


Figure 6. Potential for internal rotation in fluoro-substituted vinylcyclobutanes: (———) vinylcyclobutane; (- - - -) 1-fluorovinylcyclobutane, $E(0) = -327.66723$ hartrees; (— — —) 2-fluorovinylcyclobutane, $E(0) = -327.67084$ hartrees.

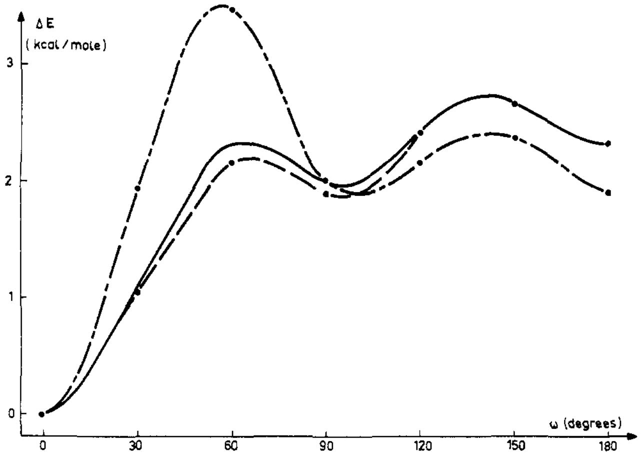


Figure 7. Potential for internal rotation in cyano-substituted vinylcyclobutane: (———) vinylcyclobutane; (- - - -) 1-cyanovinylcyclobutane, $E(0) = -320.76504$ hartrees; (— — —) 2-cyanovinylcyclobutane, $E(0) = -320.76205$ hartrees.

orbitals of cyclobutane[37] and an adjacent p function again of unspecified occupation. As pointed out by Hoffmann and Davidson, the degree of interaction between the cyclobutane valence functions and the p orbital is not expected to be greatly different in the two conformations. Thus, while a bisected arrangement is conducive to interaction of the p with the antisymmetric cyclobutane component, structure VI, a similar degree of interaction is expected to occur with the symmetric component, structure VII, in an eclipsed conformation. One might, however, expect slightly more interaction between the p orbital and the antisymmetric cyclobutane component in the bisected conformation than between the p and the corresponding symmetric function in an eclipsed arrangement. This is simply because the symmetric cyclobutane component would have some 2s character (at the position of substitution) thus reducing the effectiveness of the π–π overlap.[38]

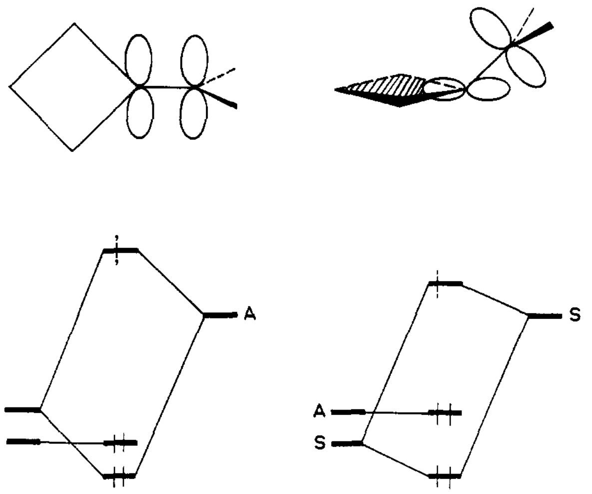
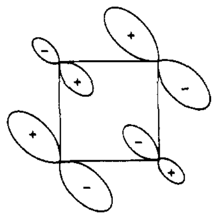
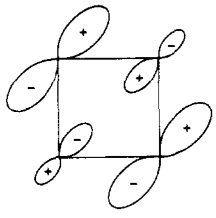


Figure 8. Interaction of the valence orbitals of cyclobutane with an external p orbital in the bisected (left) and perpendicular (right) conformations. Symmetry labels S and A refer to the plane perpendicular to the cyclobutane ring (following Hoffmann and Davidson, ref 28).



VI



VII

This argument leads to the interaction diagram given in Figure 8 and to the prediction, as was the case with the cyclopropyl systems, that small p-orbital populations (cationic and radical centers) lead to bisected conformations while increasing the electron density on p leads to a favoring of eclipsed arrangements. While the model cyclobutylcarbinyl system would appear to faithfully follow these predictions,[39] our data on substituted vinylcyclobutanes are not entirely in agreement. Although 2-fluoro substitution (leading to a building of positive charge on the carbon adjacent to the ring) results in a preferential stabilization of the bisected conformers, equivalent substitution by the strong π donor, cyano, does not reverse this trend, as our model would suggest. It is possible that steric effects are involved (note also the significant increase in the barrier to s-trans-gauche interconversion) and the matter warrents further consideration.

Interaction Energies

In order that we might obtain a more quantitative picture of the degree of interaction between the small ring molecules and the vinyl group, relative to the interactions between vinyl and formally saturated or unsaturated molecules, we consider the energies of the isodesmic processes.[40]

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(37) These have been constructed in numerous manners, and the pertinent references are summarized by Hoffmann and Davidson, ref 28. See, also, J. S. Wright and L. Salem, *J. Amer. Chem. Soc.*, **94**, 322 (1972). We shall consider the representation given by Hoffmann and Davidson.

(38) The author acknowledges and thanks Professor R. Hoffmann (Cornell) for this interesting observation.

(39) Indeed, the STO-3G method predicts bisected cyclobutylcarbinyl to be favored over the eclipsed form, but only by 2.1 kcal/mol, while the eclipsed cyclobutyl carbanion is found to possess a threefold rotational potential with gauche and eclipsed conformations being nearly equal in energy. The cyclobutylcarbinyl free radical has a slight preference for a bisected conformation. For related theoretical studies see ref 25.

(40) W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 4796 (1970); L. Radom, W. J. Hehre, and J. A. Pople, *J. Chem. Soc. A*, 2299 (1971).

Table I. Interaction Energies[a]

	Reaction	Energy, kcal/mol[b]
I	$\mathrm{\overline{CH_2CH_2C}HCH{=}CH_2 + CH_4 \rightarrow \overline{CH_2CH_2CH_2} + CH_3CH{=}CH_2}$	3.5 [3.2]
II	$\mathrm{\overline{CH_2CH_2C}HCH{=}CHF + CH_4 \rightarrow \overline{CH_2CH_2CH_2} + CH_3CH{=}CHF}$	3.3
III	$\mathrm{\overline{CH_2CH_2C}HCH{=}CH(CN) + CH_4 \rightarrow \overline{CH_2CH_2CH_2} + CH_3CH{=}CH(CN)}$	3.6
IV	$\mathrm{\overline{CH_2CH_2C}HCF{=}CH_2 + CH_4 \rightarrow \overline{CH_2CH_2CH_2} + CH_3CF{=}CH_2}$	3.6
V	$\mathrm{\overline{CH_2CH_2C}HC(CN){=}CH_2 + CH_4 \rightarrow \overline{CH_2CH_2CH_2} + CH_3C(CN){=}CH_2}$	2.7
VI	$\mathrm{\overline{CH_2CH_2CH_2C}HCH{=}CH_2 + CH_4 \rightarrow \overline{CH_2CH_2CH_2CH_2} + CH_3CH{=}CH_2}$	1.7
VII	$\mathrm{\overline{CH_2CH_2CH_2C}HCH{=}CHF + CH_4 \rightarrow \overline{CH_2CH_2CH_2CH_2} + CH_3CH{=}CHF}$	1.7
VIII	$\mathrm{\overline{CH_2CH_2CH_2C}HCH{=}CH(CN) + CH_4 \rightarrow \overline{CH_2CH_2CH_2CH_2} + CH_3CH{=}CH(CN)}$	1.9
IX	$\mathrm{\overline{CH_2CH_2CH_2C}HCF{=}CH_2 + CH_4 \rightarrow \overline{CH_2CH_2CH_2CH_2} + CH_3CF{=}CH_2}$	2.0
X	$\mathrm{\overline{CH_2CH_2CH_2C}HC(CN){=}CH_2 + CH_4 \rightarrow \overline{CH_2CH_2CH_2CH_2} + CH_3C(CN){=}CH_2}$	1.5
XI	$\mathrm{CH_3CH_2CH{=}CH_2 + CH_4 \rightarrow CH_3CH_3 + CH_3CH{=}CH_2}$	−1.2 [0.1] (2.6)
XII	$\mathrm{CH_2{=}CHCH{=}CH_2 + CH_4 \rightarrow CH_2{=}CH_2 + CH_3CH{=}CH_2}$	5.8 [7.1] (8.9)

[a] Single bond conformations: vinylcyclopropane and vinylcyclobutane molecules, s-trans; 1-butene, gauche; 1,3-butadiene, trans. Following our practice for the substituted vinylcycloalkane systems only trans 1-substituted propenes are considered. Theoretical STO-3G energies for methane, ethane, ethylene, propene, and cyclopropane, ref 8; for cyclobutane, ref 9; for 1-butene and 1,3-butadiene, ref 4; for the fluoro- and cyano-substituted propenes, we have used the optimum STO-3G geometry of the parent (ref 8) and have attached standard fluoro and cyano groups thus paralleling our procedure for the specification of the geometries of the substituted vinylcycloalkanes. STO-3G energies as follows: *trans*-1-fluoropropene, −213.11742; *trans*-1-cyanopropene, −206.21498; 2-fluoropropene, −213.12060; 2-cyanopropene, −206.21269. Theoretical 4-31G energies for methane, ethane, ethylene, propene, and cyclopropane, ref 8; for 1-butene and 1,3-butadiene, ref 9. [b] STO-3G except: [ ], 4-31G; ( ), experimental, computed from heats of formation at 298°K [S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969)].

$$\mathrm{\overline{CH_2CH_2C}HCH{=}CH_2 + CH_4 \longrightarrow \overline{CH_2CH_2CH_2} + CH_3CH{=}CH_2}$$

$$\mathrm{\overline{CH_2CH_2CH_2C}HCH{=}CH_2 + CH_4 \longrightarrow \overline{CH_2CH_2CH_2CH_2} + CH_3CH{=}CH_2}$$

$$\mathrm{CH_3CH_2CH{=}CH_2 + CH_4 \longrightarrow CH_3CH_3 + CH_3CH{=}CH_2}$$

$$\mathrm{CH_2{=}CHCH{=}CH_2 + CH_4 \longrightarrow CH_2{=}CH_2 + CH_3CH{=}CH_2}$$

Previous studies have shown that we might expect the heats of reactions such as these to be adequately described by single-determinant molecular orbital theory using only a minimal basis set.[40] It may easily be seen that the cyclopropane and cyclobutane rings (entries I and VI in Table I) stabilize vinyl to a degree intermediate between that of a formally saturated molecule, ethane, and an unsaturated one, ethylene (entries XI and XII). As could be anticipated, the stabilization due to cyclopropane is larger than that due to cyclobutane. Also of interest in Table I are the effects of substituents on vinyl on the interaction energies.[41] The pattern is quite regular and the two small rings behave in an identical manner. The 1 substitution by fluorine decreases the energy of interaction while corresponding 2 substitution leads to an increased degree of interaction. Substitution by cyano reverses the pattern.

Conclusion

From the research described in this paper the following conclusions may be made.

1. In accordance with available spectroscopic evidence, *ab initio* molecular orbital theory using the STO-3G minimal basis set predicts vinylcyclopropane and vinylcyclobutane to have s-trans rotational conformations in their respective ground states. In addition, each molecule is found to possess two additional rotational minima, corresponding to s-cis and gauche conformers. Calculations on vinylcyclopropane using the 4-31G extended basis set substantiate the assignment of a s-trans ground state and strengthen the case for a secondary gauche minimum. They uncover, however, no evidence for an additional s-cis minimum.

2. Substituents which lead to a buildup of positive charge on the π system of the 2 carbon in vinylcyclopropane lead to a shallowing of the gauche minimum. Substituents leading to increased negative charge have the opposite effect. The only significant substituent effects observed for vinylcyclobutane increase the tendency for a twofold rotational potential.

3. Both the cyclopropyl and cyclobutyl rings interact with ethylene to a degree between that characteristic for formally saturated and unsaturated substituents.

Acknowledgments. The comments and criticism of two diligent referees and of Professor Roald Hoffmann (Cornell) are gratefully acknowledged.

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(41) The effects of substituents on the rotational potentials in vinylcyclopropane and vinylcyclobutane (Figures 3, 4, and 6 and 7, respectively) might alternatively have been displayed in a manner in which the base lines were adjusted to take account of the relative stabilities of the ground-state conformers. Thus, considering Figure 3, for example, the curve for 1-fluorovinylcyclopropane might be displaced 0.2 kcal/mol up in energy (relative to the unsubstituted parent) while that for the 2-fluoro system pushed down by 0.1 kcal/mol.