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APPLICATION OF THE POPLE-SANTRY-SEGAL CNDO METHOD TO THE CYCLOPROPYLCARBINYL AND CYCLOBUTYL CATION AND TO BICYCLOBUTANE[1]

K. B. WIBERG

Department of Chemistry, Yale University, New Haven, Connecticut

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Abstract—The CNDO method has been applied to the cyclopropylcarbinyl and cyclobutyl cations, and has given results which are in very good accord with experimental data. A cross-ring interaction is calculated to be of importance with cyclobutyl derivatives, and agrees with the large difference in rate observed with equatorial and axial leaving groups. Some properties of bicyclobutane as well as the relative energies for some models of the activated complex for the thermal rearrangement of bicyclobutane have also been calculated and compared with experimental data. The CNDO method appears to have considerable promise in the investigation of organic chemical phenomena.

MUCH of the recent progress in the study of unsaturated organic molecules has its origin in the MO calculations based on the π-electron approximation. A similar treatment of saturated compounds would allow an examination of a wider range of phenomena. A number of approaches to such a treatment have been suggested.[2–5] One of them, the extended Hückel method, has been very successfully applied by Hoffmann to a variety of organic chemical problems,[6] and provides the theoretical basis for the Woodward–Hoffmann rules for electrocyclic and related reactions.[7]

The extended Hückel method has a major drawback in that it is a one electron approximation. Recently, Pople *et al.*[4,5] have developed an approximate SCF treatment (CNDO-complete neglect of differential overlap) which has the virtue of being independent of the coordinate system used. This paper will explore the application of the CNDO method to the cyclopropylcarbinyl-cyclobutyl cation problem, and to the properties and thermal rearrangement of bicyclobutane.

The CNDO treatment begins with extended Hückel molecular orbitals derived from the 2*s* and 2*p* atomic orbitals on carbon and the 1*s* atomic orbital on hydrogen. The proper linear combinations of these orbitals are obtained by constructing and diagonalizing the Hückel secular determinant in which the on-diagonal elements are the average ionization potentials and the off-diagonal elements are made proportional to the overlap integral between the atomic orbitals. The bond orders and electron densities are calculated using the occupied molecular orbitals, and from this the approximate Hartree–Fock matrix is constructed in a fashion similar to that previously used by Pople for π-electronic systems.[8] Diagonalization of the latter leads to a new set of molecular orbitals. The procedure is repeated until there is no longer a significant change in the coefficients.

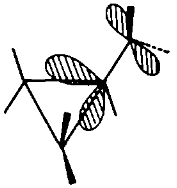
The hybridization at a given carbon is not specified at the beginning of the calculation; only the coordinate of the atoms, the average ionization potential of each type of atomic orbital used, the core charge, the β proportionality constant, and the exponent for the Slater type atomic orbital are required. The values used are summarized in Table 1. The final hybridization is determined by the geometry initially supplied and by the difference in the above parameters between 2*s* and 2*p* orbitals.

TABLE 1. PARAMETERS USED IN CNDO CALCULATIONS

Orbital	Average ionization potential	Core charge	Slater exponent	β proportionality constant
C, 2*s*	14·051	4	1·625	21.
C, 2*p*	5·572	4	1·625	21.
H, 1*s*	7·1761	1	1·2	9.

A. *Cyclopropylmethyl and cyclobutyl cations*

The structure and energy of the cyclopropylmethyl cation has received much attention in the recent literature,[9, 10] and has been considered by Hoffmann using the extended Hückel theory.[6] All of these results are in accord with the "bisected" structure as the more stable, the stabilization being derived from overlap between the empty *p* orbital and the C—C bond orbitals of the cyclopropane ring:



A fairly large barrier to rotation of the carbinyl carbon is suggested by the NMR data of Olah *et al.*[9]

The energies required for the removal of a hydrogen atom and an electron from a series of hydrocarbons have been calculated by the CNDO method, giving the results in Table 2.* The energies for forming the methyl, ethyl, 2-propyl and t-butyl cations from the hydrocarbons fall in a reasonable order and provide a guide for interpreting the following entries. With the isobutyl, cyclopropylmethyl and cyclobutyl cations, two conformations are possible. One corresponds to the conformation of the cyclopropylcarbinyl cation described above (out of plane or bisected) and the other has the plane of the CH_2 group roughly parallel to that of the rest of the molecule (referred to as "in plane").

The calculated difference in energy between the two conformations is large for cyclopropylmethyl, much smaller for cyclobutylmethyl and quite small for the isobutyl cation. The *in plane* conformation for the cyclopropylmethyl cation is

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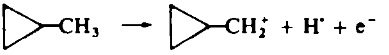
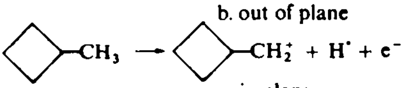
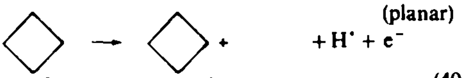
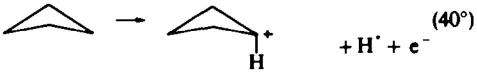
* The parameters used by Pople *et al.*[4, 5] lead to somewhat short equilibrium C—C bond lengths (1·44 Å). In the calculations reported herein, the experimental bond lengths and angles were used whenever possible; analogous values were chosen when experimental data were not available. This approach has been used by Hoffmann in his extended Hückel calculations. For the cyclopropane ring, r(C—C) was 1·53 Å and r(C—H) was 1·09 Å, for the bond to a methyl group, r(C—C) was 1·54 Å, and in a methyl group, r(C—H) was 1·11 Å. The HCH bond angle in cyclopropane was taken as 116°, and for cyclobutane it was taken as 114°. The C—C bond length in cyclobutane was 1·55 Å, and the other C—C lengths were taken as 1·54 Å.

TABLE 2. ENERGIES OF FORMATION OF SOME CATIONS*

Reaction			ΔE(a.u.)	
CH_4	→	$CH_3^+ + H^\cdot + e$	0·9190	
C_2H_6	→	$CH_3CH_2^+ + H^\cdot + e^-$	0·8230	
C_3H_8	→	$CH_3\overset{+}{C}HCH_3 + H^\cdot + e^-$	0·7559	
$i\text{-}C_4H_{10}$	→	$t\text{-}C_4H_9^+ + H^\cdot + e^-$	0·7004	
$i\text{-}C_4H_{10}$	→	$i\text{-}C_4H_9^+ + H^\cdot + e^-$		
		a. in plane	0·8045	$\Delta\Delta E = 0·0061$
		b. out of plane	0·7984	
				
		a. in plane	0·8178	$\Delta\Delta E = 0·0400$
		b. out of plane	0·7778	
				
		a. in plane	0·8016	$\Delta\Delta E = 0·0118$
		b. out of plane	0·7896	
		(planar) $+H^\cdot + e^-$	0·8124 (tetrahedral) 0·7651 (trigonal)	
		(40°) $+H^\cdot + e^-$	0·8539	
		(40°) $+H^\cdot + e^-$	0·7764	

* Although the energies are calculated in a.u., the values obtained using the CNDO method are invariably too large by a factor of about 3. A detailed comparison of calculated and observed energies will be made elsewhere.

predicted to be destabilized in comparison to the isobutyl cation, whereas the *out of plane* conformation is predicted to have a considerably lower energy than the isobutyl cation. The latter result is in good agreement with experiment and with previous calculations.

It is interesting that whereas the *in plane* conformation of the cyclobutylmethyl cation is calculated to have about the same energy as the isobutyl cation, the *out of plane* conformation is predicted to have a significantly lower energy. It is, however, difficult to test this prediction since rearrangement to a cyclopentyl cation would give a secondary ion and relieve 20 kcal/mole of ring strain.

A comparison of the results obtained by the extended Hückel method and the CNDO method is shown in Fig. 1. It is valuable first to consider the results for methylcyclopropane. The extended Hückel method generally gives exaggerated charge distributions, in contrast to the CNDO method which predicts relatively small charge separation.* The same is true in the present case.

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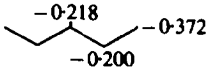
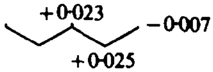
* For example, the carbon charges for n-pentane by the two methods are:

Extended Hückel[6]



CNDO



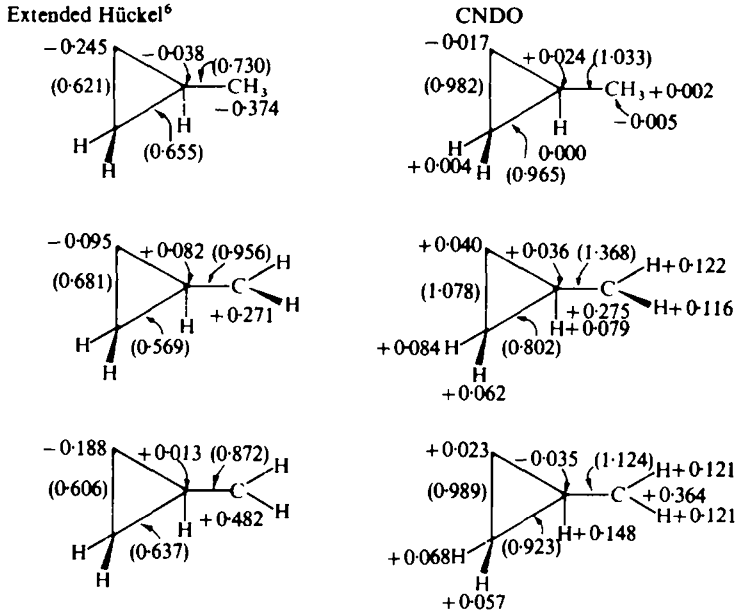


FIG. 1. Comparison of the results obtained using the extended Hückel and CNDO methods. The charge densities are given as signed numbers; the overlap populations for the extended Hückel method and the bond indices for the CNDO method are given in parentheses.

The bond populations given for the extended Hückel calculation are those derived by the method of Mulliken.[11] In the case of the CNDO results, the values given are the sum of the squares of the bond orders between the atoms in question. This sum of squares, which we should like to call "bond indices" appear to be closely related to the bond character.*

If the change in parameters on going from the hydrocarbon to the ion is compared for the two calculations, it is seen that the results are in good agreement. The *in plane* conformation has a relatively small change in bond index to the carbinyl carbon, and a relatively small transfer of charge into the cyclopropane ring as compared to the *out of plane* conformation. For the latter, the C_1—C_2 bond index is markedly reduced whereas the C_2—C_3 bond index increases.*

The results are in accord not only with the structural data on the cyclopropyl-

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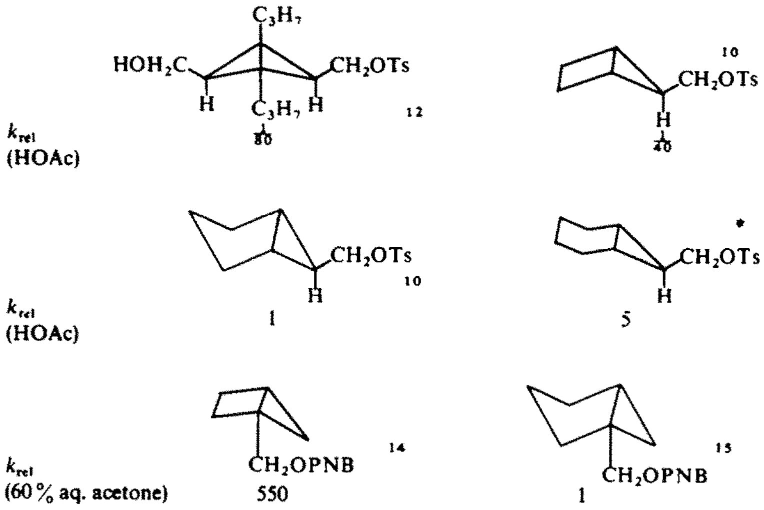
* The sum of the squares of the bond orders (p_{jk}) between any one atomic orbital and all other orbitals in a molecule can be shown by a derivation similar to that given by L. Salem, *Molecular Orbital Theory of Conjugated Systems*, p. 39. W. A. Benjamin, New York (1966), to be two times the charge density in that orbital (p_{jj}) less the square of the charge density:

$$\sum_k p_{jk}^2 = 2p_{jj} - p_{jj}^2.$$

For a unit charge density, the value is 1 whereas it goes to zero for $p_{jj} = 2$ (a non-bonded pair) or for $p_{jj} = 0$ (an empty orbital). Correspondingly, the sum of the squares of the bond orders to an atom corresponds to the number of covalent bonds formed by that atom, corrected for the ionic character in each bond.

carbinyl ion, but also with the effect of bridging the cyclopropane ring with a second ring. Some significant data are:



With the 2,3-bridged compounds, the normal trend is toward slightly lower rates when the bridging ring is decreased in size. The calculations predict an increase in the 2,3 bond index, which should result in a decrease in the 2,3-bond length. If such a change in bond length occurred, the strain energy would increase for the smaller bridging ring and should lead to a small decrease in the rate of reaction.

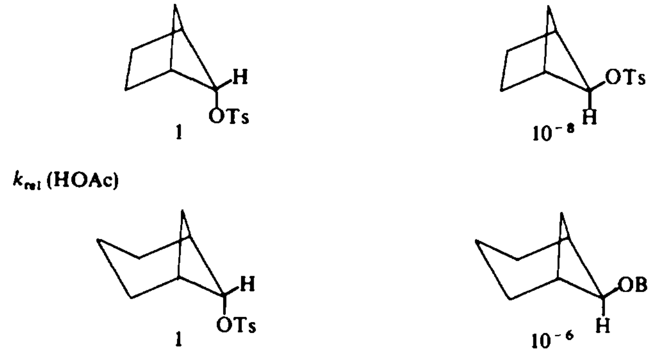
With the 1,2-bridged compounds, a decrease in ring size leads to a marked increase in rate. The calculations predict a considerable decrease in the 1,2 bond order on going to the cation, which should lead to an increase in bond length and a relief of strain for the smaller ring. This may, of course, not be the only effect contributing to the changes in rate constant, but it is in the correct direction.

The energy of the cyclobutyl cation also was calculated. The planar conformation with a trigonal cationic center was calculated to be slightly destabilized with respect to the 2-propyl cation as would be expected. However, the trigonal cation may not be a good model for the activated complex formed in the solvolysis of a cyclobutyl derivative. Bonding to the leaving group will still be important in the activated complex, and so, an ion with a tetrahedral arrangement about the cationic center might be a better model.

The energy of a cyclobutyl cation with a puckered conformation (as found in cyclobutane itself) and a tetrahedral cationic center was found to be dependent on the orientation of the empty orbital. The structure derived from an equatorial leaving

* Estimated from data on 3,5-dinitrobenzoates.[13]

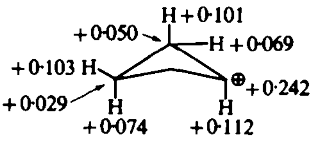
group was calculated to have considerably lower energy than one derived from an axial leaving group.* This is in good accord with our experimental results:[17]

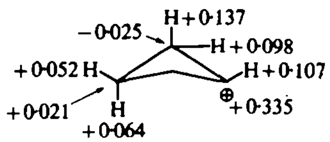


A marked difference in reactivity is noted and the isomer with the equatorial tosylate group is in each case the more reactive one.

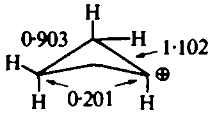
The calculated charge densities and bond indices for the two conformations are summarized below:

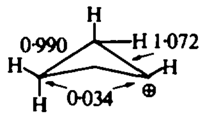
Charge densities





Bond indices





It can be seen that the equatorial leaving group leads to a cation which has a large cross-ring bond index, and a better charge distribution than the other cation. The cross-ring bond index results largely from a $2p$–$2p$ interaction, and thus involves the cationic orbital and the p-component of the cross ring C—H bond orbital to the equatorial hydrogen. Correspondingly, considerable charge is transferred to this hydrogen.

The interaction referred to above leads to what might be described as a symmetrical bicyclobutonium ion (as contrasted to the unsymmetrical ion proposed by Roberts and his co-workers).[18] Such an ion (or at least an activated complex) leads to a ready explanation of a variety of observations concerning the solvolytic reactivity of cyclobutyl derivatives. For example, Wilcox and Nealy[19] have shown that *trans*-3-hydroxy-2,2,4,4-tetramethylcyclobutyl tosylate is 800 times as reactive as the *cis*-isomer, and is about as reactive as 2,2,4,4-tetramethylcyclobutyl tosylate. The decreased reactivity of the *cis*-isomer may result from the introduction of the electron

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* The same conclusions have been reached using the extended Hückel method.[16]

withdrawing hydroxy group into the cross ring equatorial position which interacts strongly with the developing cationic center.

TABLE 3. BOND INDICES AND CHARGES

Compound	Hydrogen	Charge	Bond indices 1s–2s ⟶	 1s–2p	$J_{C_{13}-H}$
Propane	CH_2	0·998	0·220	0·739	123
Cyclobutane	equatorial	1·024	0·237	0·724	
	axial	0·995	0·265	0·700	134[a]
Cyclopropane		0·995	0·288	0·680	161
Bicyclobutane	exo	1·009	0·283	0·686	152
	endo	1·014	0·301	0·663	170
	bridgehead	0·979	0·366	0·600	203

Compound	C–C bond	 2s–2s	Bond indices 2s–2p	 2p–2p
Propane		0·067	0·422	0·552
Cyclobutane		0·046	0·389	0·557
Cyclopropane		0·049	0·308	0·629
Bicyclobutane	side	0·050	0·327	0·596
	central	0·037	0·168	0·688

[a] The coupling is averaged over the two hydrogen positions because of the rapid conformation inversion. The 1s–2s bond index for the planar conformation is 0·244.

We should like to be able to make a direct comparison of the calculated energies of the planar and non-planar cyclobutyl cations and the cyclopropylcarbinyl cation. However, in order to do this, it would first be necessary to minimize the energy with respect to structure. This, in turn, requires that the Pople parameters used be adjusted to give the best fit for the ground state structures. The problem of obtaining such parameters is currently under investigation.

B. *Bicyclobutane and its thermal rearrangements*

Bicyclobutane is an unusually interesting hydrocarbon. It has been found to have a dipole moment of 0·7 D[20] which is remarkably high for a saturated hydrocarbon. The bridgehead hydrogens are found to be remarkably acidic, and to have an unusually large C^{13}-H NMR coupling constant.[21] The electronic structure of bicyclobutane has been discussed using two models differing in hybridization,[22,*] but no calculations have been reported.

Using the bond lengths suggested by the microwave data, the energy was calculated as a function of the dihedral angle between the two cyclopropane planes. A 60° angle

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[*] It is unfortunate that the Coulson–Moffitt representation of cyclopropane[23] has been considered as basically different than that of Walsh.[24] Coulson and Moffitt started with 2s and 2p atomic orbitals as the basis functions and calculated the coefficients of the basis functions which led to the lowest energy bond orbitals. Walsh developed a model which used sp^2 hybrid orbitals and p orbitals. However, Walsh did not minimize the energy with respect to hybridization (in fact, he did not calculate the energy). If he did, and both calculations were done correctly using the same method, the final results should be the same.

gave a significantly lower energy than either 50° or 70°, and this is in good accord with the available data.[29] The dipole moment was calculated to be 1·1 D, which again is in good accord with the experimental value.

The calculated data for the C—H bonds of bicyclobutane and other hydrocarbons are summarized in Table 3. The 1*s*–2*s* bond index is higher for the bridgehead protons of bicyclobutane than for any of the other compounds.* In order to see if the 1*s*–2*s* bond indices are correlated with the C^{13}-H NMR coupling constants, a plot of the data was prepared (Fig. 2). It is seen that a good linear relationship is found, and this is in accord with the postulated relationship between the coupling constant and the *s*-character of the bond orbitals.[26]

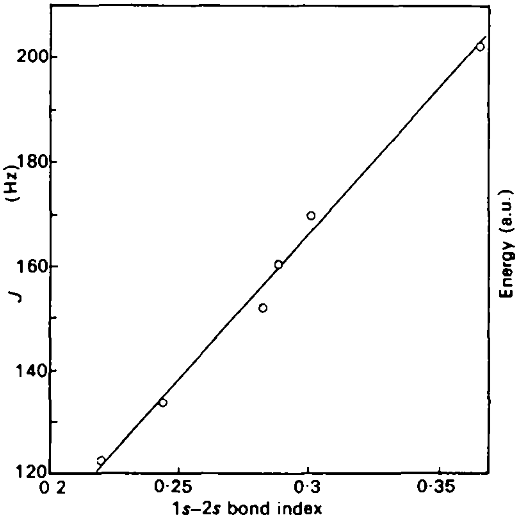

FIG. 2. Correlation of C^{13}-H NMR coupling constants with 1*s*–2*s* bond indices.

The calculations also suggest that the central bond of bicyclobutane has considerably more *p*-character than the C—C bonds of cyclopropane. Consequently, the facile reaction with electrophiles and the reaction with carbenes is not surprising.[27] The large 1*s*–2*s* bond index for the bridgehead protons, coupled with the calculated low electron density, provides a rationale for the acidity of these protons. It can be seen that the CNDO method gives results which are in good accord with the properties of bicyclobutane.

It was then of interest to extend the calculation to the activated complex formed in the thermal decomposition of bicyclobutane to butadiene. The reaction leading directly to butadiene may proceed in any one of six ways. First, the reaction may lead either to *cis*- or *trans*-butadiene as the initial product.

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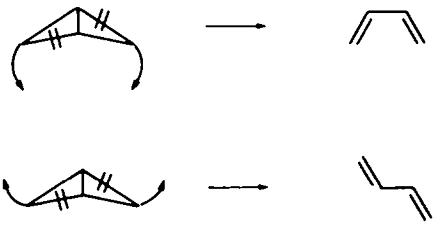
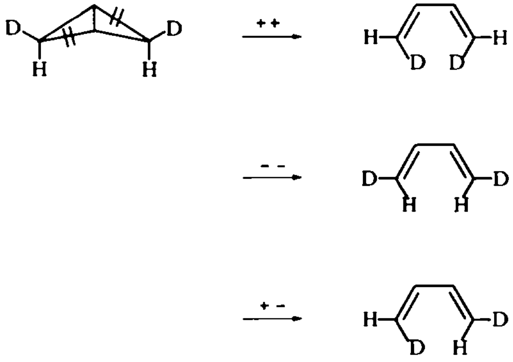
* Just as the sum of the squares of the bond orders to a given orbital gives the bond index, the square of the bond order between two orbitals is related to hybridization. For example, with methane, the 1*s*–2*s* bond order is 0·50 and the 1*s*–2*p* bond order is 0·866, whereas the squares are 0·25 and 0·75 and correspond to the hybridization (sp^3).

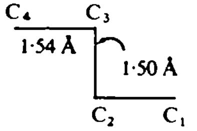


For each of these modes of reaction, the two CH_2 groups may rotate so that the *exo*-hydrogens move toward the bonds being broken (hereafter referred to as + +); they may rotate so that the *exo*-hydrogens move away from the bonds being broken (− −); and they may move so that one hydrogen moves toward and the other away from the bonds being broken (+ −). The geometrical consequences are:



Corresponding results are found for opening to *trans*-butadiene.

Models of the possible activated complexes were constructed as follows. First, the bonds to be broken were stretched from 1·54 Å to 2·15 Å:



Then, the energy was calculated as a function of the C_1–C_2–C_3–C_4 dihedral angle. The change in energy with dihedral angle is shown in Fig. 3, and the corresponding changes in bond indices are shown in Fig. 4. It can be seen that the *trans*-conformation (180°) represents a maximum in energy, and that when the dihedral angle is reduced to a value below that in bicyclobutane (120°), the energy drops rapidly and reaches a minimum with the *cis*-conformation (0°). The product of the reaction, as described above, is, of course, cyclobutene.

The bond index curve shows a smooth transition from a C_2—C_3 single bond to a double bond, with the C_1—C_3 bond index essentially vanishing. Besides indicating the nature of the bonding changes which occur in the reactions, the fact that the bond indices are continuous functions of the dihedral angle indicates that the process is electronically allowed. If there were an interchange of bonding and antibonding orbitals at some point during the change in angle, the curves would be discontinuous. The above result suggests that a possible mechanism for the reaction is one in which

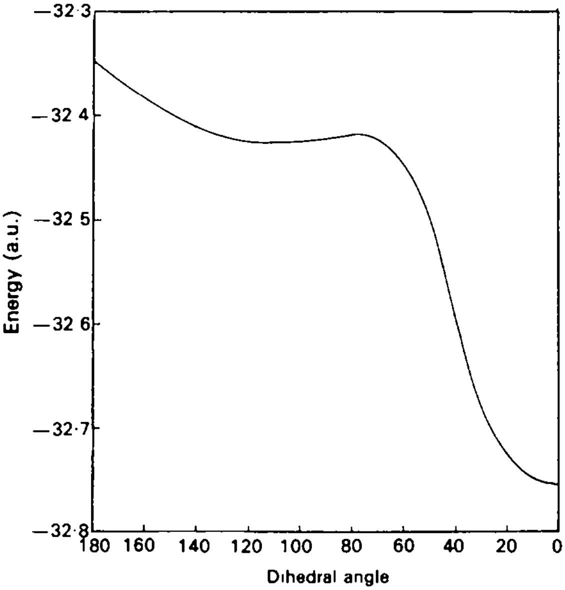


FIG. 3. Effect of dihedral angle on the energy of the model of the activated complex for bicyclobutane isomerization

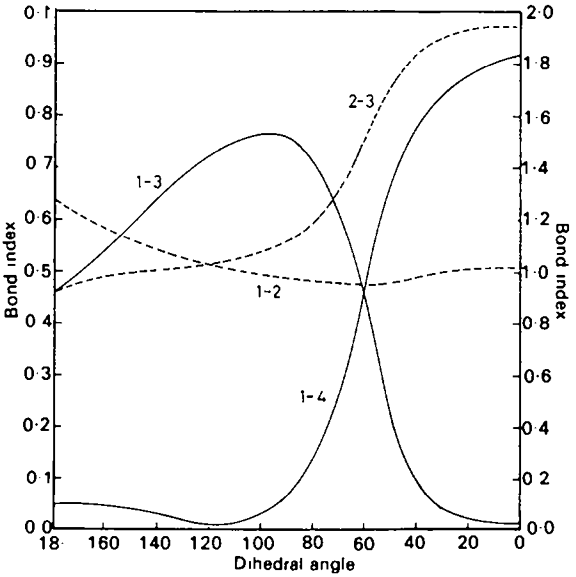
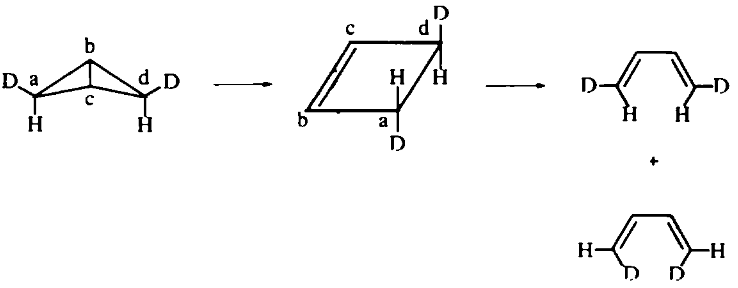


FIG. 4. Effect of dihedral angle on the bond indices for the model of the activated complex for bicyclobutane isomerization. The solid lines refers to the lefthand axis; the dashed lines to the righthand axis.

a vibrationally excited cyclobutene is the initial product, and then rapidly rearranges to butadiene. The geometrical consequences of such a process are:



The rearrangement of the cyclobutene would be expected to be a conrotatory process,[28] and since there is no steric difference between hydrogen and deuterium, the product should be an equal mixture of *cis*- and *trans*-dideuterobutadienes. This would be in accord with our experimental result[29] in which bicyclobutane-2-*exo*-d_1 gave a 1:1 mixture of butadiene-*cis*-1-d_1 and butadiene-*trans*-1-d_1.

The effect of twisting the CH_2 groups was then examined. When a dihedral angle of 150° was used, any direction of twist led to an increase in the calculated energy. Thus, the calculations suggest that the formation of *trans*-butadiene is not a favored process.[*] A dihedral angle of 90° was then chosen and the effect of the three possible modes of CH_2 twist was examined. The + − mode led to a decrease in energy, but the + + and − − modes initially led to an increase in energy. The C_1–C_2 bond index is plotted as a function of the angle of twist in Fig. 5. The + − mode leads to a continuous function of the angle but the + + and − − modes lead to a discontunity indicating that these modes are not allowed.[†] [‡] Thus, a direct reaction leading

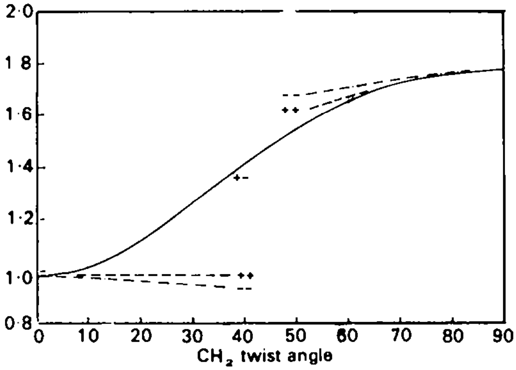


FIG. 5. Effect of CH_2 twist on the C_1–C_2 bond index for a model of the activated complex for bicyclobutane isomerization. The dihedral angle is 90°.

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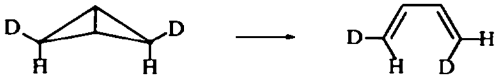
[*] Since only a limited number of models were examined, it is possible that a geometry exists which would favor opening to *trans*-butadiene. However, of the three possible twisting modes, only the + − mode is allowed. The + + and − − modes were shown not to be allowed in the same fashion as later described for opening to *cis*-butadiene.

[†] The same conclusion may be reached in a qualitative way starting with the two bonding π-orbitals of *cis*-butadiene. In the + + and − − modes, one of the π-orbitals will give a bonding orbital whereas the other will give an antibonding orbital. In the + − mode, each of the π-orbitals will give one bonding C—C bond orbital. The simple orbital representation we have earlier[29] should be disregarded for it, among other things, would lead to a *trans*-fused bicyclobutane!

[‡] Corresponding results were obtained when a shorter C_1—C_3 distance of 2·0 Å was used in the calculations.

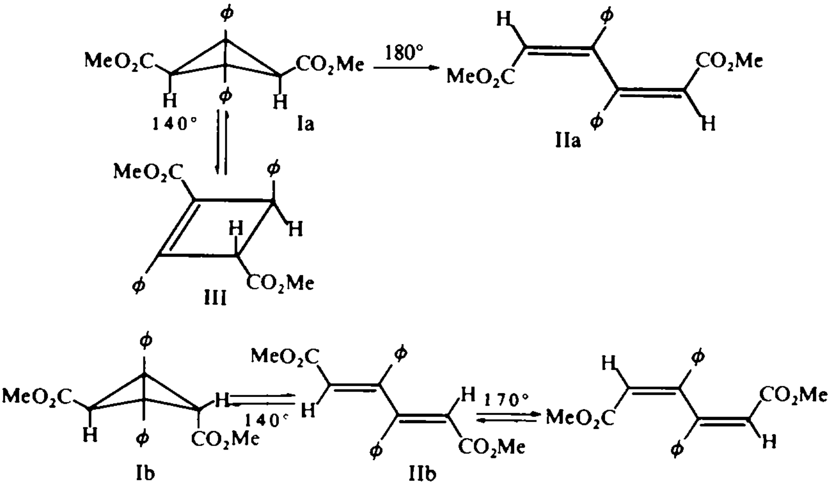
to butadiene would occur as follows:



This, again, is in accord with our experimental findings.[29] It is clear that a study of the rearrangement of bicyclobutane-2,4-d_2 will be required in order to establish the course of the reaction.

Because of the large number of geometrical variables, it is not practical to search out the minimum energy path between bicyclobutane and butadiene. Since the calculations indicate that a decrease in energy may occur with less dihedral angle distortion if the CH_2 group is twisted during the reaction, it appears likely that the lowest energy path is the one which leads directly to *cis*-butadiene.* However, even if this is the case, suitable structural modification may lead to a cyclobutene as an intermediate.

The above conclusions permit a reexamination of the interesting results reported by D'yakonov *et al.*[30] in their study of the thermal rearrangement of a highly substituted bicyclobutane:



Whereas bicyclobutane and 1,3-dimethylbicyclobutane[31] have been shown not to form a cyclobutene during thermal rearrangement, the diphenyl substituted bicyclobutane, Ia, not only gives the cyclobutene III, but the latter is in thermal equilibrium with Ia. This indicates that phenyl substitution has markedly stabilized the bicyclobutane since the rearrangement of bicyclobutane to cyclobutene would be exothermic, by 17 kcal/mole.

The rearrangement of Ia to III would require a mechanism in which the central bond of Ia is opened to a diradical, which then undergoes a hydrogen migration to give III. It might be reasoned that phenyl substitution would stabilize the intermediate diradical and permit a mode of reaction which is not realized with bicyclobutane.

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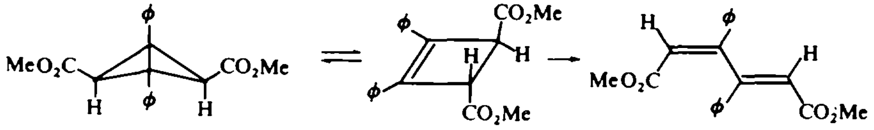
* The conversion of bicyclobutane to cyclobutene has ΔH = −16 kcal/mole whereas the reaction to butadiene has ΔH = −27 kcal/mole. Thus, the energetics of the reaction also favor the direct process.

However, it should be noted that the NMR spectrum reported for III is unusual and corresponds to a more symmetrical structure. It is tempting to postulate that the product is actually IV, formed by the process suggested by the CNDO calculations:



Ia IV IIa

The product obtained at a higher temperature, IIa, is the one which would be expected from the normal conrotatory ring opening of IV. The reaction could lead either to the *cis-cis* or *trans-trans* isomer (IIb or IIa). The latter is the more stable and presumably is therefore formed.

The rearrangement of Ib to IIb does not appear to involve a cyclobutene intermediate (at least none was found under the conditions employed for Ia). If the reaction proceeded directly to a butadiene, it should involve the + – mode of methylene rotation. The observed product, IIb, corresponds to this prediction. A further electronic effect must also be operative, since the product is the less stable of the two isomers which could be formed via the + – mode of reaction.

EXPERIMENTAL

The calculations described above were carried out using the program written by G. A. Segal[5] which was made available through the Quantum Chemistry Program Exchange at Indiana University. The matrix diagonalization subroutine in this program was found not to be satisfactory with some of the matrices involved in these calculations, and was replaced by the M.I.T. subroutine HDIAG. Also, the program was modified so that the bond indices were calculated.

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