

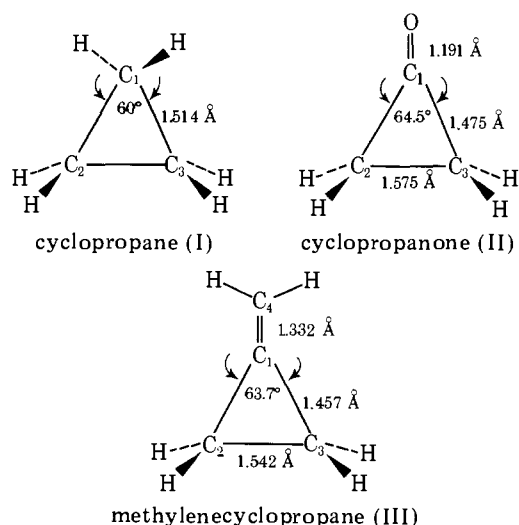
# Bond Length Changes Resulting from Substitution and Ring Opening in Three-Membered Systems

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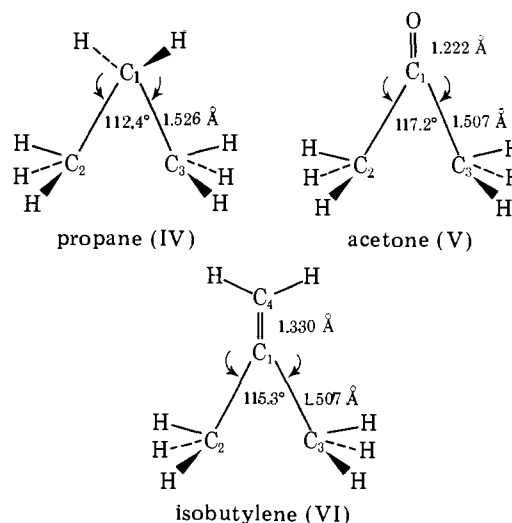
**Abstract:** Substituents on cyclopropane are known to alter the bond lengths in the cyclopropane ring. In particular, oxygen and methylene both shorten the adjacent ( $C_1-C_2$  and  $C_1-C_3$ ) bonds and lengthen the opposite ( $C_2-C_3$ ) bond, the oxygen substituent shortening the adjacent bonds less and lengthening the opposite bond more. It is known also that forming the cyclopropane ring shortens the  $C=O$  bond but does not affect the  $C=C$  bond distance in these molecules. Ab initio wave functions were obtained for cyclopropane, cyclopropanone, methylenecyclopropane, propane, acetone, and isobutylene. Comparison of orbital composition, energies, and overlap populations of the parent with the substituted molecules was utilized to ascertain the origin of these substituent and ring closure effects. The analysis shows that the substituent induced electron withdrawal and charge redistribution in the cyclopropane orbitals of SS and AS symmetry shorten the adjacent bonds while the charge redistribution in the cyclopropane orbitals of SA symmetry lengthens the opposite bond. Since the oxygen interacts to a larger extent than the methylene group with the pertinent cyclopropane (and propane) orbital of SA symmetry, the opposite bond is longer in cyclopropanone than in methylenecyclopropane. This more efficient oxygen-parent molecule interaction is also responsible for the differential shortening of the adjacent bonds in the cyclopropane ring and for the observed  $C=O$  and  $C=C$  bond length changes upon ring closing. A second method which takes into account the relative filling of an unoccupied  $C-C-C$  antibonding cyclopropane orbital of SA symmetry in the substituted cyclopropanes can also explain the different cyclopropane geometries. This approach provides a complementary view of geometry changes. In addition to rationalizing and systematizing observed results, the electronic structure analysis procedure presented here is able to discriminate between discrepant experimental data in the literature concerning the carbonyl and  $C-C$  bond lengths in acetone. Many contemporary studies of electronic structure employ semiempirical methods and in order to help test these schemes parallel semiempirical and ab initio calculations were carried out. The same general conclusions arise from both techniques although some molecular properties differ.

The effect of substitution on the geometry of cyclopropane has generated widespread interest and numerous theoretical<sup>1-10</sup> and experimental<sup>11-20</sup> studies in recent years. In particular, the equilibrium geometries obtained from microwave and Raman studies on cyclopropane (I),<sup>21</sup> cyclopropanone (II),<sup>11</sup> and methylenecyclopropane (III)<sup>12</sup> show that the oxygen and methylene substituents both shorten the adjacent bonds ( $C_1-C_2$  and  $C_1-C_3$ ) and lengthen the opposite bond ( $C_2-C_3$ ) in the cyclopropane ring with oxygen producing a less shortened adjacent bond but a more lengthened opposite bond.



Microwave studies on propane (IV),<sup>22</sup> acetone (V),<sup>23</sup> and isobutylene (VI)<sup>24</sup> have also been carried out. The geometries obtained for these molecules are ambiguous as to the relative effect of oxygen and methylene substituents on the propane  $C-C$  bond length. It is also evident from these structural results that ring formation shortens the  $C=O$  bond but leaves the  $C=C$  bond distance unaffected. This latter observation is unexpected on the basis of a rehybridization argument sug-

gested by Laurie and Stigliani<sup>12</sup> (since forming the cyclopropane ring should lead to a decrease in the  $s$  character of the  $C-C$  single bonds and a concomitant increase in the  $s$  character of the double bonds, the  $C_1=C_4$  bond would be predicted to behave the same as  $C=O$ ).



In order to elucidate the origin of these substituent and ring closure effects, we have carried out ab initio electronic structure calculations on the above six molecules. Other wavefunctions have been already constructed for all of these molecules.<sup>8-10,25-34</sup> Some were computed at different geometries and all were carried out with a different purpose in mind. Our approach made use of cyclopropane (I) and propane (IV) as reference molecules and compared their orbital compositions, orbital energies, and overlap populations with those of the substituted molecules. Therefore, we retained the cyclopropane skeleton in II and III and the propane skeleton in V and VI, varying only the  $C=O$  and  $C=C$  bond lengths (Hoffmann et al.<sup>4</sup> used a similar technique for some three-membered rings containing sulfur). A second approach to the substituted cy-

Table I. Geometrical Parameters

Molecule	$R_{C_1-C_2,3}$ , Å	$E_{CH}$ , Å	$R_{C_1-X}$ , <sup>a</sup> Å	$R_{C_4-H}$ , Å	$C_2C_1C_3$ , deg	HCH, deg	HCX, <sup>a</sup> deg	HC <sub>4</sub> H, deg
I. Cyclopropane	1.514	1.080	1.080		60.0	116.0	116.0	
II. Cyclopropanone	1.514	1.080	1.191		60.0	116.0	147.8	
II'. Lengthen C=O in II	1.514	1.080	1.222		60.0	116.0	147.8	
III. Methylene cyclopropane	1.514	1.080	1.322	1.088	60.0	116.0	148.0	114.3
III'. Shorten C=C in III	1.514	1.080	1.302	1.088	60.0	116.0	148.0	114.3
IV. Propane	1.526	1.091	1.076		112.4	107.7	106.1	
V. Acetone	1.526	1.091	1.222		112.4	107.7	121.4	
VI. Isobutylene	1.526	1.091	1.330	1.088	112.4	107.7	122.4	118.5

<sup>a</sup> X = H, O, CH<sub>2</sub>.

clopropanes (which follows a method employed by Hoffmann<sup>2,3</sup>) is based on the relative filling of an unoccupied C-C-C antibonding cyclopropane orbital of SA<sup>35</sup> symmetry and this scheme is also able to rationalize the differential substituent effects. However, it does not completely explain the overall effects since it considers the  $\pi$ -donating ability only, overlooking substituent electronegativity.

It is shown that the use of overlap population as a measure of bond length changes has serious shortcomings and this is characteristic of strained systems.<sup>4,5</sup> In particular, overlap populations would predict substituent-induced adjacent bond lengthening rather than the shortening known to occur. The origin of this failure is found to lie in their inability to discriminate between overlaps in the center of the ring and those along C-C internuclear axes. Examination of orbital schematics enables one to anticipate when overlap population failures will occur. Splitting magnitudes in the orbital energy correlation diagrams enables one to correctly predict bond length changes even when overlap populations cannot.

As shown in a forthcoming paper, our techniques are applicable to molecules other than those considered here, specifically, 1,1-difluorocyclopropane,<sup>13</sup> 1,1-dichlorocyclopropane,<sup>15,16</sup> and 1,1-difluorocyclopropene.<sup>36</sup> We have also demonstrated that the present analysis is invariant to small geometry changes: an additional calculation of II with the carbonyl bond lengthened to equal the C=O bond distance in V and one shortening the C=C bond in III by 0.03 Å do not alter results.

This latter conclusion is useful since experiments performed by different methods do not agree on the carbonyl and C-C bond lengths in acetone (V).<sup>23,37-39</sup> Our theory indicates that the microwave value for C=O<sup>37,38</sup> is correct rather than that obtained from electron diffraction while earlier microwave and electron diffraction results are more accurate than the latest microwave measurements for the C-C length.<sup>23</sup>

Many contemporary studies employ the semiempirical CNDO/2 or INDO schemes and in a continuing effort to establish the successes and failures of these methods we have carried out parallel semiempirical calculations on cyclopropane and cyclopropanone. We find that for the type of information we seek in this paper, use of these techniques is qualitatively successful.

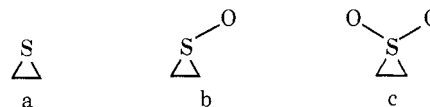
### Computational Details

The calculations were carried out ab initio utilizing the GAUSSIAN 70 computer program and the minimal STO-3G s, p basis set<sup>25,40</sup> on an IBM 360-91 computer. The STO-3G basis set reproduces quite well nearly all of the important trends in the bond lengths and bond angles of the first row polyatomic molecules considered by Newton et al.<sup>41</sup> Hydrocarbon geometries appear to be particularly well represented by this basis set.<sup>29</sup>

Since we employ charge distributions in our analysis, it is important to show that the STO-3G basis set yields reasonable

electric dipole moments. Hehre and Pople<sup>25</sup> have reported that the calculated dipole moments of a series of organic molecules are in moderate agreement with the experimental dipole moments. All of the calculated dipole moments for the hydrocarbons and the oxygen-containing molecules are too small indicating that charge polarization is underemphasized and that back-donating<sup>25,42</sup> in the latter molecules may be overemphasized by this minimal basis set. Nevertheless, the relative values of the dipole moments along a series of molecules are well reproduced, therefore lending credence to the charge distributions predicted by these calculations. Thus the alternating charge distributions found in molecules with polar substituents are believed to be a real effect.<sup>25,42</sup>

Hariharan and Pople<sup>30</sup> have shown that the bonding in strained cyclic systems is much better represented if d functions are included in the basis set. Likewise, Rohmer and Roos<sup>5</sup> have found from their ab initio calculations on the series of molecules



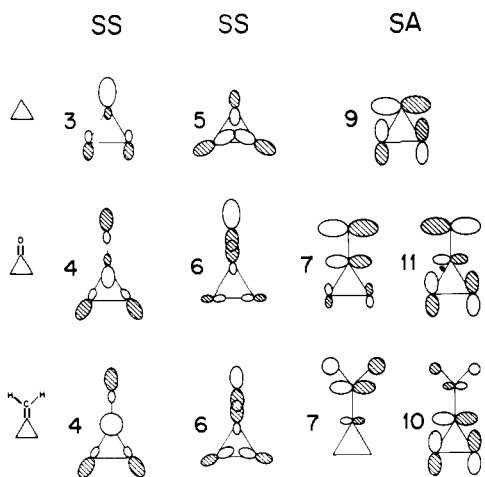
that d functions are important in order to correctly describe the electronic structure in the three-membered rings. But these authors find that d functions do not contribute to substituent effects. It follows then that polarization functions are not necessary in our calculations.

Molecules I, II, and III were calculated with experimental C-C and C-H bond lengths and the  $C_2C_1C_3$  and CCH bond angles of I<sup>21</sup> (Table I). The C=O bond length and CCO bond angle in II<sup>11</sup> and the  $C_1=C_4$  and  $C_4-H$  bond lengths and  $C_1C_4H$  and  $HC_2H$  bond angles in III<sup>12</sup> are the experimentally determined values. Molecules IV, V, and VI were calculated with the observed C-C and C-H bond lengths and the  $C_2C_1C_3$  and CCH angles of IV.<sup>22</sup> The other bond lengths and angles are again the experimentally obtained parameters.<sup>23,24</sup>

The strategy of geometry choice was suggested by work of Hoffmann et al.<sup>4</sup> on a series of three-membered rings containing sulfur. They pointed out that comparing Mulliken overlap populations<sup>43</sup> of parent and substituted molecules with the same skeletal geometry should reflect whether the substituents will weaken or strengthen the ring bonds.

Two additional calculations were carried out ab initio varying the double bond lengths in cyclopropanone (II) and methylenecyclopropane (III). The C=O bond length in II was lengthened to 1.222 Å (II'); the C=C bond length in III was shortened to 1.302 Å (III') (see Table I). Molecules I and II were also calculated utilizing the INDO semiempirical basis set.<sup>44</sup>

Many other theoretical calculations are available for cyclopropane (I).<sup>25-33</sup> Some of them have been carried out to calibrate different methods such as the iterative maximum overlap approximation<sup>31</sup> or electrostatic force theory.<sup>32</sup> Wave



**Figure 1.** Molecular orbital diagrams for carbonyl and methylene addition to cyclopropane. The orbitals are classified according to the reflections in the plane of the molecule and perpendicular to it (SS, SS, SA). Related orbitals of a given type are shown vertically under the symmetry heading.

functions for cyclopropane,<sup>29</sup> propane,<sup>25,26</sup> acetone,<sup>25</sup> and isobutylene<sup>26</sup> have already been computed at the STO-3G level, but overlap populations, orbital energies, and the MO coefficients were not reported, and all were determined at geometries different from ours. Cyclopropane,<sup>33</sup> cyclopropanone,<sup>39</sup> and methylenecyclopropane<sup>10</sup> have also been studied via the CNDO method.

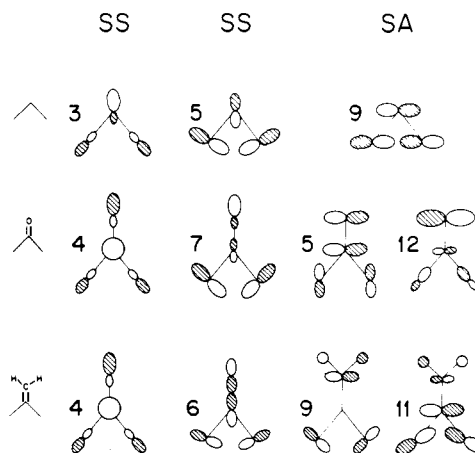
### Results and Analysis of Results

The effectiveness of the interaction between the orbitals on the substituents and parent molecules is dependent on three factors:<sup>45</sup> (1) the relative energy of the orbitals, (2) their symmetry properties, (3) the magnitude of their overlap. The CH<sub>2</sub> bonding orbital of SA symmetry will be more stable than the corresponding oxygen orbital since the latter is a lone pair whereas the CH<sub>2</sub> orbital is delocalized over all three atoms.<sup>4</sup> An additional consequence of this delocalization is the diminished size of the coefficient on C<sub>4</sub>. This further reduces the magnitude of the C<sub>1</sub>-C<sub>4</sub> overlap. As a result, the oxygen substituent interacts more effectively with the cyclopropane and propane orbitals of SA symmetry. This is likewise true for the orbitals of SS symmetry. In contrast, the CH<sub>2</sub> and O orbitals of AS symmetry interact almost equally well with the parent molecule orbitals since both substituent orbitals are lone pairs. Overall, the oxygen substituent-parent molecule interaction is larger. This conclusion is supported by the charge redistributions, coefficient changes (Figures 1 and 2), and orbital energy level splittings (Figure 3).<sup>46</sup>

**The Adjacent Bond.** The molecular orbitals (MO's) predominantly affected by the substituents and ring closure are shown schematically in Figures 1 and 2. For the substituted molecules these are the symmetry allowed bonding and antibonding combinations of substituent orbitals mixed with parent molecule orbitals. SS symmetry<sup>35</sup> leads to one relevant combination; SA produces two.

The orbitals of cyclopropane which are primarily involved in the substituent effects on the adjacent bonds are MO's 1, 3, and 5. Figure 1 shows that oxygen and methylene interaction with MO 3 of cyclopropane will strengthen the adjacent (C<sub>1</sub>-C<sub>2,3</sub>) bonds by removing the antibonding overlap in this cyclopropane orbital and by directing the charge density more effectively along the C<sub>1</sub>-C<sub>2,3</sub> bond axes.<sup>47</sup>

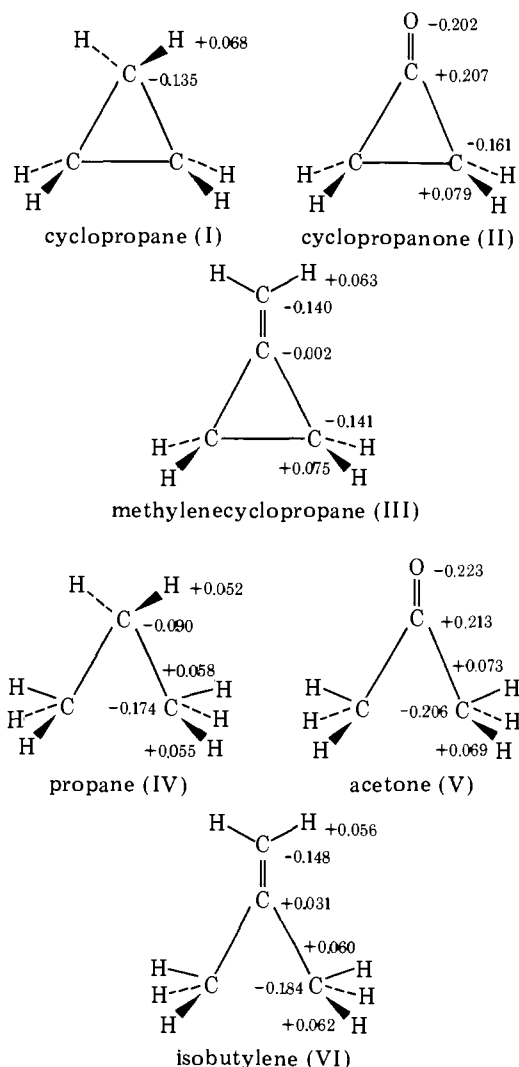
The interaction of the substituents with MO 1 of cyclopropane also strengthens the adjacent bonds but to a lesser extent than the interaction with MO 3. (We have not included MO



**Figure 2.** Molecular orbital diagrams for carbonyl and methylene addition to propane. The orbitals are classified according to the reflections in the plane of the molecule and perpendicular to it (SS, SS, SA). Related orbitals of a given type are shown vertically under the symmetry heading.

1 in Figure 1 since the adjacent bond strengthening via MO 1 is in the same direction as produced by MO 3 and is shown more clearly by the latter.)

Atomic charges from population analysis are given below for molecules I-VI. It is evident that the oxygen substituent



is imposing an alternating charge distribution<sup>25,42</sup> which causes C<sub>1</sub> and the H's to be more positive and C<sub>2</sub> and C<sub>3</sub> more negative in cyclopropanone and acetone than are the corresponding

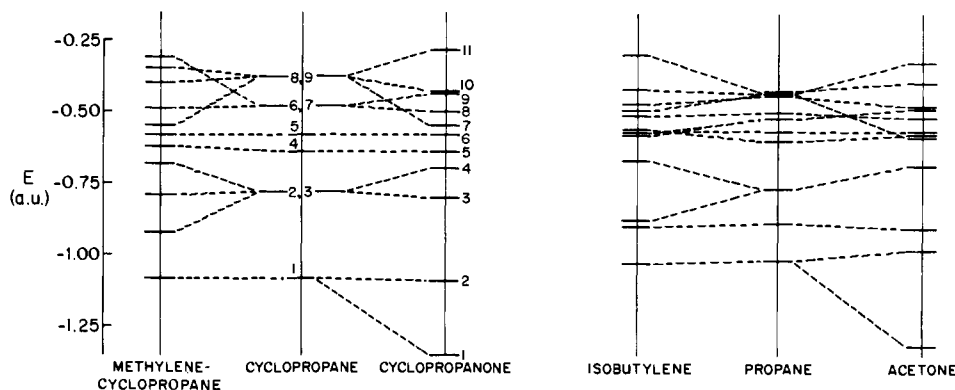


Figure 3. Orbital energy correlation diagrams for carbonyl and methylene addition to cyclopropane(left) and to propane (right).

atoms in cyclopropane and propane. The methylene group is inducing the same type of charge redistribution but to a lesser extent.

O and  $\text{CH}_2$  both produce a charge transfer in MO 3 from  $\text{C}_1$  to carbons 2 and 3 and a reversal of sign for the  $\text{C}_1$  ( $2p_z$ ) AO leading to a  $\text{C}_1\text{-C}_{2,3}$  overlap change from antibonding to bonding. Thus, adjacent bond shortening appears to be at least partially due to the charge alternation effect<sup>25,42</sup> induced in the  $\sigma$  orbitals by these substituents. The O-MO 1 interaction transfers charge density from the  $\text{C}_1$  ( $2s$ ) AO to the  $\text{C}_1$  ( $2p_z$ ) AO increasing the  $\text{C}_1\text{-C}_{2,3}$  bonding overlap.

Oxygen and methylene induce adjacent bond *weakening* via MO 5 of cyclopropane by decreasing the magnitude and the effectiveness of the charge density in the bonding region thereby reducing the bond overlap (Figure 1).

The orbital energy splitting diagram (Figure 3) enables us to determine whether the substituent-MO 1, MO 3 or substituent-MO 5 interactions will dominate.<sup>48</sup> This diagram shows which parent molecule orbitals are affected by substitution and the relative magnitude of the parent molecule-substituent interaction.<sup>46</sup> The left-hand side of Figure 3 shows: (1) the splitting between oxygen and MO 1 of cyclopropane is the principal source of stabilization for cyclopropanone; (2) the methylene-MO 3 interaction is the principal source of methylenecyclopropane stabilization; (3) the oxygen-MO 3 interaction is actually destabilizing but is overridden by the oxygen-MO 1 interaction; (4) the oxygen-MO 5 and methylene-MO 5 combinations produce essentially no energy change; (5) the oxygen-MO 9 and methylene-MO 9 combinations are also sources of stabilization for the substituted molecules. Since the O-MO 1 and methylene-MO 3 interactions lead to stabilization, the substituent effects associated with these interactions will dominate and the adjacent bonds will shorten. This conclusion agrees with the experimental results.<sup>11,12,21</sup>

In general, comparing the Mulliken overlap populations<sup>43</sup> (Tables II, III, IV) of the parent and substituted molecules reflects whether substituents weaken or strengthen bonds. Examining Table II shows  $\text{C}_1\text{-C}_{2,3}$  overlap population increases for MO's of AS symmetry with both substituents; decreases for SA symmetry MO's with oxygen substituent, no change for methylene; decreases for SS symmetry MO's with oxygen, and slight increases with methylene. Overall, oxygen appears to induce a decrease in overlap implying adjacent bond lengthening<sup>49</sup> while the methylene-induced net overlap changes suggest a slight adjacent bond shortening. These results are contrary to our conclusion from the orbital schematics, energy correlation diagram, and experimental facts.<sup>11,12,21</sup> The immediate reason for this error is a too large overlap loss from the substituent-MO 5 interaction in the SS orbitals. As noted originally by Bader,<sup>47</sup> a basic problem in bonding interpretations employing population analysis occurs because this

measure considers only the magnitude of charge in a region and not its spacial placement. For the problem at hand, it is apparent from Figure 1 that the orbitals comprising MO 5 are pointed to the center of the ring rather than directed along the  $\text{C}_1\text{-C}_{2,3}$  internuclear axes as those of MO 3. The potential energy is higher at the ring center than along the internuclear line, thus a given overlap population off line contributes less to bonding strength than along the C-C line. In terms of force vectors, orbitals pointing along the internuclear axis pull nuclei together with undiminished magnitude compared to orbitals pointing at an angle to the internuclear line which only contribute a component of their force vectors. The same holds for MO 5 compared to MO 1, and this is the origin of the invalid correlation between overlap population and bond length. The cases where this measure will fail can be easily evaluated from orbital schematics. On the other hand, use of orbital energy correlation diagrams should always provide a correct method of analysis. We list here several examples of strained systems from the literature where overlap populations do not correlate with bond length changes, although the above analysis of the problem does not seem to have been given previously: (1) Rohmer and Roos<sup>5,49</sup> on the series a, b, c; (2) Lehn and Wipff<sup>50</sup> on bicyclo[2.1.1]hexane and bicyclo[1.1.1]pentane; and (3) Newton and Schulman<sup>51</sup> on bicyclobutane.

Our results also lead to the conclusion that the C-C bond length in acetone should be approximately 1.52 Å, a value in agreement with earlier experiments<sup>23b,c</sup> rather than the shorter bond obtained by the more recent microwave determination.<sup>23a</sup> Examination of the orbital energy level diagrams, overlap populations, and MO's shows that the effect of an oxygen substituent is similar in propane and cyclopropane suggesting that the C-C bond distance in acetone is longer than the distance in isobutylene but shorter than the distance in propane. This differential shortening is due primarily to the differences in the effectiveness of the interaction between the substituent SA orbitals and the parent molecules. The combined result of the substituted induced electron withdrawal and the  $\pi$  back-bonding in MO 9 (on I and IV) is a charge decrease on  $\text{C}_1$  and a charge increase on  $\text{C}_2$  and  $\text{C}_3$ . This charge redistribution generates a lengthening of the  $\text{C}_1\text{-C}_2$  and  $\text{C}_1\text{-C}_3$  bonds because it reduces their bonding overlap. Since this particular substituent-parent molecule interaction is much smaller for  $\text{CH}_2$  than for O, it contributes principally to the overall oxygen substituent effect and reduces the  $\text{C}_1\text{-C}_{2,3}$  bond shortening for oxygen.

**The Opposite Bonds.** In contrast to the adjacent bonds, analysis of the orbital (Figure 1) and energy level (Figure 2) diagrams and of the Mulliken overlap populations (Tables III and IV) leads to conclusions concerning the opposite bonds in molecules I-III which uniformly agree with the experimental results.<sup>11,12,21</sup> The orbital on cyclopropane (I) primarily involved in the substituent-induced changes in the  $\text{C}_2\text{-C}_3$  bond

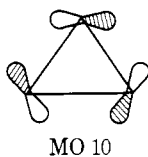
Table II. Adjacent Bond Overlap Populations<sup>35,a</sup>

Molecule	SS	SA	AS
I. Cyclopropane	0.308	0.294	-0.003
II. Cyclopropanone	0.298	0.277	0.009
III. Methylene-cyclopropane	0.312	0.296	0.010
IV. Propane	0.380	0.358	-0.002
V. Acetone	0.372	0.332	0.010
VI. Isobutylene	0.383	0.358	0.013

<sup>a</sup> Summed over valence orbitals.

is MO 9 (SA symmetry). As Figure 1 shows, the oxygen-MO 9 and methylene-MO 9 interactions generate an increase in the charge density on C<sub>2</sub> and C<sub>3</sub> in MO 9 leading to an increase in the antibonding interaction between these carbons and to C<sub>2</sub>-C<sub>3</sub> bond weakening. The overlap populations (Tables III and IV) also indicate that substitution produces C<sub>2</sub>-C<sub>3</sub> bond weakening via interaction with the SA symmetry orbitals. Figure 3 shows that these interactions are stabilizing. Therefore, the C<sub>2</sub>-C<sub>3</sub> bonds in molecules II and III will be longer than the C<sub>2</sub>-C<sub>3</sub> bond in I. Since the oxygen substituent interacts with MO 9 to a much larger extent than the methylene group, the opposite bond is longer in II than in III. Our conclusion on the origin of the opposite bond lengthening agrees with the work of Hoffmann, et al.<sup>4</sup> on a, b, and c.

**An Alternative Explanation.** Hoffmann<sup>2,3</sup> has postulated that the effect of a  $\pi$ -donating substituent<sup>45</sup> on a cyclopropane ring would be to lengthen all three bonds in the ring. This prediction was based on the supposition that a  $\pi$  donor will interact effectively with only the unoccupied cyclopropane orbitals of SA symmetry. The interaction between the  $\pi$  donor and the occupied cyclopropane SA orbitals is expected to produce a charge transfer from the donor to the ring which is cancelled by the charge transfer from the ring to the donor. Hoffmann surmised that the dominating interaction would be that between the  $\pi$  donor and the unoccupied SA C-C-C antibonding cyclopropane orbital (MO 10) leading to partial occupancy of this orbital in the substituted molecule. This would lead to a lengthening of all the ring bonds. Our results clearly demonstrate that the effect of the oxygen substituent on the cyclopropane orbitals of SA symmetry is indeed to lengthen all three bonds. However, we find that for the adjacent bonds this is overridden by the oxygen  $\sigma$  interaction with MO's 1 and 3. Thus the  $\pi$ -donor interaction will not explain the overall substituent effects, but it does explain the difference between O and CH<sub>2</sub> substituents because CH<sub>2</sub> is a poor  $\pi$  donor whereas O is a good one.



In later work on a series of thiirane molecules, Hoffmann et al.<sup>4</sup> concluded that the experimentally observed bond length changes resulted partly from a larger sulfur 3d contribution to the bonding in c than in a, thereby shortening C-S and lengthening C-C. They also pointed out that this explanation would lead to a shorter C-S bond in b than in a which is contrary to experiment. In addition, Rohmer and Roos<sup>5</sup> have found from ab initio calculations on these molecules that the variation in the C-C and C-S bond lengths is independent of the d functions. It follows that d functions will not contribute to the cyclopropane substituent effects.<sup>30</sup>

The second part of the Hoffmann et al.<sup>4</sup> explanation for the C-C bond lengthening for c involves the orbital of a which is similar to MO 9 of I. Applying their analysis to II predicts that

Table III. Opposite Bond Overlap Populations<sup>35,a</sup>

Molecule	SS	SA	AS	AA
I. Cyclopropane	0.855	-0.253	0.100	-0.113
II. Cyclopropanone	0.839	-0.314	0.111	-0.115
III. Methylene-cyclopropane	0.847	-0.272	0.110	-0.114

<sup>a</sup> Summed over valence orbitals.

Table IV. Total Overlap Populations<sup>a</sup>

Molecule	C <sub>1</sub> -C <sub>2,3</sub>	C <sub>2</sub> -C <sub>3</sub>	C-X <sup>b</sup>
I. Cyclopropane	0.596	0.596	0.0
II. Cyclopropanone	0.580	0.518	0.894
III. Methylene-cyclopropane	0.615	0.568	1.207
IV. Propane	0.732		
V. Acetone	0.714		0.882
VI. Isobutylene	0.750		1.205

<sup>a</sup> The total overlap populations may not be exactly equal to SS + SA + AS + AA in Tables I and II since those values represent only the valence orbitals. <sup>b</sup> X  $\equiv$  H, O, CH<sub>2</sub>.

the interaction of the  $\pi$ -donating oxygen with MO 9 is the dominant source of the C-C bond lengthening in II, a result in agreement with our conclusion.

**Ring Closure.** Total overlap population (Table IV) shows that forming the cyclopropane ring shortens the carbonyl bond but does not affect the alkenyl bond. The explanation for the differential effect on the double bonds lies in the relative strengths of the oxygen and methylene interactions with the cyclopropane and propane orbitals of SA symmetry. The C=O bond is shorter in II than in V as a result of the transfer of charge from carbons two and three to carbon one upon ring closure.

Because of its charge delocalization and relatively large energy separation, the interaction between the CH<sub>2</sub> group and the parent molecule SA symmetry orbitals is comparatively small. The C<sub>1</sub>=C<sub>4</sub> overlap population resulting from this interaction is approximately 1% of the total C<sub>1</sub>=C<sub>4</sub> overlap population in III and VI. Since this interaction is making essentially no contribution to the double bond in either III or VI, the SA symmetry orbitals are not important for understanding the relationship between C<sub>1</sub>=C<sub>4</sub> bond length and ring closure. In contrast, the corresponding interaction between the oxygen substituent and the parent molecules makes a contribution of approximately 9% to the total C=O bond overlap population. Thus, these orbitals are more important for understanding the relationship between C=O bond length and ring closure.

The highest occupied propane orbital of SA symmetry has a coefficient of 0.46 on C<sub>1</sub> while this orbital in cyclopropane has a coefficient of 0.62 on C<sub>1</sub>. The variation in the C<sub>1</sub> coefficient arises from the antibonding interaction between carbons two and three in these orbitals. Closing the ring leads to a build-up of charge on C<sub>1</sub> and reduces the C<sub>2</sub>-C<sub>3</sub> antibonding overlap. Because of the larger C<sub>1</sub> coefficient in I, oxygen will interact more efficiently with the cyclopropane orbital than with the propane orbital thus forming a stronger bond in II than in V. The smaller bond overlap in V is partially compensated by the interaction between the oxygen and the second highest occupied propane orbital of SA symmetry. Cyclopropane has no equivalent occupied orbital available for bonding. Since the C<sub>1</sub> coefficient in the second highest propane SA orbital is only 0.24, it does not interact very effectively with the oxygen. Consequently, the C=O bond in II is shorter than the bond in V.

Both substituents interact to approximately the same extent with the orbitals of AS symmetry in I and IV. This is expected

since the orbitals on both C<sub>4</sub> and O which mix with the AS symmetry orbitals of the parent molecule are a lone pair. As a result, these interactions contribute little to the observed differential effect of ring closing on the C=O and C<sub>1</sub>=C<sub>4</sub> bond lengths.

**Rehybridization Effects.** The rehybridization argument presented by Laurie and Stigliani<sup>12</sup> contends that since forming the cyclopropane ring increases the s character (via the SS symmetry orbitals) in both the carbonyl and the alkenyl bonds, both bonds should shorten. The analysis given below, however, shows: (a) ring-closure-induced sp rehybridization in the SS symmetry orbitals does not shorten the double bonds, (b) rehybridization does not behave the same for C=O and C=C bonds. The experimental results support the present interpretation.

For both the carbonyl and the alkenyl systems, the highest occupied SS symmetry orbital is the orbital for which the greatest increase in the s character of the C<sub>1</sub>=X bond occurs upon ring formation. For this orbital, the C<sub>1</sub>(2s)-X(2s) interaction is antibonding and the C<sub>1</sub>(2p<sub>z</sub>)-X(2p<sub>z</sub>) interaction is bonding. Consequently, increasing the s character (or decreasing the p character) weakens this bond. This is substantiated by the double bond overlap population decreases upon ring formation (by 0.054 for C=O and 0.174 for C=C).

The bond weakening noted above is offset in the alkenyl systems by the charge increase in the double bond of III which occurs in the second highest occupied SS symmetry orbital. In this orbital, the C<sub>1</sub>(2s)-C<sub>4</sub>(2s) interaction is antibonding and the C<sub>1</sub>(2p<sub>z</sub>)-C<sub>4</sub>(2p<sub>z</sub>) interaction is bonding for both III and VI. Since the latter interaction dominates, the C<sub>1</sub>=C<sub>4</sub> overlap is bonding, and the increase in charge leads to a net strengthening of the double bond in III. For the corresponding orbitals in the carbonyl systems, the antibonding C<sub>1</sub>(2s)-O(2s) interaction dominates the bonding C<sub>1</sub>(2p<sub>z</sub>)-O(2p<sub>z</sub>) interaction and the orbitals are antibonding with respect to the double bond. Closing the ring also leads to a charge gain in the double bond in this orbital for molecule II. But the resulting increase in the antibonding interaction is greater than the increase in the bonding overlap. Hence, the double bond in II is weakened by the charge gain. The net result is a total overlap population for the SS symmetry orbitals which is slightly smaller in II (0.468) than in V (0.479) but the same in III (0.810) and VI (0.811).

**Validity of Semiempirical Schemes.** Molecules I and II were also calculated via the INDO method.<sup>44</sup> A comparison of the INDO and STO-3G results yields the following observations: (1) The INDO C-H bond charge polarization is smaller whereas the INDO C=O bond charge polarization is larger. In fact the C-H bond in I is polarized in the opposite direction for the two methods. (2) The 2s orbital population for both the C and O atoms is smaller with INDO. The INDO loss in the 2s orbital population on C<sub>1</sub> of I with oxygen substitution is much less whereas the INDO C<sub>1</sub>(2p<sub>z</sub>) loss and C<sub>2,3</sub>(2p<sub>z</sub>) gain in orbital population is greater. (3) The occupied orbitals in I and II have the same general appearance and the same energy ordering for both methods although the INDO energies for the corresponding MO's are all more stable and more closely spaced. All of the above is also true for the unoccupied orbitals except that the MO energy ordering is not identical for both methods. (4) The magnitudes obtained for the AO coefficients in the LCAO expansions are similar for both methods on I and II. For the most stable orbitals the s and p AO coefficients are larger in the INDO MO's. At higher orbital energies the AO coefficient magnitudes begin to equalize and finally the STO-3G AO coefficients are larger for the unoccupied orbitals. (5) The effect of the oxygen substituent on the cyclopropane AO coefficients is essentially the same for both methods. Although the magnitudes of the charge redistributions are not identical, the charge transfers go in the same direction for both

methods. It follows that the analysis of the STO-3G calculations applies equally well to the INDO results. (6) The INDO Mulliken overlap populations are larger for both molecules studied. Fortunately, the INDO overlap populations for the adjacent bonds are larger for II than for I yielding a one-to-one correspondence between calculated overlap population and observed bond length (it is to be recalled that this was not obtained from the STO-3G calculations). The INDO opposite bond overlap decreases in parallel with the ab initio result.

**Generalization to Other Systems.** Since the above analyses of the substituent and ring opening effects are based solely on the extent of orbital mixing and the consequent charge transfer and overlap changes it should be general. This is verified for the substituent effects by the observation that our approach also explains the bond length changes for 1,1-difluorocyclopropane,<sup>12</sup> *cis*-1,2,3-trifluorocyclopropane,<sup>14</sup> 1,1-difluorocyclopropene,<sup>36</sup> and 1,1-dichlorocyclopropane.<sup>15,16</sup> A forthcoming publication shows that the analysis is also capable of predicting approximate geometries for fluorocyclopropane, 1,2-*cis*-difluorocyclopropane, and 1,1,2,2-tetrafluorocyclopropane.

One check on the approach is the demonstration that it is invariant under arbitrary changes in the geometry at which the calculations were carried out. Thus we found no qualitative difference in the extent of orbital mixing or the charge delocalizations when the C=O bond in II is lengthened or the C=C bond in III is shortened by 0.03 Å. This also indicates that the unequal effects of the ring opening on these two double bonds are a real and necessary consequence of their differing efficiency in substituent-parent interaction and their differing capacity for charge delocalization. Thus, the carbonyl bond in II must be shorter than the carbonyl bond in V. This conclusion suggests that in the disagreement between the electron diffraction<sup>37-39</sup> and the microwave<sup>23</sup> results for the carbonyl bond length in acetone (V), the microwave results are the more accurate. This assertion is further substantiated by noticing that the length of the C=O bond in formaldehyde should be between the cyclopropanone (II) and acetone (V) C=O bond lengths since the capacity for charge delocalization in the appropriate formaldehyde SA symmetry orbital is greater than that for II but less than that for V. Electron diffraction data indicate that the formaldehyde and acetone (V) carbonyl bond lengths are similar (1.209 and 1.221 Å, respectively) while the microwave results for these two molecules vary (1.20 vs. 1.22 Å, respectively).

Analogous reasoning leads to the conclusion that the C-C bond length in acetone had been more accurately determined by earlier<sup>23b,c</sup> rather than the most recent experimental investigation.<sup>23a</sup>

## Summary

(1) Oxygen and methylene substitution of cyclopropane induces adjacent (C<sub>1</sub>-C<sub>2,3</sub>) bond shortening by shifting charge density in the SS symmetry orbitals from C<sub>1</sub> into the region along the C<sub>1</sub>-C<sub>2,3</sub> internuclear axes.

(2) Oxygen and methylene substitution of cyclopropane induces opposite (C<sub>2</sub>-C<sub>3</sub>) bond lengthening by increasing the C<sub>2</sub>-C<sub>3</sub> antibonding overlap in the SA symmetry orbitals.

(3) Analysis of the substituted cyclopropanes based on the relative filling of an unoccupied C-C-C antibonding cyclopropane orbital of SA symmetry accounts for the differential substituent effects but not the overall effects.

(4) Our results suggest that oxygen and methylene substitution of propane leads to bond length changes analogous to those observed for the cyclopropane adjacent bonds, in opposition to the current interpretation of experimental data. We believe that an experimental reevaluation of this question is now appropriate.

(5) The analysis presented here explains halogen substituent

effects on cyclopropane and cyclopropene as well as oxygen and methylene substituent effects (see also a forthcoming paper on halogen induced bond length changes).

(6) Ring closure shortens the C=O bond but does not change the C=C bond due to the differential strengths of the substituent interactions with SA symmetry orbitals.

(7) Ab initio and semiempirical methods yield analogous results for the problems addressed here.

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