Effect of Successive Fluorination on the Structure of Cyclopropane

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Boggs, J. E. and Fan, K., 1988. Effect of Successive Fluorination on the Structure of Cyclopropane. – Acta Chem. Scand., Ser. A 42: 595–602.

The structures of cyclopropane and all 12 of its possible fluorinated derivatives have been calculated using a 4–21 basis set. Variations in C–F bond lengths and in the ring C–C distances are examined with respect to the number and location of fluorine substituents. Mulliken population analyses show the trends of net charges and overlap populations as increasing number of fluorine atoms are substituted on the ring.

Dedicated to Professor Otto Bastiansen on his 70th birthday

Over 40 years ago, a bright young Norwegian chemist working with one of the pioneers of Norwegian structural chemistry determined the structure of cyclopropane by the new experimental technique of gas-phase electron diffraction.[1] The structural observation that the HCH angle is $118 \pm 2°$, close to the sp^2-hybridized carbon valence angle of 120° and remote from the expected angle for sp^3 hybridization, opened the valve for a torrent of speculation, interpretation, and additional research which has continued unabated to the present day. A later experimental study[2] refined the HCH angle to $115 \pm 1.0°$, still indicating a hybridization with significant sp^2 character.

The experimental bond angle led Walsh[3] to propose his well-known model for the structure of cyclopropane based on the assumption of sp^2 hybridization of the carbon atoms with the three sp^2 orbitals directed toward the two hydrogen atoms and the center of the ring. The remaining p orbitals of adjacent carbon atoms were thought to overlap well outside the internuclear line, producing "banana bonds" linking the carbon atoms. The model was later refined by Coulson and Moffitt[4] and by others.

The first structural studies of substituted cyclopropanes were concerned primarily with determination of the preferred orientation of asymmetric substituents as probes of differing types of interaction with the ring. Observations that substituents having a lone pair of electrons on the atom attached directly to the ring, such as in $-NH_2$[5] or $-PH_2$,[6] adopt a conformation with the symmetry plane of the substituent perpendicular to the plane of the ring were rationalized in terms of Walsh-like models as reflecting a donation of electron density from the lone pairs into the electron-poor ring center. Substituents which contain double bonds, such as $-CHO$[7,8] or $-NO_2$,[9] are found to bisect the plane of the ring in a manner such that they achieve the maximum overlap with the extraannular ring region which is high in electron density. A partial review of this work has been given in the paper on nitrocyclopropane.[9]

Additional information about substituent interactions with the ring can be obtained by observing the variations in the ring C–C distances adjacent to and opposite the point of substitution. A combination of experimental errors and overly optimistic assignment of experimental uncertainties made this a confusing situation at first, and one set of aurhors[10] was led to the discouraged conclusion that "it appears that the effects of saturated substituents are not as clearly describable as are those of the unsaturated substituents."

The consistency of the data is now considerably improved and there is a general confirmation of

the predictions of Hoffmann[11] that withdrawal of electrons from the highest occupied ring orbital into substituents capable of acting as π-electron acceptors would lead to a shortening of the C–C bond opposite the substituent and to a lengthening of the adjacent bond, while electron density transfer from a π-electron donor into the lowest unoccupied molecular orbital of the ring should lead to a lengthening of all the ring C–C bonds. An extensive survey by Penn and Boggs[12] in which second moments were calculated from microwave spectral data for a variety of substituted cyclopropanes corroborated this conclusion as far as the effect on the opposite bond was concerned, although this analysis could give no information on the adjacent bond. Confirmation is also found in data on a number of individual compounds. In cyclopropyl cyanide, for example, the substituent is a π-electron acceptor, and the electron density transfer is said to be the cause of the observed shortening of the opposite bond and lengthening of the adjacent bond, compared with the parent cyclopropane.[13,14] Similar behaviour is observed for cyclopropyl aldehyde.[7,8]

A major difficulty in seeking significance in small structural differences in structures obtained from microwave spectroscopy (the source of most of the available data on substituted cyclopropanes) is the uncorrelated nature of the error introduced into the structure by the complex and varying nature of the data analyses that transform highly precise measured frequencies into the reported bond distances. This difficulty was surmounted in a limited way in the survey by Penn and Boggs[12] which extracted the desired information from the more nearly directly measured moments of inertia rather than from final derived structures. An alternative approach is to look for a source of information where whatever error exists is correlated in the sense that, at least to a major extent, it affects a given bond parameter (such as a C–C or C–F distance) in the same way in different molecules. Such a technique is now available in the form of structures derived from *ab initio* calculation of equilibrium structures.

The time may not be far away when systematic surveys of a range of molecules such as those reported here can be done quickly at a level of *ab initio* calculation such that the results can be relied on directly to an accuracy of one or two thousandths of an Ångstrom. At the moment, however, that is not possible, nor is it necessary. There is now a great deal of evidence that calculations with medium-sized basis sets, even with complete neglect of electron correlation, can give bond lengths in related molecules such that the *relative* accuracy is within the desired limits. This arises from the fact that the source of the error is similar in the different molecules, producing nearly identical errors that cancel when comparisons are made.[15–17] A recent study[18] of the effect of successive fluorination on the structure of benzene has given evidence of the utility of this approach.

The present paper reports a study of the computed structures of all of the possible fluorinated cyclopropanes. All of the calculations were done at the same quantum-chemical level and with completely similar procedures. It is expected that inaccuracies in bond lengths found under these conditions should be highly systematic, so that comparisons between the different structures can reveal significant trends due to interactions of the substituents with the ring and with each other.

Procedure

All geometries were fully optimized using the program TEXAS[19] and the 4-21 Gaussian split-valence basis set.[15] Convergence criteria were such that all bond distances and angles are converged to a level until the last figure given is meaningful. Absolute accuracy, of course, is lower. It is known that at this level, computed C–C bond lengths can be corrected to give estimates of the true equilibrium bond lengths by adding about 0.005 Å, and that the computed C–F bond lengths will be approximately 0.02 Å greater than the experimental ones.[16,20] The latter error is largely a basis set effect that could be lessened by the inclusion of *d* functions in the atomic basis for fluorine, but it is not thought that this would improve the reproducibility of the error sufficiently to warrant the added cost in computer time. The optimized geometries found by this procedure are given in Fig. 1. While *ab initio* computations on some of the individual molecules in the series have been reported previously, there has been no systematic study of the entire family carried out at the same level of computational accuracy with the intent to facilitate intercomparisons.

Table 1. Comparison of computed C–C bond lengths (Å) with experimental values.

Molecule	C_1-C_2		C_2-C_3		Ref.
	Comp.	Exp.	Comp.	Exp.	
Cyclopropane	1.515	1.510(1)	1.515	1.510(1)	2
1,1-Difluoro-	1.477	1.464(2)	1.550	1.553(1)	21
cis-1,2-Difluoro-	1.494	1.488(3)	1.506	1.503(4)	22
trans-1,2-Difluoro-	1.485	1.466(4)	1.506	1.488(5)	23
cis,cis-1,2,3-Trifluoro-	1.504	1.507(1)	1.504	1.507(1)	24
cis,trans-1,2,3-Trifluoro-	1.505	1.500(3)	1.493	1.478(10)	25
1,1,2,2-Tetrafluoro-	1.476	1.471(3)	1.503	1.497(10)	26
Hexafluoro-	1.502	1.503(3)	1.502	1.505(3)	27

Discussion of results

Absolute values of the structural parameters. While the absolute bond lengths and angles obtained are of less importance for the purpose of this work than are their relative values, it is interesting to compare them with experimental values where these are known. Two purposes are served. First, the comparison can furnish at least a few spot checks on the reliability of the procedure used. Also, the detailed comparison may point out instances in which it would be of interest to check one or more of the experimental results. The comparisons that are available are shown in Table 1.

For cyclopropane itself, the C–C bond is computed to be 0.005 Å longer than found experimentally by Bastiansen *et al.*[2] The HCH angle is within the experimental error of the reported value of $115.1 \pm 1.0°$. Using an overall average, the computed C–C bond lengths shown in Table 1 are greater than the experimental ones by 0.007 ± 0.006 Å. The agreement is noticeably less satisfactory than in general for both of the bond lengths in *trans*-1,2-difluorocyclopropane.

As expected, the C–F bond lengths show a greater offset value between computed and experimental values, with the computed lengths being too great by an average of 0.016 ± 0.006 Å. Both here and for the C–C bond lengths, no variation in the size of this offset value with increasing fluorination is apparent. In general, the agreement is very pleasing and lends credibility to trends that can be observed, which of course should have even greater reliability than the absolute values themselves.

As shown in Table 1, the microwave studies showed a very marked difference between the ring geometries of *cis*- and *trans*-difluorocyclopropane, with the entire ring being appreciably smaller for the *trans* isomer. Only a small difference is indicated by the computed geometries, and, as mentioned above, the difference between computation and experiment is larger for the *trans*-difluoro compound than for any other. It may be worthwhile to examine the possibility that the experimental analysis could have led to an incorrect conclusion.

The microwave moments of inertia are presumably correct, but these could also be fit by a structure with a larger ring and a smaller C–F distance. While the absolute values of the computed C–F distances are not as accurate as other parameters, it is noteworthy that for the *trans*-1,2 compound the computed C–F distance differs from the experimental one by only 0.007 rather than the average 0.016 Å. The microwave isotope substitution method is known to produce errors under certain circumstances and for the compounds in this study there is the added handicap that there are no isotopes of fluorine. The situation is reminiscent of that for 1,1-dichlorocyclopropane for which a microwave r_s structure[28] yielded an excessively long C_1-C_2 bond, as demonstrated by subsequent theoretical[29] and experimental [30,31] studies.

It may also be noted that the experimental C–F distance in *cis,cis*-1,2,3-trifluorocyclopropane is smaller than the computed one by an amount distinctly greater than average. At the same time, the C–C bonds are longer than the computed ones. Once again this means that the

direct spectroscopic observations, the moments of inertia, are compatible with the computed values as well as the experimental ones. The discrepancies may be too small to be convincing individually, but it is significant that in every instance the correlation of the errors is such that the discrepancy could be attributed to problems with the microwave substitution method just as well as to lack of consistency in the computations. A cautious reader could believe that the uncertainties in the microwave structures are somewhat larger than those reported as arising solely from the fit.

It is meaningless to compare computed and experimental C–H distances, in view of the differences between the computed equilibrium r_e values and the experimental r_s substitution distances. In general, the differences are of the magnitude and in the direction expected.

For the molecules in Table 1, the computed FCF and HCF angles are consistently larger than the experimental ones by $1.6 \pm 0.3°$. This may reflect an inadequacy in the calculation or it may arise from the vibrational averaging error remaining in the experimental substitution structure obtained without the availability of fluorine isotopes. Computed HCH angles agree with the experimental ones with an average deviation of only 0.3°.

Systematic trends in the ring bond lengths. The significant structural parameters resulting from the calculations are shown in Fig. 1. Readers interested in wag, rock or twist angles of the

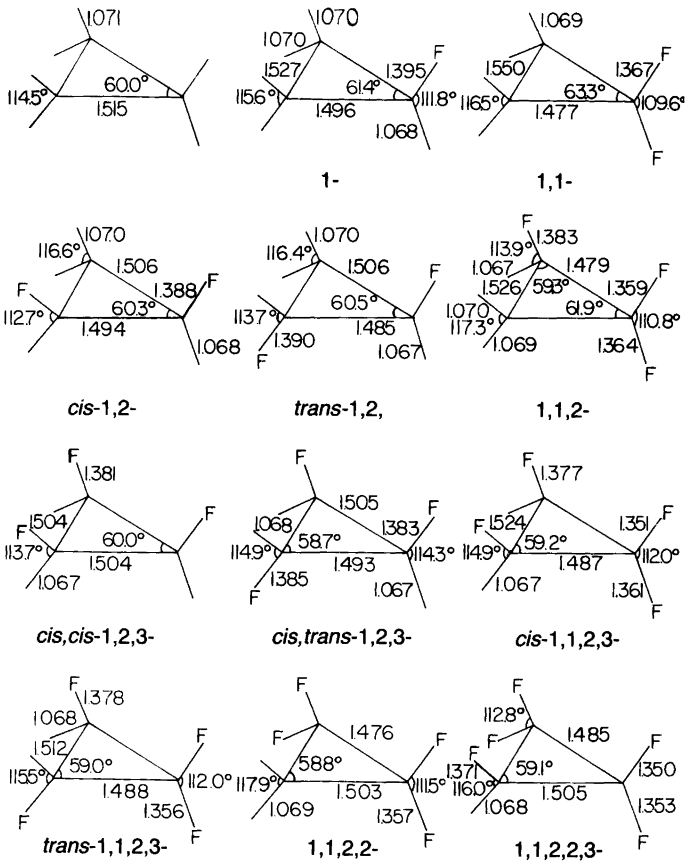

Fig. 1. Computed structures of cyclopropane and the fluorinated cyclopropanes. Hexafluorocyclopropane (not shown) has C–C = 1.502 Å, C–F = 1.347 Å, and ∠FCF = 113.5°.

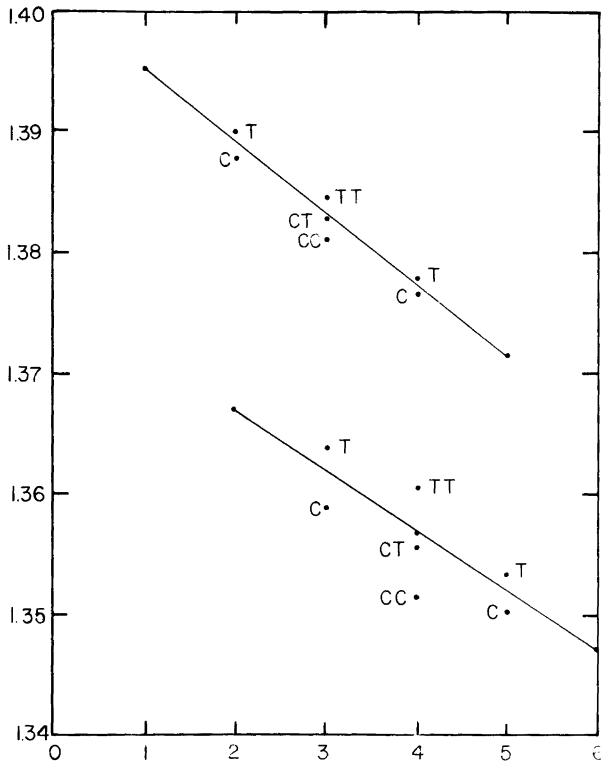

Fig. 2. Computed C–F bond lengths in CHF (upper line) and CF_2 (lower line) as a function of the number of fluorine atoms.

$-CH_2$, $-CHF$ and $-CF_2$ groups can obtain complete data from the authors on request.

The change in the C–F bond distance is found to vary in a remarkably uniform manner, which is best visualized by reference to Fig. 2. The upper line refers to C–F distances when only one fluorine atom is attached to the carbon atom. For the compounds containing 2, 3 or 4 fluorine atoms, the precise C–F distance is dependent on the relative location of the fluorine atoms, but their average gives a nearly perfect straight line. Even the small variation with *cis/trans* isomerism is consistent. For the 1,2-difluoro compound, the C–F bond is slightly shorter for the *cis* isomer, presumably reflecting a greater extent of interaction with the ring orbitals in this form. The trend continues in the 1,2,3-trifluoro compounds with the C–F bond being shortest when it is *cis* to two other fluorine atoms, intermediate when it is *trans* to one and *cis* to the other, and longest when it is *trans* to both of the others. Again, the same result is observed for the tetrafluorocyclopropanes. While these differences are quite small, the regularity in the trends involved lends additional credibility to the method used in this investigation.

The lower line in Fig. 2 shows similar relationships among the C–F distances involving two fluorine atoms attached to the same carbon. Again, the trend with increasing fluorination is very regular and the results for the trifluoro, tetrafluoro and pentafluoro compounds show shorter C–F bond lengths when the two C–F groups are *cis* to each other.

The C–H bond distances show very little variation, the difference between the longest and shortest being only 0.003 Å. Still, the variation is quite systematic, with C–H bond-shortening accompanying increased fluorination.

Interpretation. For the C–C bond, the first qualitative observation from the results shown in Fig. 1 is that, quite generally, the effect of a fluorine atom is indeed to shorten the adjacent C–C bond and lengthen the opposite one. In the earliest interpretation,[21] it was assumed that fluorine

would act as an electron donor. Later, however, it was clearly shown[29] that in cyclopropyl compounds, fluorine acts as an electron-withdrawing substituent. Hoffmann suggested[11] that electron density would flow from the highest occupied molecular orbitals, but it was shown that for mono- and 1,1-difluorocyclopropane, these orbitals have the wrong symmetry and that electrons are withdrawn instead from orbitals $11a'$ and $9a_1$. As demonstrated in the previous paper,[29] this results in a shortening of the adjacent bond and a lengthening of the opposite bond for substitution of fluorine on a given carbon atom, as observed.

In an important article by Deakyne, Allen and Craig,[32] it was predicted that the effect of fluorination on a ring bond lengths should be additive for multiple fluorination. However, it is not yet clear that this is universally true,[26] and inspection of Fig. 1 suggests that the response to successive fluorination is somewhat more complex.

Substitution of one fluorine atom or of two fluorine atoms on the same carbon reduces the adjacent ring C–C length by 0.019 and 0.038 Å, respectively, while the opposite bonds are lengthened by 0.012 and 0.035 Å. Thus, the effect on the adjacent bond is strictly additive, but the second fluorine atom has a considerably larger effect than the first one on the opposite bond.

In the two 1,2-difluorocyclopropanes, the longer C–C bond is opposite one CHF group and adjacent to the other, so it might be expected to be changed by $+0.012 - 0.019 = -0.007$ Å. In both cases, the change relative to cyclopropane is -0.009 Å, remarkably good agreement. Similar reasoning would predict that the length of the C–C bond between the two CHF groups would be altered by $2(-0.019) = -0.038$ Å. As shown in Fig. 1, however, the changes are -0.021 Å for the *cis* isomer and -0.030 Å for the *trans*, somewhat less than expected on the basis of additicity. Even though we do not find as large a difference between the effects of *cis* vs. *trans* substitution as does the Gillies group,[22,23] it is clear that the effect is real.

In *cis,cis*-1,2,3-trifluorocyclopropane, each C–C bond is opposite one CHF group and adjacent to two others, so strict additivity would predict a bond length change of $(+0.012) + 2(-0.019) = -0.026$ Å. The computed change is -0.011 Å. Similar results are seen for other flu-

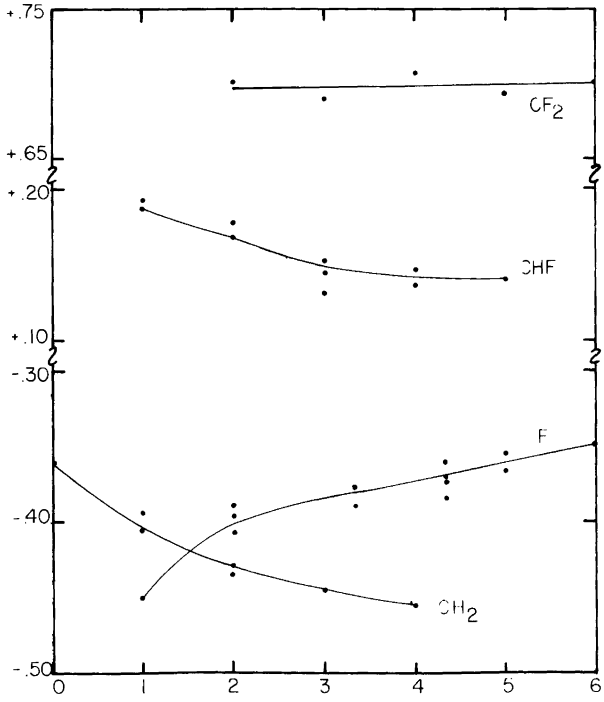

Fig. 3. Net charges on the atoms as a function of the number of fluorine atoms. Lines labeled CF_2, CHF and CH_2 show the charges on the carbon atom in those groups.

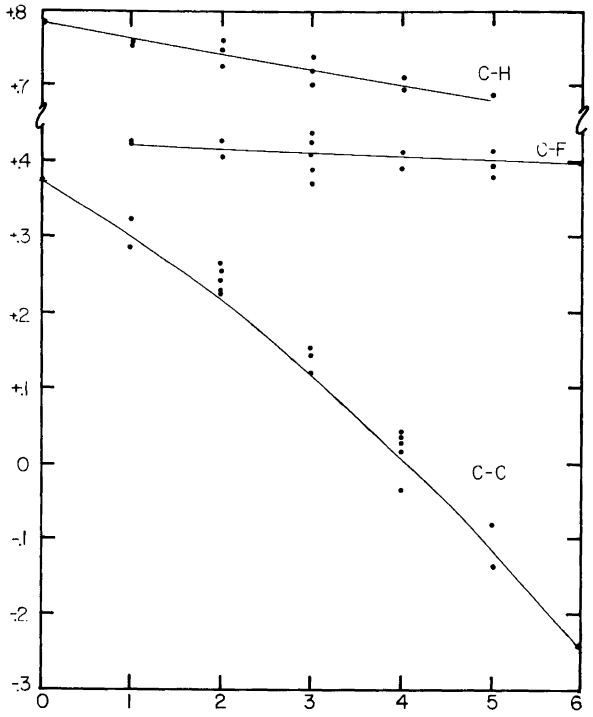

Fig. 4. Mulliken overlap populations of C–H, C–F and C–C bonds as a function of the number of fluorine atoms.

orinated compounds. Additivity seems to be approximate, but not exact.

It may be noted that the effect of *cis/trans* isomerism on C–C bond lengths is opposite to that seen for C–F bonds. Two C–F bonds *cis* to each other are shortened more (compared with monofluorocyclopropane) than are two C–F bonds in a *trans* position. However, the C–C bond between two C–F bonds is affected more when their orientation is *trans*.

Mulliken population analysis. While Mulliken population analyses,[33] like other methods for partitioning the molecular wavefunction, are justifiably subject to criticism, useful qualitative insight can often be obtained. Fig. 3 shows some trends in net charges as obtained by this technique. As is expected, a fluorine atom withdraws electron density from the carbon atom to which it is substituted while an opposite carbon becomes more positive.

The effect of multiple fluorination can be seen from the comparisons shown in Fig. 3, and can be summarized in the following generalizations:

(a) The net charge on a fluorine atom becomes slightly less negative as an increasing number of fluorines is added to the ring.
(b) The net charge on a carbon atom in a CHF group increases sharply when that fluorine atom is the only one in the molecule, but then decreases slightly as other fluorine atoms are substituted on the ring.
(c) In a CF_2 group, the carbon is quite positive ($\sim +0.7$ compared with the -0.36 found in the parent cyclopropane), but then changes very little as more fluorine atoms are substituted elsewhere in the ring.
(d) The net charge on the carbon in a CH_2 group decreases slightly and regularly as fluorine atoms are substituted elsewhere in the ring.
(e) The net charge on a hydrogen atom becomes slightly more positive as fluorine atoms are substituted anywhere on the ring.

Further information about the ring-substituent interaction can be obtained by examining the Mulliken overlap populations which are summarized in Fig. 4. While there are small trends in the

overlaps for the C–H and C–F bonds, by far the major effect is seen in the C–C bond, for which the overlap population varies from +0.378 in C_3H_6 to −0.245 in C_3F_6. Charge transferred to the fluorine atom comes primarily from the ring bonds. While significant differences can be seen between the contributions from C–C bonds adjacent to CH_2, CHF or CF_2 groups, the effect as read from the Mulliken overlap populations is probably too small to warrant interpretations.

Acknowledgements. This work was supported by a grant from The Robert A. Welch Foundation and all calculations were done on the computers at the University of Texas at Austin Computation Center. The authors would also like to express their appreciation to Dr. Charles W. Gillies for useful discussion and information about unpublished work.

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Received March 23, 1988.