

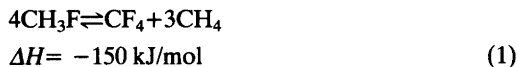
A Theoretical Investigation of Relative Stabilities and Interconversion Barriers in *gem* Di- and Tetrafluoromethylene Cyclopropane

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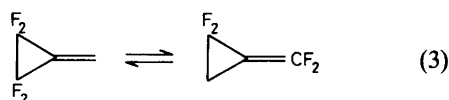
Ab initio calculations on the SCF level have been undertaken in order to investigate *gem* di- and tetrafluoromethylene cyclopropane with respect to charge distribution, relative stabilities and interconversion potential barriers to sigmatropic migration. Anticipated geometric trends are reproduced by the calculations, and the relative reactivity characteristics of the different molecules can be interpreted in terms of differences in the charge distributions. For the interconversion reactions, the orbitally allowed transition state for the tetrafluoro substituted species is found to be very high in energy, thus making an orbitally allowed migration unlikely in this case.

Thermodynamic stabilization is normally observed in successive fluorination reactions, for instance eqn. (1).¹



In contrast to this, there is an observed kinetic destabilization when fluorine is successively added to a cyclopropane system.² Although changes in strain energy of reactants and products seem to explain nicely the thermodynamics of a number of *gem*-difluorocyclopropane reactions,³ an understanding of the reaction kinetics and mechanisms makes it necessary to study reaction intermediates as well as ground states.

We have in the present work studied some aspects of the reactions (2) and (3).



Ab initio calculations³ of the reactant and product of eqn. (2) gave as a result a good agreement with the experimental enthalpy difference [$H(\text{exp}) = -7.9 \text{ kJ/mol}$, $E(\text{theor}) = -2.6 \text{ kJ/mol}$]. The calculations were carried out with complete geometry optimizations using a 4-21⁵ basis set and a final 4-31G basis set at the end point. Our previous experience is that bond length changes are a sensitive measure of the electronic impact of various substituents on the cyclopropane ring.⁶⁻¹² Complete geometry optimizations of the reactant of eqn. (3) and the parent methylene cyclopropane are performed on the same level of sophistication as our previously published study of the species in eqn. (2).³

We have also carried out calculations of various possible diradical intermediates for reactions (2) and (3). The hydrocarbon analogous rearrangement reaction (4)



has been studied theoretically by Hehre *et al.*¹³ Since those calculations were carried out at the

same level of sophistication as ours, they provide an interesting comparison.

The present work includes investigations of the effect of fluorine on the stable species, on the reaction intermediates and various forms of the fluorinated trimethylene methane diradical.

METHODS

The geometry optimizations were carried out at the SCF level using 4-21 basis set⁵ using the computer programme TEXAS¹⁴ which calculates the forces on all atoms making possible a simultaneous optimization of all internal coordinates. The gradient method is very convenient for complicated geometry optimizations, and offers a straightforward way to determine molecular structures.

The triplet forms of the diradical were calculated with the Gaussian 76 programme, using an unrestricted Hartree Fock procedure. Standard geometry parameters were employed.

The open shell singlet states deserve some special considerations. For some conformers of the activated states, the two open shells appear in the same symmetry, thus rendering the usual Brillouin theorem (which states that an SCF wave function does not interact with singly excited states) inapplicable. The proper condition is in this case provided by the extended Brillouin theorem,¹⁵ which states that (at self-consistency) the matrix element between the open shell singlet

and the difference between the two corresponding closed shell configuration is zero. The matrix element between the open shell wave function and each of the closed shell excitations may, in fact, be quite large, as is the case *e.g.* for some Auger states on water.¹⁶

Labelling the two open shells *a* and *b*, the configuration of interest (only indicating the orbitals *a* and *b*) are:

1. $1/\sqrt{2} [\{a\bar{b}\} - \{\bar{a}b\}]$
2. $\{a\bar{a}\}$
3. $\{b\bar{b}\}$

It is easily shown that the off diagonal matrix elements between these states are:

$$H_{12} = \sqrt{2} F(a^2)_{ab}$$

$$H_{13} = \sqrt{2} F(b^2)_{ab}$$

$$H_{23} = K_{ab}$$

where $F(a^2)$ and $F(b^2)$ signify the Fock-operators for the closed shell configurations formed with the canonical orbitals for the open shell state.

All matrix elements needed to calculate proper non-interacting states are thus easily obtained. In the present study the open shell calculations on the open shell singlet states for the difluorinated species were carried out using the restricted OS-SCF method followed by the above described 3×3 CI. The effect of the 3×3 CI was, however, minimal, and no corrections were deemed necessary for the tetra-substituted systems.

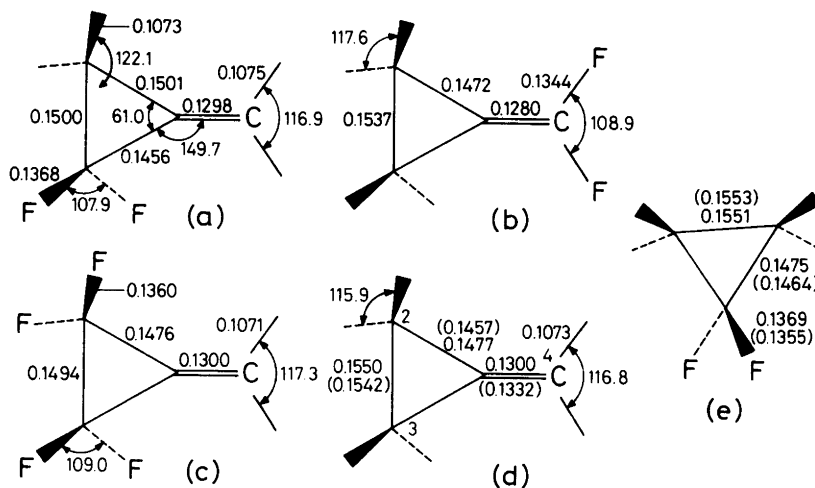


Fig. 1. Results of structure analysis. Distances in nm. See text.

For the latter species, calculations on the singlet form were carried out only on the high symmetry forms. This was decided partly from the results on the difluorinated forms and partly for economic reasons.

RESULTS AND DISCUSSION

(a) *Structure analysis.* We have in a series of articles⁶⁻¹² exploited the effect of various substituents upon a cyclopropane ring. For the cases where comparison with experimental structure works was possible, our calculations were generally in good agreement with experiment, e.g. for 1,1-difluorocyclopropane, where the main trends of a short C₁-C₂ bond and a long C₂-C₃ bond found in a microwave investigation was reproduced in our calculations. The often reported¹⁷ but perhaps not fully understood shortening of the C-F bond upon successive fluorination was also reproduced in our calculations.

The results of the present calculations are given in Fig. 1, where also our previously reported data for the molecules in reaction (2) and 1,1-difluorocyclopropane⁶ are given for comparison.

Experimental values from microwave spectroscopy for methylene cyclopropane and 1,1-difluorocyclopropane are given in parentheses. The agreement is in general satisfactory although for methylene cyclopropane, the calculated differences in bond lengths between the double bond and the C-C bond adjacent to it is somewhat too large.¹⁶ Some of our previous works⁷ in this series triggered reinvestigation of microwave

work. In these cases, errors had been made in determining the location of the C₁ atom with corresponding errors in the C₁-C₂ and C₁-X distances. The overall size of the molecule had, however, been determined with good precision. In the present case, however, the difference between the calculated and the experimentally determined value of the C₁-C₄ double bond parallels the findings for the double bond in vinylcyclopropane⁸ and cyclobutene.¹⁹ The disagreement for methylene cyclopropane seems to reflect a shortcoming in the theoretical work (presumably a basis set deficiency) rather than a misassignment of the experimental spectrum. For the present discussion this is not crucial, since it is the trend in geometry parameters within the series *a-e* that is our prime interest.

Some features may be deduced from Fig. 1:

(1) When *gem*-difluoro or methylene groups are substituents on cyclopropane rings, they have the same ability of shortening the adjacent and lengthening the opposite bond (see *d* and *a*).

(2) When these substituents are simultaneously introduced, they have a nearly additive effect upon ring structure. This is seen in *a* where the C₁-C₂ bond is shortened about twice as much as in *b* and *c*. (The parent cyclopropane has computed C-C bond lengths of 1.5153 Å within the same approximation.) The C₂-C₃ and C₃-C₁ bonds being adjacent to one substituent and opposite to another, have intermediate bond lengths.

A further picture of the electronic distribution of the systems may be achieved by inspection of Table 1 where atomic gross charges are given. Summation of charges of the ring carbons reveals

Table 1. Gross atomic populations, total energies and dipole moments. Basis set 4-31G/4-21.^a Energies in a.u. Dipole moments in debyes.

Gross atom	Molecule			
	a	b	c	d
C1	6.05	6.13	6.06	6.05
C2	5.26	6.27	5.26	6.31
C3	6.33			
C4	6.34	5.31	6.29	6.38
F	9.41	9.42	9.39	
C1+C2+C3	17.64	18.67	16.58	18.67
<i>E</i> (total)	-352.11522	-352.11622	-549.55566	-154.65886
Dipole	3.3	3.2	4.3	0.3

^a See Ref. 25 for definition of nomenclature.

that *a* and *c*, both molecules with fluorine on the ring, have considerably less electron density than the hydrocarbon ring. According to Table 1, a whole electron is removed from the ring by introduction of each CF₂ group. The same summation carried out on 1,1-difluorocyclopropane yields a value of 18.25 electrons, but since the calculations on that molecule were carried out using a different basis set, the numbers are not directly comparable.

We believe that this weakening of the ring is essential in explaining the enhanced reaction rates upon successive fluorination. Note that shortened C–C bond distances do not necessarily imply stronger bonds, although this is generally true for open chains.

(b) *Energy considerations.* The total energies given in Table 1 give the energy for the isodesmic reaction



This is a measure of the preference for one or two CF₂ groups in the three-membered ring. This increased strain energy is comparable to the destabilization of 19.2 kJ/mol for monofluorocyclopropane and 41.9 kJ/mol for 1,1-difluorocyclopropane.³ The latter values were computed by non-geometry optimized 4–31G quality SCF calculations. All these values are consistent with the 19–21 kJ/mol of increased strain energy per fluorine substituent postulated by O'Neal and Benson.²

(c) *Reaction intermediates.* Following the calculations by Hehre *et al.*¹³ for the corresponding hydrocarbon reaction, we have calculated the stability of a series of possible reaction intermediates. The conformation and spin states of these, along with atomic charges and energy differences compared to corresponding closed rings are shown in Fig. 2.

We have restricted our calculations to diradical intermediates, neglecting possible concerted mechanisms. Because of the size of this problem (46 and 60 electrons for intermediates of *a* and *c* and 24 internal coordinates) we have limited the calculations to standard geometries. For both the di- and tetrasubstituted species the triplet state planar forms are astonishingly low, only about 14.6 kJ/mol above the ring system. This finding is at variance with the results of the hydrocarbon calculation. In the work by Hehre *et al.* the

	$\Delta E (E_{\text{radical}} - E_{\text{ring}})$ in kJ/mol	
	Singlet	Triplet
	164.2	69.0
	144.6	13.8
	176.4	123.3
	1663.6	437.7
		56.9
	759.5*)	116.6
	330.2	14.6

*) ΔE for closed shell ring: 448.9 kJ/mol

Fig. 2. Energies of various diradical conformers relative to closed ring system. In kJ/mol.

singlet-triplet splitting was found to be only a few kJ/mol and the transition state was found to be a singlet at 186.9 kJ/mol above the ring system. However, a paper by Yarkony and Schaefer on the trimethylene methane diradical predicts the $^3A_2' - ^1E'$ separation to be 88 kJ/mol on the basis of double zeta quality SCF calculations, and MINDO/2 calculations by Dewar and Wasson¹⁹ predict this energy difference to be about 146 kJ/mol.

As for the singlet forms, we have for the difluorinated species found three close-lying states, the planar form and both forms with orthogonal CF₂ groups, to be of nearly the same energy (144.6, 164.3 and 176.4 kJ/mol above the closed ring form). From an experimental value of

the activation energy⁴ of 160 ± 1.6 kJ/mol, it is likely that one of the above-mentioned forms is the reaction intermediate. The level of sophistication of the present calculation and the lack of geometry optimization for the open shell forms makes the proper selection from these forms an uncertain task. It is, however, interesting to note the difference at this point with the above-mentioned results and the results for the hydrocarbon by Hehre. For that higher symmetry species, the energy for the planar form was predicted to be 368 kJ/mol above the ring system. A point of some interest is the small significance of the correction factor for the open shell singlets of a_1 symmetry which were computed to be 22.6 kJ/mol for the perpendicular form of the difluorinated diradical and 0.04 kJ/mol for the planar form. These contributions are included in the energy differences given in Fig. 2.

Inspection of Fig. 2 reveals that the tetrafluorinated species also has low lying triplet states, especially for the planar form, but possesses no low lying singlet states. A kinetic study of the rearrangement reaction (3) gives an energy of activation of 123.7 ± 5 kJ/mol and a relative rate of rearrangement of (3) vs. (2) at 150 °C of 7850,²⁰ whereas at the same temperature the relative rate of reaction (2) vs. the hydrocarbon rearrangement is reported to be only 4.4. Although the lower symmetry of the reactant of reaction (2) would lead to a net retardation of (2) compared to (3), this factor could not possibly account for the difference in reaction rates. The experimental kinetic data coupled with the results of the present calculation seem to imply a different reaction mechanism for (3). *A priori* this could be either a concerted type reaction or a "forbidden" crossing to the triplet state. Although we have not attempted to perform calculations of the former, a diradical intermediate does seem to be consistent with both theoretical¹³ and experimental²³ findings. The triplet state diradical thus seems to be the most likely candidate to be intermediate of reaction (3). The possibility of a triplet intermediate has been suggested also in an experimental study²³ of analogous systems, although in that case the final products were dimers.

As a final point, we wish to comment on the charge distribution in the open shell forms. This relates to the attention that has been given over the years to the hydrocarbon analogues and

which is interestingly summarized in Ref. 20. A key point has been the large positive charge of the central carbon atom which led to its use as a zero point in the definition of the "free valence" concept introduced by Coulson.²⁴ The numerical value of this was calculated in the previously mentioned paper by Yarkony and Schaefer to be +0.62 el. on the planar form, a value not only reported to be the largest known to a hydrocarbon carbon, but in fact one of the largest encountered on any carbon atom studied by double ζ basis sets. Since it is well known that the carbon in a CF_2 group also bears a highly positive charge (+0.73 el. for 1,1-difluorocyclopropane in Ref. 6) one would assume the fluorinated radicals to be either destabilized or electronically reorganized in order to avoid neighbouring positive charges. From Fig. 2 it is seen that destabilization is clearly not taking place, and a survey of the atomic gross charges for the intermediates gives normal, negative charges ranging from 0.09 el. to 0.20 el. for the central carbon atom for all cases considered.

We wish to stress that we have not tried to determine absolute values of energies with any degree of precision in this work. The present calculations are of a qualitative nature since neither configuration interaction nor geometry optimization have been carried out. However, our prime interest has been to study trends within closely related systems, trends which can withstand a more advanced treatment. An extension of the present work would have to include geometry optimization of the intermediate diradicals, a larger basis set and configuration interaction.

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