Thermodynamics of cis-trans Isomerizations. II. The
1-Chloro-2-fluoroethylenes, 1,2-Difluorocyclopropanes, and Related Molecules

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For the cis-to-trans reaction of 1-chloro-2-fluoroethylene the equilibrium constant over the temperature range 475-760°K is given by log \( K = -171.0 + 0.0462 \). As a consequence \( \Delta H^\circ_{\text{cis}} = 780 \pm 20 \) cal/mol and \( \Delta S^\circ_{\text{cis}} = 0.21 \pm 0.04 \) cal/deg-mol. For the cis-to-trans reaction of 1,2-dichloroethylene \( K = 0.645 \pm 0.013 \) at 562°K. This gas chromatographically derived value confirms previous dielectric constant measurements.

Critically evaluated electronic energy differences for a series of cis-trans isomerizations in the gas phase are: \( \text{N}_2\text{F}_2, 3050 \pm 400; \text{C}_2\text{F}_4\text{H}_2, 1050 \pm 120; \text{C}_2\text{Cl}_4\text{H}_2, 870 \pm 110; \text{C}_2\text{Br}_4\text{H}_2, 720 \pm 160; \text{C}_2\text{Br}_4\text{H}_2, 250 \pm 330; \) and \( \text{C}_2\text{F}_4\text{H}_2, 80 \pm 230 \) cal/mol. In each case the cis isomer has the lower energy. This cis effect is rationalized in terms of “nonbonded” forces. The synthesis of the cis and trans isomers of 1,2-difluorocyclopropane is described. A preliminary value for the equilibrium constant for the cis-to-trans isomerization of these isomers is \( 11.7 \pm 0.5 \) at 850°K, from which it appears that the trans isomer has the lower energy. This result is remarkable in view of \( \Delta H^\circ_{\text{trans}} - \Delta H^\circ_{\text{cis}} = 0 \) for 1,2-difluoroethane as well as the low energy of cis-CF_2H_2.

In the 1930's Kistiakovsky and his coworkers at Harvard made a series of precise measurements of enthalpies of hydrogenation from which accurate resonance energies and energies of isomerization were derived. In particular, for the reaction

\[
\text{cis-2-butene(g)} = \text{trans-2-butene(g)}
\]

they found that the energy change at 355°K was

\(-950 \pm 120 \) cal/mol.\(^2\) Subsequent application of this method to more elaborately substituted ethylenes has given values for isomerization energies which include

\(-940 \) cal/mol for \( \text{MeHC} = \text{CH}[(\text{t-Pr})_2] \); \(-4220 \) for \( \text{EtOOC} = \text{CHCOOEt} \); \(-5700 \) for \( \text{PhHC} = \text{CHPh} \); and \(-9370 \) for \( \text{(t-t-Bu)HC} = \text{CH(t-t-Bu)} \).\(^{3a}\) The presently available spectroscopic and thermodynamic data are, however, insufficient to permit separation of the electronic energy contribution in \( \Delta E^\circ \) from the contributions due to other degrees of freedom of the molecules. Nonetheless, it seems likely that the non-electronic contributions nearly cancel out (vide infra), and thus the trans configuration has the lower electronic energy. These electronic energy differences for isomeric ethylenes are a part of the experimental basis for the concept of steric crowding, which is apparently important even in the case of 2-butenes.\(^4\)

In contrast to the foregoing examples, a growing body of experimental data on haloethylenes (and a diazene) strongly suggests that cis isomers can have the lower electronic energy. Reasonably well established gas-phase examples of this effect include the 1,2-dichloroethylenes,\(^5\) the 1,2-difluoroethylenes,\(^6\) and the 1,2-difluorodiazenes.\(^7\) Fragmentary data exist for many others.\(^8\) In mixed dihaloethylenes the preference (free energy) for the cis configuration is sustained throughout the series \( \text{C}_2\text{F}_4\text{H}_2 \) to \( \text{C}_2\text{F}_4\text{H}_2 \).\(^{5a,b}\) Enthalpy differences ranging from 700 to 3000 cal/mol are found in fluorine- and chlorine-substituted species. Haloethylenes are sufficiently simple that complete spectroscopic data may be confidently sought and employed to isolate the electronic energy change. In addition to giving experimental results from the isomerization equilibrium of the 1-chloro-2-fluoroethylenes and, secondarily, confirmatory data for the 1,2-dichloroethylenes, the main purpose of the present paper is to provide a thorough analysis for the whole series of halogenated ethylenes (and a diazene) for which reasonably complete data are now available.

\(^{(5)}\) (a) L. Ebert and R. Bull, Z. Physik Chem. Abt. A, 152, 451 (1931); (b) A. R. Olson and W. Maroney, J. Amer. Chem. Soc., 56, 1320 (1934); (c) R. E. Wood and D. F. Stevenson, ibid., 63, 1050 (1941).
Preference (free energy) for the cis configuration is apparently not limited to halogenated ethylenes. It is also found in 1-halopropylenes8 with 1-chloropropylene9 and 1-bromopropylene,10 being the best documented examples in the recent literature. For crotononitrile (CH3CH=CHCN), Butler and McAlpine have obtained a positive enthalpy change for the cis-to-trans reaction from the temperature coefficient of the equilibrium constant.11 These propylene examples have been rationalized in terms of polar attraction between CH and CX bonds with and without hyperconjugation. Such an explanation has also been given for the re-12 and published nmr observations13 that support reaction from the temperature coefficient of the equilibrium constant.11 These propylene examples have been rationalized in terms of polar attraction between CH and CX bonds with and without hyperconjugation. Such an explanation has also been given for the remarkably low barriers for CH2-group rotation in cis-1-fluoropropylene12 and in cis-1-chloropropylene.13 A dipole attraction argument will not serve, however, to explain the effect in the symmetrically substituted haloethylenes.

There is evidence that the double bond is not required for an apparent net attraction to occur between two identical (or neighboring) halogen atoms.14 From vibrational spectroscopic studies Klabo and Nielsen deduced a 0 $\pm$ 200 cal/mol energy difference between gauche and trans conformers of 1,2-difluoroethene near room temperature.16 Abraham and Parry have alluded to unpublished nmr observations19 that support the conclusions of Klabo and Nielsen. El Bermani and Jonathan found only $-200 \pm 80$ cal/mol for the gauche-to-trans conversion in 1-chloro-2-fluoroethane.17 These particular ethane cases are made all the more noteworthy by the failure of Abraham and Parry’s empirical potential function to account for the rotameric energy differences. In contrast, their function which includes an ethane-like threefold barrier term, a pair of Buckingham-like van der Waals terms, and a dipole term, was moderately successful in accounting for conformational energy differences in many other halogenated ethanes.16 Yet, Dellepiane and Zerbi have recently shown that similar empirical potential functions for internal rotation give a poor account of the shape of the barrier for a number of experimentally well-developed cases.18 Nmr studies, supported by a partial vibrational assignment, also suggest that 1,2-dimethoxyethane is another example in which the gauche configuration is of lower energy than the trans.19,20 Further evidence for a cis preference in the absence of a double bond comes from the studies by Eliel and Kaldunston of the equilibrium for the cis-trans isomerization of 5-substituted 2-isopropyl-1,3-dioxanes such as

$$\text{CH}_2=\text{CH} \text{- trans} \rightarrow \text{CH}_2=\text{CH} \text{- gauche}$$

for which $\Delta G^\circ_{298} = 380$ cal/mol for the cis-to-trans conversion in benzene.21 It has seemed to us that a thorough investigation of the 1,2-difluorocyclopropanes, which are spectroscopi-cally manageable and configurationally well defined, would clarify the importance of the double bond in the cis effect. Models show that the FF distance in the cis and trans isomers of these cyclopropanes should be within 0.1 Å of the corresponding distances in the 1,2-difluoroethylenes and 1,2-difluoroethanes. Preliminary results of the cyclopropane study are reported in this paper.

**Experimental Section**

1-Chloro-2-fluoroethylenes. The preparation and characterization of the cis and trans isomers of C2F2H2 have been described before.22 As in the earlier study of the C2F2H2 isomerization equilibrium,2 gas chromatography was employed to analyze the equilibrium mixtures of the iodine-catalyzed, gas-phase isomerization. Samples were handled on a vacuum system as described before, but the oven was improved. A Bayley Instrument Co. (Model 117) controller was installed with its resistance element in the aluminum cylinder which enclosed the reaction cell, and three chromel-alumel thermocouples were positioned in and around the cell to check for temperature uniformity. At most the temperature varied about 1° over the cell volume. At each temperature equilibrium was approached from both the cis-rich and trans-rich sides. Gas chromatographic analyses were performed at 65° on a 4-m column packed with dibutyl phthalate on firebrick. Peaks representing the two isomers were well separated and had near-Gaussian shapes. Areas of the peaks were calculated by the triangle approximation after initial planimeter measurements gave the same results for ratios of areas within experimental error. Measurements on prepared mixtures showed that no correction was needed to observe trans/cis ratios within 0.5%. In most cases samples were equilibrated for several days and showed little evidence of volatile side products and only slow pressure decreases due to polymerization.

(13) (a) R. A. Beaudet, ibid., 40, 2705 (1964); (b) V. W. Weiss, P. Bank, and W. H. Flygare, ibid., 45, 981 (1967).
Pressures in the reaction vessel ranged from 100 to 300 Torr.

**1,2-Dichloroethylenes.** Samples of Aldrich Chemical Co. cis-C₂Cl₂H₂ and trans-C₂Cl₂H₂ were used without further purification other than degassing and vacuum distillation. The equilibrium study at 288° followed the same procedure as for the 1-chloro-2-fluoroethylenes. For the gas chromatographic analyses a 4-m column packed with silicone oil on firebrick was used at 90°. Sketching was employed to untangle the small region of overlap between the two peaks, and areas were measured with a planimeter. Side reactions were not extensive.

**1,2-Difluorocyclopropanes.** cis- and trans-1,2-difluorocyclopropanes were prepared by a photolytic reaction between diazomethane and 1,2-difluoroethylene (source, Peninsular Chem Research Co.). Photolysis of approximately 1:1 mixtures of diazomethane and olefin in the liquid phase at −50° gave a yield of cyclopropanes of about 20%.24 The vented reaction tube was immersed in an ethanol-Dry Ice mixture in an unsilvered Pyrex dewar flask and irradiated from the outside with light from a medium pressure mercury arc. Pure samples of cis and trans isomers were obtained by gas chromatographic fractionation on a 4-m column packed with tricresyl phosphate on firebrick. After the trans isomer (bp −11°) was eluted at room temperature, the column temperature was raised to 75° to hasten the elution of the cis isomer (bp −46°). Iden-
tifications based on the rigid-rotor, harmonic oscillator model were performed with program STATHERM on an IBM 360/44 computer. Input consisted of Cartesian coordinates and masses for atoms, vibrational fundamentals, and rotational symmetry numbers. Output included principal moments of inertia as well as tables of thermodynamic functions of 100 to 2000°K in 100° intervals. Tables of output data are on file.

**Results**

For the reaction

\[ \text{cis-C}_2\text{FClH}_2(g) = \text{trans-C}_2\text{FClH}_2(g) \]

Table I summarizes the equilibrium constant measurements and Figure 1 shows the temperature dependence of log *K* over the 280° range. A least-squares fit gives

\[ \log K = \frac{(-171.0 \pm 4.9\text{K})}{T} + (0.0462 \pm 0.0083) \]

from which $\Delta E^\circ_\text{vib} = 780 \pm 20$ cal/mol and $\Delta S^\circ_\text{vib} = 0.21 \pm 0.04$ cal/deg-mol. Figure 1 also includes two "ungefähr" values of the equilibrium constant reported by Viehe.6 They were not used in the least-squares analysis. A rigid-rotor, harmonic-oscillator treatment of the spectroscopic data gives $\Delta S^\circ_\text{vib} = 0.24 \pm 0.2$ cal/deg-mol, $\Delta E^\circ_\text{vib} = 185 \pm 20$ cal/mol, and $\Delta E_\text{vib} = -270 \pm 70$ cal/mol.21,27 As a consequence $\Delta E_\text{vib} = \Delta E^\circ_\text{vib} - \Delta E^\circ_\text{phot} - \Delta E^\circ_\text{vib} = 860 \pm 110$ cal/mol. The excellent agreement between the entropy change derived from the equilibrium constant measurements and the entropy change calculated from the spectroscopic data is reassuring. The ±0.2 uncertainty in the calculated $\Delta S^\circ$ is due primarily to the estimated uncertainties in the assignments of the vibrational fundamentals.

**Table 1:** Observed Equilibrium Constants for the Reaction

<table>
<thead>
<tr>
<th>Temp, °K</th>
<th>cis-rich</th>
<th>trans-rich</th>
<th>Equilibrium constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>474</td>
<td>1</td>
<td>3</td>
<td>0.485</td>
</tr>
<tr>
<td>540</td>
<td>4</td>
<td>4</td>
<td>0.536 ± 0.003</td>
</tr>
<tr>
<td>554</td>
<td>4</td>
<td>5</td>
<td>0.594 ± 0.002</td>
</tr>
<tr>
<td>615</td>
<td>5</td>
<td>6</td>
<td>0.587 ± 0.007</td>
</tr>
<tr>
<td>681</td>
<td>5</td>
<td>3</td>
<td>0.621 ± 0.007</td>
</tr>
<tr>
<td>756</td>
<td>5</td>
<td>2</td>
<td>0.661 ± 0.004</td>
</tr>
</tbody>
</table>

* After mixture had apparently reached equilibrium. With average difference from the average. All 55 values of the equilibrium constant were used in the least-squares analysis.

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(24) This methylene reaction was not stereospecific. No reaction was observed in repeated attempts to photolyze ketene-difluoro-
ethylene mixtures in the liquid phase at −86°. Gas-phase photolysis of the ketene-ethylene mixtures gave complex product mixtures and low yields of the difluorocyclopropanes.

(25) Paper II, 23rd Symposium on Molecular Structure and Spec-
troscopy, Columbus, Ohio, September 1968.


(27) $\theta$ = thermal energy; $zp$ = zero point vibrational energy; e = electronic energy.
Figure 1. Temperature dependence of the equilibrium constant for the cis–trans isomerization of C$_2$ClF$_2$. Viehe (ref 6) carried out this research: cis-rich, O; trans-rich, △. Line is from least-squares analysis.

Figure 2 is a composite of all of the published values for the equilibrium constant for the reaction

cis-C$_2$Cl$_2$H$_2$(g) = trans-C$_2$Cl$_2$H$_2$(g)

Our single equilibrium constant measurement, $K = 0.645 \pm 0.013$ at 562 ± 1 K, is also included. The agreement of this gas chromatographically derived value with the ones based on dielectric constant measurements decreases the possibility that the latter method was confounded by side reactions (vide infra). All of the published values except the one of Ebert and Bull were obtained from dielectric constant measurements. The line in Figure 2 was drawn by eye. In drawing this line the single value of Ebert and Bull, based on boiling point measurements, was disregarded as were the two high temperature measurements of Maroney. Side reactions were probably significant at these high temperatures. Nonetheless, the line fits the two high temperature values reasonably well. The equation for this line is

$$\log K = \left( -141^\circ K \right)/T + 0.066$$

from which $\Delta E_0^{\circ} = 650 \pm 70$ cal/mol and $\Delta S_0^{\circ} = 0.30 \pm 0.20$ cal/deg-mol. The upper limits on these values are based on the line which fits the data of Wood and Stevenson alone.56

From the published spectroscopic data we calculate $\Delta S_0^{\circ} = 80.40 - 80.05 = 0.35 \pm 0.2$ cal/deg-mol, $\Delta E_0^{\circ} = 8010 - 7800 = 210 \pm 20$ cal/mol, $\Delta E_{vib} = 20500 - 20775 = -275 \pm 80$ cal/mol. Consequently, $\Delta E_0^{\circ}$ is 720 ± 160 cal/mol. The small differences between these statistical thermodynamic quantities and those given by Pitzer and Hollenberg are due to the use of the updated vibrational assignment of Hopper and the geometric parameters preferred by Bernstein and Ramsay.

The present value of 650 cal/mol for $\Delta E_0^{\circ}$ is consistent with the value of $\Delta E_0^{\circ} = 200 \pm 50$ cal/mol obtained from the enthalpy of combustion of C$_2$Cl$_2$H$_2$ isomers in the liquid phase and the enthalpies of vaporization. Compared with the present value of $\Delta E_0^{\circ} = 440$ cal/mol, values of 530 and 500 were calculated from Wood and Stevenson equilibrium constant data alone and a value of 445 was calculated from the combined lower temperature data.

Statistical thermodynamic calculations were also carried out for cis- and trans-N$_2$F$_2$. The vibrational fundamentals were from King and Overend's assignment augmented with gas-phase Raman bands for the

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trans isomer observed by Shamir and Hyman.\textsuperscript{32} Separate geometric parameters used for the two isomers were those reported by Bohn and Bauer from an electron diffraction study.\textsuperscript{34} Microwave measurements concur on the cis geometry,\textsuperscript{35} and high resolution infrared measurements concur on the trans.\textsuperscript{36} For use with \(\Delta E^{0}_{298} = 3000 \pm 300\) cal/mol obtained by Armstrong and Marantz from enthalpies of reduction with ammonia,\textsuperscript{37} \(\Delta E^{0}_{298} = 2915 - 2850 = 65 \pm 40\) cal/mol, and \(\Delta E^{0}_{100} = 7030 - 7145 = -115 \pm 75\) cal/mol. Also \(\Delta S^{0}_{298} = 62.00 - 61.85 = -0.25 \pm 0.2\) cal/deg-mol. The difference in electronic energy between the two isomers is 3050 ± 400 cal/mol. All of these thermodynamic quantities are for the reaction

\[
\text{cis-N}_2\text{F}_2(g) = \text{trans-N}_2\text{F}_2(g)
\]

Colburn and coworkers have reported several measurements of the cis-trans equilibrium at 553°K.\textsuperscript{38} From the average equilibrium constant, \(K = 1.023\), and calculated values of \(\Delta S^{0}_{100} = -0.15\) cal/deg-mol and \(\Delta H^{0}_{298} - \Delta H^{0}_{298} = 40\) cal/mol, one calculates \(\Delta E^{0}_{298} = 1990\) cal/mol. Given the difficulty of making equilibrium measurements on this highly reactive system, this value appears to be in reasonable agreement with the thermochemical one.

For the iodine-catalyzed reaction

\[
\text{cis-C}_2\text{F}_4\text{H}_4(g) = \text{trans-C}_2\text{F}_4\text{H}_4(g)
\]

at 586 ± 5°K, the equilibrium constant is 11.7 ± 0.5, from which \(\Delta G^{0}_{298} = -2900 \pm 200\) cal/mol. Although considerable infrared and Raman data are in hand, we do not yet have a complete assignment of the fundamentals for the two isomers. Therefore, for the present we assume \(\Delta S^{0}_{100} \approx 0\) and \(\Delta E^{0} = \Delta E^{0}_{298} = \Delta E^{0}_{100}\). In this cyclopropane case, the trans isomer has lower electronic energy. In view of the difficulties in obtaining equilibrium in this system we consider this result to be preliminary.

**Discussion**

Table II is a compilation of thermodynamic quantities for the cis-to-trans isomerization of haloethylenes (and difluorodiene) for which rather complete spectroscopic and thermodynamic data are available. The quantity of particular interest, the difference in electronic energy of the two isomers, is given in the last column. In addition to the data for difluorodiene, chlorofluoroethylene, and dichloroethylene which were presented in the Results section, Table II includes data for 1,2-difluoroethylene, 1,2-dibromoethylene, 1,2-diodoethylene, and one trihaloethylene.

Pertinent thermodynamic quantities for the iodine-catalyzed isomerization of \(\text{C}_2\text{F}_4\text{H}_4\) have been reported previously.\textsuperscript{1,47} A shock tube study of the rate of isomerization from both the cis and trans directions gives \(\Delta E^{0}_{298} = 2700 \pm 2400\) cal/mol\textsuperscript{18} in general agreement with the value derived from the temperature dependence of the equilibrium constant.

Two sets of measurements of the gas-phase, iodine-catalyzed isomerization of \(\text{C}_2\text{Br}_2\text{H}_4\) have been reported.\textsuperscript{39,40} The 80° temperature range is too small to reveal a believable temperature dependence of the equilibrium constant. In choosing \(K = 0.960 \pm 0.06\), for the cis-to-trans reaction we have placed somewhat greater weight on the more recent measurements, which are based on gas chromatographic analysis. Statistical thermodynamic values of \(\Delta S^{0}_{298} = 0.58 \pm 0.5\) cal/deg-mol and \(\Delta E^{0}_{298} = 220 \pm 40\) cal/mol\textsuperscript{41} have been used to extract \(\Delta E^{0}_{298}\) and \(\Delta E^{0}\) from \(\Delta G^{0}_{298}\). Dowling and coworkers gave \(\Delta E^{0}_{298} = -100 \pm 160\) cal/mol (present value 90 ± 240) based on the dubious \(\Delta E^{0}\) calculated by Noyes and Dickinson.\textsuperscript{42} In the liquid phase the polar, cis isomer is favored \((K = 0.59-0.67\) at 25–150°\textsuperscript{43} over the gas phase as expected.\textsuperscript{15}

The published spectroscopic data for the diiodoethylenes do not permit meaningful statistical thermodynamic calculations. Although the assignment for the cis isomer\textsuperscript{44} appears to be sound, the assignment for the cis isomer is in doubt. The cis assignment is based on spectra measured on the eutectic mixture (20% trans, 80% cis).\textsuperscript{14} A number of bands of the two isomers are overlapped. The standing assignment gives \(\Sigma^{p}_{i}f_{i}^{cis} < \Sigma^{p}_{i}f_{i}^{trans}\) in contrast to all of the other dihalo cases considered in this paper. Also two of the frequencies for \(cis-C_2I_4H_4\) (\(\nu = 664\) and \(\gamma = 176\) cm\(^{-1}\)) fall below values that would fit the group frequency pattern established by the other dihaloethylenes. In contrast, a similar group frequency comparison for the trans isomer is satisfactory.\textsuperscript{42}

Furuyama, Golden, and Benson have recently reported the equilibrium constant \((K = 1.69 \pm 0.13)\) for the gas phase isomerization (inherently iodine catalyzed) and have found no significant temperature dependence over a 140° range.\textsuperscript{44} They give \(\Delta E^{0}_{298} = -0.15\) cal/deg-mol.

**References**

(34) R. K. Bohn and S. H. Bauer, *Inorg. Chem.*, 6, 369 (1967). Calculated moments of inertia were: \(cis-N_2F_2\): \(I_1 = 20.58, I_2 = 64.04, I_3 = 90.62\); \(trans-N_2F_2\): \(I_1 = 6.633, I_2 = 109.80, I_3 = 116.42\).


(40) Viehe and Franchimont (ref 8b) have shown an equilibrium is established between HBrC=CBrH, HBrC=CIH, and HIC=CIH, all of which were present in significant amounts in their system. We have not observed any such halogen exchange in the fluorochloroethylene systems.


430°K in the liquid phase in decalin gave sufficient to accurately determine a small 

revised somewhat as a consequence of the present com-

trihaloethylene, 

However, this liquid phase value is a re-

calculated one. In the original report the eutectic mix-

E. Further doubt is in-

tration interaction, Fermi resonance, and gas nonideality

strong support for the existence of this effect. The

pattern of the entropy and energy values is reasonable,

sufficient to accurately determine a small ΔE°.

The thermodynamic values in Table II for the one 
thrihaloethylene, 1,2-difluoro-1-chloroethylene, are from 
a previous paper. Error estimates have been re-

somewhat as a consequence of the present compar-

ative analysis.

Although much of the evidence for the cis effect de-

pends on small differences between large numbers, the data in Table II, considered as a whole, provide rather 

strong support for the existence of this effect. The pattern of the entropy and energy values is reasonable, 

and, where checks on the entropy change from second-

law and third-law treatments are possible, the agree-

ment is good. Of course, contributions from second-

order effects including anharmonicity, rotation–vibra-

tion interaction, Fermi resonance, and gas nonideality 
have been neglected in the statistical thermodynamic 
calculations. It is reasonable, however, to assume that 
these contributions tend to cancel out for molecules as 
similar as pairs of cis–trans isomers.

At first thought gas nonideality, particularly in the form of strong hydrogen bonding between pairs of cis 
isomers, is of greater concern. Qualitatively, dimer-

ization of cis isomers (an exothermic process) could pro-
duce an apparent positive temperature coefficient for 
the overall cis–trans isomerization that could domi-

nate a true negative temperature coefficient (exo-

thermic) for the simple isomerization involving mono-

mers. Evaluation of expressions for the competing equilibria with representative values for the overall 
temperature coefficient and trans/cis ratio showed that 
the necessary degree of dimerization of the cis isomer 

would be unreasonably large. At room temperature 
the dimerization would be essentially complete. Yet, 
separate gas density measurements for the cis (and trans) isomers of C₂F₂H₂ gave molar weights within a 
few per cent of ideal gas values. Also, enthalpies and 
entropies of vaporization are normal for both cis- and 
trans–C₂H₂H₂. 

In every instance in Table II the observed, composite ΔE° reflects the difference in electronic energy rather 

well, as has been often assumed. Since ΔS° = 0, particularly for the fluoro systems, the approximation 

ΔE° = ΔG° is useful.

At least one kind of nonthermodynamic evidence ex-

ists in support of the cis effect. It is the difference in 
torsional force constants for cis- and trans–C₂F₂H₂ 
and cis- and trans–C₂ClF₂H₂. In both cases the cis isomer 
has the larger force constant for incipient torsion around 
the double bond. The difference is well outside the un-

certainty in these force constants as calculated by a 

normal coordinate analysis of complete hydrogen–deu-

terium isotopic sets. In contrast, the force constants 

for CH out-of-plane wagging are very nearly the same 
in each case. The larger torsional force constant for cis 

isomer presumably reflects some additional force 

holding this isomer in the planar configuration.

Though more supporting evidence would be desirable, the cis effect in haloethylenes now seems to be rather 


(47) From unpublished vapor pressure equations, for cis-C₂F₂H₂: ΔH° = 4970 
cal/mol and ΔS° = 22.6 gibbs/mol.

Table II: Thermodynamic Functions for cis–trans Isomerization of Haloethylenes 

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temperature, °K</th>
<th>ΔS°calc.</th>
<th>ΔS°calc.</th>
<th>ΔS°calc.</th>
<th>ΔS°calc.</th>
<th>ΔS°calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>FN = NF</td>
<td>300</td>
<td>-0.25 ± 0.2</td>
<td>3000 ± 300</td>
<td>2930 ± 380</td>
<td>3050 ± 400</td>
<td></td>
</tr>
<tr>
<td>HFC = CFH</td>
<td>620</td>
<td>0.14 ± 0.03</td>
<td>930 ± 20</td>
<td>780 ± 40</td>
<td>1080 ± 120</td>
<td></td>
</tr>
<tr>
<td>HFC = CCH (450–760)</td>
<td>615</td>
<td>0.21 ± 0.04</td>
<td>780 ± 20</td>
<td>600 ± 40</td>
<td>870 ± 110</td>
<td></td>
</tr>
<tr>
<td>HFC = CCH (475–760)</td>
<td>540</td>
<td>0.30 ± 0.20</td>
<td>650 ± 70</td>
<td>440 ± 90</td>
<td>720 ± 160</td>
<td></td>
</tr>
<tr>
<td>HBrC = CBrH (420–500)</td>
<td>475</td>
<td>0.58 ± 0.3</td>
<td>(320 ± 200)</td>
<td>90 ± 240</td>
<td>250 ± 330</td>
<td></td>
</tr>
<tr>
<td>HIC = CICH (470–610)</td>
<td>540</td>
<td>1.1 ± 0.1</td>
<td>0 ± 200</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HFC = CClI</td>
<td>590</td>
<td>-0.12 ± 0.3</td>
<td>(10 ± 180)</td>
<td>30 ± 20</td>
<td>80 ± 230</td>
<td></td>
</tr>
</tbody>
</table>

* Calculated from a single equilibrium and ΔS°calc. Literature citations are given in the text.
well established in experiment. Rationalizations for it are, however, a much more uncertain matter. At first glance the 3000 cal difference in energy between the isomers of \( \text{N}_{2} \text{F}_{2} \) (Table II) appears anomalously large compared with the 1100 cal difference for the isomers of \( \text{C}_{2} \text{F}_{2} \text{H}_{2} \). However, in \( \text{C}_{2} \text{F}_{2} \text{H}_{2} \) the repulsion energy between the CF bond dipoles is approximately 1400 cal greater in the cis isomer.\(^{46}\) The corresponding difference in dipole–dipole repulsion in \( \text{N}_{2} \text{F}_{2} \) must be considerably smaller since the cis isomer has a dipole moment of only 0.16 D.\(^{52}\) Thus, for comparative purposes each for the electronic energy difference for a dihaloethylene pair in Table II should be increased from about 1400 to 400 cal, the latter being for \( \text{C}_{2} \text{I}_{2} \text{H}_{2} \).\(^{16}\)

At the present time no quantum mechanical calculations appear to be available that are sufficiently precise to corroborate the experimental evidence for the cis effect and to explain it. However, Pitzer and Hollenberg\(^{29}\) and others have ascribed this effect to contributions from resonance structures of the type

\[
\begin{align*}
\text{F}^+ & \quad \text{F}^- \\
\text{H} & \quad \text{C} & \quad \text{F}^+ & \quad \text{F}^- \\
\text{H} & \quad \text{H}
\end{align*}
\]

More recently Hoffmann and Olofson\(^{49}\) have argued for a preferred cis structure of electronically excited or anionic butadiene due to overlap of the \( \pi \) orbital in the HOMO.

This molecular orbital argument applies to cis-\( \text{C}_{2} \text{C}_{l} \) \( \text{F}_{2} \text{H}_{2} \), which may be considered to have a six-electron \( \pi \) system if a nonbonded pair from each fluorine atom is involved. Both the valence bond and the MO arguments require double bond character in the CX bonds at the expense of the unshared pairs on each of the halogen atoms. The nuclear quadrupole coupling constants for chloroethylenes have been interpreted as indicating about 5% double bond character for CCl bonds.\(^{50}\) The corresponding double bond character for cis-\( \text{C}_{2} \text{C}_{l} \) \( \text{Cl}_{2} \text{H}_{2} \) is not exceptional, however, and no data are available for trans-\( \text{C}_{2} \text{Cl}_{2} \text{H}_{2} \). An apparent weakness in this electron delocalization explanation is the trend in the \( \Delta E_{a} \) values in Table II. These \( \Delta E_{a} \) values do not seem to decrease in proportion to the presumed weakening of the p–p overlap between carbon and larger halogen atoms. Steric repulsion of nonbonding electrons might also be expected to add to this rate of decrease in \( \Delta E_{a} \).\(^{16}\) However, these effects are offset to some extent by the previously cited decrease in the CX dipole–dipole repulsion. If the polar valence bond structures (1) were important, the cis effect would be marked in the mixed chlorofluoroethylenes. Yet, the electronic energy differences for the two chlorofluoro examples in Table II seem to fit a smooth trend between \( \text{CFH} = \text{CFH} \) and \( \text{CCl} = \text{CCl} \). (The fragmentary data for \( \text{CFH} = \text{CBrH} \) and \( \text{CFH} = \text{CII} \) suggest otherwise, however.\(^{4,8}\) Although the case for the electron delocalization interpretation of the cis effect is far from complete, it seems the most reasonable proposal for haloethylenes (and diazenes).\(^{41}\)

The electron delocalization argument will not serve to explain the apparent cis effect in saturated compounds. Although \( H^0_{\text{gauche}} - H^0_{\text{trans}} = 0 \) for 1,2-difluoroethane, allowance for about 1000 kcal/mol greater CF dipole–dipole repulsion in the gauche conformer makes \( \Delta H^0 \) 0 more significant. It must be emphasized, however, that \( \Delta H^0 = 0 \) for the \( \text{C}_{2} \text{F}_{2} \text{H}_{2} \) conformers is tentative, and further, \( \Delta E_{a} \) might yet prove to favor the trans form. However, on the basis of presently available data (see the Introduction for other examples) a nonbonded, van der Waals attraction between the halogen atoms may be important. van der Waals attractions based on potential energy parameters obtained from noble gases are too small to support this hypothesis,\(^{16}\) although it is possible that noble gas parameters are inadequate for bound halogen atoms. Thus, for 1,2-dihaloethanes containing fluorine Abraham and Parry's calculations were 0.5–1.0 kcal too low for the gauche-to-trans conversion. Figure 3 is a schematic representation of the location of various fluorocyclopropanes on a deepened \(-F\ldots F\ldots F\ldots\) potential curve. Based on rotation barriers in various fluoroethanes\(^{16}\) it appears that the cis (eclipsed) form of \( \text{C}_{2} \text{F}_{2} \text{H}_{2} \) falls in the repul-

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\( \text{CCHH=CH} = \text{CCH} \). (The fragmentary data for \( \text{CFH} = \text{CBrH} \) and \( \text{CFH} = \text{CII} \) suggest otherwise, however.\(^{4,8}\) Although the case for the electron delocalization interpretation of the cis effect is far from complete, it seems the most reasonable proposal for haloethylenes (and diazenes).\(^{41}\)

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\( \text{(48)} \) Estimated from a point charge model based on the geometry and dipole moment from the microwave study (ref 36). Neglect of moment for the CH bond favors the cis isomer.


\( \text{(51)} \) For 1-halopropenes simple dipole–dipole attraction seems to be an adequate explanation as shown by Abraham and Parry's calculation for rotamers of 1-halopropenes (ref 19).

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sive region. Of course, the steepness of the potential curve on the repulsive side implies that small differences in geometry would cause sizeable changes in the van der Waals interaction energy. Unfortunately, the fact that the rotation barrier in cis-1-fluoropropylene is little different from that for 1,1-difluoropropylene, in which the apparent equilibrium HF distance is 0.05 Å longer, seems to contradict this explanation—if the $-H \cdot \cdot \cdot F-$ van der Waals potential is anything like that for $-F \cdot \cdot \cdot F-$. For cis haloethylenes both double bond induced and direct van der Waals attractions may be involved, since the FF distance in cis-1,2-C\(_2\)F\(_2\)H\(_4\) is close to that in gauche-1,2-C\(_2\)F\(_2\)H\(_4\).

cis-1,2-Difluorocyclopropane with a predicted FF distance\(^{53}\) close to that of gauche-C\(_2\)F\(_2\)H\(_4\) might be expected to exhibit the single bond cis effect alone. However, our preliminary equilibrium constant value implies a remarkably low energy for the trans configuration. Of course, it is possible that the true FF distance in the cis-cyclopropane is sufficiently small to place it well up the repulsive side of the van der Waals potential. Such a shortened FF distance could possibly be related to diminished opportunity for steric relief in the cyclopropane, which should be reflected in a large HCF bending force constant. It is also possible that the difluorocyclopropane result is the only one permitting direct interpretation, in which case the true cis effect is only to be found along with double bonds. In the near future we expect to have more critical vibrational and thermodynamic data on the difluorocyclopropanes. It is also hoped that the trans cyclopropane isomer has a sufficient dipole moment to make possible a detailed microwave investigation of it as well as the cis isomer.\(^{15}\)

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\(^{52}\) FF distance in cis-C\(_2\)F\(_2\)H\(_2\) is 2.74 Å (V. W. Laurie and D. T. Pence, J. Chem. Phys., 38, 2689 (1963)); in the corresponding trans isomer it is 3.50 Å. Based on the geometric parameters (ref 15): $r_{CF} = 1.37$, $r_{CC} = 1.54$ Å, $\angle CCF = 109.5^\circ$, and dihedral angle in gauche of 60°; the FF distance in cis-C\(_2\)F\(_2\)H\(_2\) is 2.45 Å, in gauche-C\(_2\)F\(_2\)H\(_2\) is 2.77 Å, and in trans-C\(_2\)F\(_2\)H\(_2\) is 3.56 Å.

\(^{53}\) With $r_{CF} = 1.38$, $r_{CC} = 1.52$ Å, $\angle CCC = 60^\circ$, $\angle HCF = 115^\circ$, and $\angle CCF = 116.5^\circ$, the FF distance in cis-C\(_2\)F\(_2\)H\(_2\) is 2.71 Å. See Ha. H. Gunthard, R. C. Lord, and T. K. McCubbin, Jr., J. Chem. Phys., 25, 768 (1956), for cyclopropane geometric parameters.

\(^{54}\) NOTE ADDED IN PROOF. D. Sianesi and R. Fontanelli, Ann. Chim. (Rome), 55, 860 (1965), have measured the bromine-catalyzed isomerization of 1H-pentafluoropropylene over the temperature range 300–550°. For the cis-to-trans reaction $\Delta H^\circ = 3.9$ kcal/mol (sign changed to conform to the data) and $\Delta S^\circ = 1.45$ cal/deg-mol.