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# The Infrared Absorption Spectra of Cis and Trans−1,2 Dichlorohexafluorocyclobutane

John R. Lacher, Alfred Büchler, and J. D. Park

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volume increase above 0°K, 0.209 experimental *vs* 0.162 computed, the result looks poorer, as only 80 percent of the true expansion has been computed.

Table IV, giving the vapor pressures, shows most dramatically how poor the equations really are. The computed value of $Pv/u_0$ in Table IV is sevenfold too high at $kT/u_0=0.7$, showing that the Gibbs free energy is too high by $RT\ln 7$ per mole, or $\mu_r/kT$ too high by $\ln 7=2$. The quantity $(\mu_r/kT)-\ln v$ is the difference between $\mu/kT$ for the system and that of a perfect gas at the same volume as the system. This is the configurational free energy per molecule, divided by $kT$. At $kT/u_0=0.7056$ the experimental value is $-6.2$ whereas our computed value is only $-4.2$. This means that our restrictions on the form of the distribution function permit the nonequilibrium ensemble to utilize only 68 percent of the reduction in free energy which is available to an equilibrium configuration.

The main advantage which we may claim for the method used here is that of logic and self-consistency. We have defined a nonequilibrium ensemble with definite prescribed characteristics, and, except for the one remedial error of neglecting interactions between more distant than neighboring cells, we have computed its thermodynamic characteristics correctly. These are necessarily such that at fixed $V$ and $T$ the Helmholtz free energy is too large, at fixed $P$ and $T$ the Gibbs free energy is too large, and at fixed $\mu$ and $T$ the $PV$ product is too small.

Since the prescription of the distribution is exact, one may proceed to investigate improvements. The most obvious one, and the one which appears to offer the greatest hope of improvement, is the introduction of a correlation function between the positions of two molecules in neighboring cells. It would not appear to be impossible to handle such a distribution.

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# The Infrared Absorption Spectra of *Cis*- and *Trans*-1,2-Dichlorohexafluorocyclobutane*

JOHN R. LACHER, ALFRED BÜCHLER, AND J. D. PARK
*University of Colorado, Boulder, Colorado*

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The thermal dimerization of chlorotrifluoroethylene leads to 1,2-dichlorohexafluorocyclobutane consisting mainly of the high boiling isomer. On the other hand, the photochemical or catalytic chlorination of hexafluorocyclobutene yields a dichloride consisting mainly of the low boiling isomer. These isomers may be readily separated by fractional distillation. Dielectric constant measurements permit one to indicate that the high boiling one is *cis* and the low boiling is the *trans*. The infrared spectra in the sodium chloride region were measured and compared with the existing data on the Raman spectra.

HENNE and Ruh[1] first prepared 1,2-dichlorohexafluorocyclobutane. They showed that the thermal dimer of monochlorotrifluoroethylene consisted entirely of the "head-to-head" compound.[2] However, no attempt was made to separate the *cis*- and *trans*-isomers. The Raman spectrum of the unresolved mixture of the two isomers has been reported by Edgell and Kite.[3]

## PREPARATION OF THE ISOMERS

The high boiling isomer of 1,2-dichlorohexafluorocyclobutane was obtained by the dimerization of monochlorotrifluoroethylene[4] under autogenous pressure at 200° in the presence of du Pont Terpene *B* inhibitor.[1] The dimer was distilled on a Podbielniak column having 100 theoretical plates. The last cut and pot residue were identified as the pure high boiling isomer by an inspection of their freezing point curve. The estimated purity was 99 percent. It is believed that the thermal dimer produced in this way consisted of at least 80 percent of the high boiling isomer.

TABLE I. *Cis* and *trans* isomers of 1,2-dichlorohexafluorocyclobutane.

| | *cis* | *trans* |
|---|---|---|
| B.P. | 54°/630 mm | 51.3°/630 mm |
| F.P. | −14.2° | −24.2° |
| $n_D^{20}$ | 1.3340 | 1.3340 |

The low boiling isomer was produced by either photochemical or catalytic chlorination of hexafluorocyclobutene. 1,2-dichlorohexafluorocyclobutane (thermal dimer) was dechlorinated with zinc in boiling *n*-butanol to give hexafluorocyclobutene. The photochemical chlorination was carried out batchwise using a 5-l glass bulb in the usual fashion. The thermal chlorination was carried out over a ferric chloride-activated charcoal catalyst using methods previously described.[5] The dichloride produced by either of these

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[1] A. L. Henne and R. P. Ruh, J. Am. Chem. Soc. **69**, 279 (1947).
[2] A. L. Henne and W. J. Zimmerschied, J. Am. Chem. Soc. **69**, 281 (1947).
[3] W. F. Edgell and F. E. Kite, J. Chem. Phys. **15**, 882 (1947).
[4] A sample of monochlorotrifluoroethylene was kindly furnished us by Dr. E. G. Young of the Kinetic Chemicals Division of the du Pont Company.
[5] Lacher, McKinley, Walden, Lea, and Park, J. Am. Chem. Soc. **71**, 1334 (1949).

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methods was found on distillation to consist of at least 80 percent of the low boiling isomer. The purity of the final product was checked spectroscopically by the disappearance of the high boiling isomer's absorption band at 9.56$\mu$ and was judged to be 99 percent.

In order to identify the nature of each isomer, an attempt was made to measure their dipole moments. Theoretically, the *trans*-compound should have a zero moment, while the *cis*-compound should have a moment of the order of 0.1 Debye unit using the group moment values recently given by Myers and DeVries.[6] In practice it was found that in a 4 mole percent solution of 1,2-dichlorohexafluorocyclobutane in benzene, the dielectric constant of the low boiling isomer was the same as that of pure benzene, while the solution containing the high boiling isomer was 1 percent higher. While the instrument did not permit measurements which could be extrapolated to zero concentration, the difference of 1 percent is larger than the experimental error and permits the deduction that the low boiling isomer is *trans* and that the high boiling one is the *cis* isomer. A summary of some of their physical properties is given in Table I.

TABLE II. Infrared and Raman bands for 1,2-dichlorohexafluorocyclobutane.

| Infrared | | Raman[a] |
|---|---|---|
| *cis* | *trans* | mixture |
| 7.25$\mu$ | 7.27$\mu$ | 7.18$\mu$ |
| | 7.46 | |
| 7.80 | 7.81 | 7.77 |
| 8.07 | 8.09 | 8.04 |
| 8.18[b] | | |
| 8.45 | 8.47 | 8.40 |
| | (8.88)[c] | |
| | | 9.00 |
| 9.18 | 9.22 | |
| | | 9.31 |
| 9.56 | | |
| 9.78 | 9.80 | |
| 10.40 | 10.27 | 10.35 |
| 11.24 | | |
| 11.61 | 11.58 | 11.59 |
| 12.40 | 12.49 | 12.35 |
| (14.49)[c] | | |
| | (13.25)[b, c] | |
| | (14.54)[c] | |

[a] See reference 3.
[b] Shoulder.
[c] Not a fundamental band.

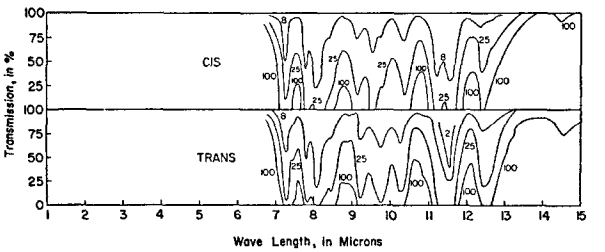


FIG. 1. Infrared absorption spectra of *cis*- and *trans*-1,2-dichlorohexafluorocyclobutane. 10-cm cell and pressures as indicated in mm.

## INFRARED ABSORPTION SPECTRA

A Perkin-Elmer mode 12B infrared spectrometer with NaCl optics was used in the region 2.15 to 15$\mu$. Using gaseous samples, the spectra were obtained in the usual way and are shown for the 2 isomers in Fig. 1. The wavelength of the absorption bands are given in Table II. If we assume a planar ring, the *cis* isomer will belong to the symmetry group $C_s$ (one plane of symmetry) and the *trans*-isomer to the symmetry group $C_2$ (one twofold axis of symmetry). The distribution of fundamentals will be: for the *cis*-isomer, $15A'+15A''$; and for the *trans*-isomer, $16A+14B$. All of these fundamentals should be both infrared and Raman active, with the $A'$ and $A$ vibrations polarized and the $A''$ and $B$ vibrations depolarized in the Raman spectrum. The probable fundamentals in this region, together with the Raman shifts reported by Edgell and Kite[3] on what was possibly a *cis-trans* mixture, are listed in Table II. The agreement is good, the Raman bands not occurring in the infrared probably involve very small changes in the dipole moment as compared to the polarizability, and vice versa. It is seen that most bands in the *trans*-spectrum are shifted slightly towards the red. The *cis*-bands at 8.18 and 9.56$\mu$ disappear in the *trans*-spectrum, while the band at 11.24$\mu$ either disappears or is shifted and masked completely by the *trans*-band at 11.58$\mu$. On the other hand, the band at 10.40$\mu$ in the *cis*-spectrum is shifted to 10.27$\mu$ in case of the *trans*.

The bands at 7.25, 7.80, 8.07, and 8.18$\mu$ for the *cis*-isomer, and at 7.27, 7.81, and 8.09$\mu$ for the *trans*-isomer probably involve C—F stretching vibrations. Of the other bands, those at 9.56, 10.40, and 11.24$\mu$ for the *cis*-isomer obviously involve the —CFCl—CFCl— part of the ring as a whole and therefore are shifted or disappear altogether in the *trans*-spectrum; while the bands whose location changes only very slightly apparently involve CF, $CF_2$ and perhaps CFCl and CCl group motions unaffected by the structure of the ring.

[6] A. L. Myers and T. DeVries, J. Am. Chem. Soc. **73**, 1813 (1951).

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