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## Physical and Inorganic Chemistry

### Infrared and Raman Spectra of *cis*- and *trans*-1,2-Dichloro-1,2-difluoroethylene

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*cis*- and *trans*-CFClCFCl have been separated by fractional melting, and infrared and Raman spectra of the nearly pure isomers have been obtained. Configurational assignments are established and are in agreement with a larger fluorine-fluorine coupling constant for the *trans* isomer. For both isomers complete assignments of the fundamental vibrations are given. For the *cis* isomer, however, some doubt surrounds the assignment of the two  $a_2$  modes. Zero-order normal coordinate calculations are in satisfying agreement with the observed fundamental frequencies.

*cis*- and *trans*-1,2-dichloro-1,2-difluoroethylene are members of a series of pairs of geometric isomers of chlorofluoroethylenes which are of particular interest in studies of interactions between nonbonded atoms.<sup>1</sup> An important step in this work is the development of complete assignments of vibrational fundamentals for the several *cis-trans* pairs. Since separation of *cis*- and *trans*-CFClCFCl by distillation had been reported twice<sup>2,3</sup> and since the vibrational spectra and assignment for the *trans* isomer were available,<sup>4</sup> we sought initially the *cis* isomer by gas chromatographic fractionation of crude C<sub>2</sub>F<sub>2</sub>Cl<sub>2</sub>. Two fractions were isolated. One gave an infrared spectrum identical with that reported for the *trans* isomer, but the other proved to be the asymmetric isomer CCl<sub>2</sub>CF<sub>2</sub>.<sup>5</sup> It then seemed likely

that the reported *trans* spectrum was in fact that of the *cis-trans* mixture. Separation by a combination of distillation and fractional melting confirmed this interpretation and showed that a significant purification of the two isomers had been obtained for the first time. Meanwhile, Tiers and Lauterbur had achieved a partial separation of these isomers by prolonged distillation and had made a tentative assignment of configuration as part of a study of the splitting of the F<sup>19</sup> n.m.r. spectrum by C<sup>13</sup>.<sup>6</sup>

Mann, Shimanouchi, Meal, and Fano have calculated the fundamental vibration frequencies of *cis*- and *trans*-CCl<sub>2</sub>FCCl<sub>2</sub>F with force constants transferred from C<sub>2</sub>F<sub>4</sub> and C<sub>2</sub>Cl<sub>4</sub>.<sup>7</sup> They used a Urey-Bradley force field for the planar modes and a simple valence force field for the out-of-plane modes. We have repeated the calculation for the planar modes and have obtained very nearly the same frequencies. These frequencies along with the selection rules for infrared and Raman activity and the expected band shapes for the gas phase infrared spectra are summarized in Table I.<sup>4</sup>

#### Experimental Section

*Preparation of 1,2-Dichloro-1,2-difluoroethylene.* CCl<sub>2</sub>FCCl<sub>2</sub>F was dehalogenated with zinc dust in refluxing absolute ethanol, and the mixture of C<sub>2</sub>F<sub>2</sub>Cl<sub>2</sub> products was continuously distilled into a Dry Ice cooled trap. The crude product contained nearly equal amounts of the *cis* and *trans* isomers and about 10% of CF<sub>2</sub>CCl<sub>2</sub>. The unsymmetrical isomer was conveniently removed by a procedure which takes

(1) N. C. Craig, G. Y.-S. Lo, C. D. Needham, and J. Overend, *J. Am. Chem. Soc.*, **86**, 3232 (1964).

(2) E. G. Locke, W. R. Brode, and A. L. Henne, *ibid.*, **56**, 1726 (1934).

(3) R. F. Sullivan, Doctoral Thesis, University of Colorado, 1956; University Microfilms (Ann Arbor, Mich.), Publication No. 22638, 1958.

(4) D. E. Mann and E. K. Plyler, *J. Chem. Phys.*, **26**, 733 (1957).

(5) J. R. Nielsen, H. H. Claassen, and D. C. Smith, *ibid.*, **18**, 485 (1950).

(6) G. V. D. Tiers and P. C. Lauterbur, *ibid.*, **36**, 1110 (1962).

(7) D. E. Mann, T. Shimanouchi, J. H. Meal, and L. Fano, *ibid.*, **27**, 51 (1957).

**Table I.** Predictions for the Vibrational Spectra of *cis*- and *trans*-CFCICFCl<sup>a</sup>

Infrared		Raman	—Assignment—		Infrared	Raman	—Assignment—	
a <sub>1</sub>	B <sup>b</sup>	Pol.	ν <sub>1</sub>	1729 (0.0)	a <sub>g</sub>	...	ν <sub>1</sub>	1731 (0.0)
			ν <sub>2</sub>	1140 (0.3)			ν <sub>2</sub>	1207 (0.2)
			ν <sub>3</sub>	565 (3.8)			ν <sub>3</sub>	644 (1.0)
			ν <sub>4</sub>	324 (0.8)			ν <sub>4</sub>	413 (4.1)
			ν <sub>5</sub>	183 (2.5)			ν <sub>5</sub>	299 (2.0)
a <sub>2</sub>	...	Depol.	ν <sub>6</sub>	349	a <sub>u</sub>	C	ν <sub>6</sub>	358
			ν <sub>7</sub>	150		...	ν <sub>7</sub>	140
b <sub>1</sub>	A <sup>b</sup>	Depol.	ν <sub>8</sub>	1260 (0.0)	b <sub>g</sub>	...	ν <sub>8</sub>	514
			ν <sub>9</sub>	969 (1.0)				
			ν <sub>10</sub>	434 (0.8)	b <sub>u</sub>	A/B	ν <sub>9</sub>	1235 (0.0)
			ν <sub>11</sub>	411 (3.7)		...	ν <sub>10</sub>	878 (2.2)
							ν <sub>11</sub>	431 (1.7)
b <sub>2</sub>	C	Depol.	ν <sub>12</sub>	518			ν <sub>12</sub>	184 (1.1)

<sup>a</sup> Calculated Cl<sup>35</sup>Cl<sup>35</sup>-Cl<sup>35</sup>Cl<sup>37</sup> isotope splittings in parentheses; frequencies in cm.<sup>-1</sup>. <sup>b</sup> Table II in ref. 4, the A and B band-shape designations are reversed. The axis of least moment of inertia (*I<sub>A</sub>*) is parallel to the CC bond. Principal moments of inertia for the *cis* isomer are 166.7, 260.1, and 426.8 a.m.u. Å<sup>2</sup>; for the *trans* isomer: 117.6, 336.0, and 453.6 a.m.u. Å<sup>2</sup>.

advantage of the easier formation of the ether of this isomer with sodium ethoxide in ethanol.<sup>8</sup>

**Separation of Isomers.** Since separation of the *cis* and *trans* isomers by fractional distillation on a 50-plate spinning-band column was found to be inefficient, we tried a number of promising gas chromatography columns. Although a 12-ft. column with a tricresyl phosphate or silver nitrate-glycerin liquid phase on firebrick separated the CF<sub>2</sub>CCl<sub>2</sub> (b.p. 18.9°)<sup>9</sup> from the

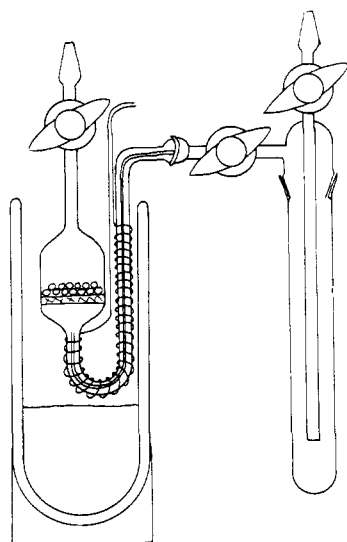


Figure 1. Fractional melting apparatus.

*cis* and *trans* mixture (b.p. 21° uncor.; lit.<sup>10</sup> b.p. 20.9°) at room temperature, no evidence of separation of the *cis-trans* pair was ever obtained. Tiers and Lauterbur also found gas chromatography to be ineffective for this separation.<sup>6</sup>

The two isomers were separated by a combination of fractional melting and fractional distillation. In this way were obtained a 20-mmole sample of *trans*-CFCICFCl of 99.6% isomeric purity and a 4-mmole sample of *cis*-CFCICFCl of 95.1% isomeric purity.

(8) J. M. Birchall, R. N. Haszeldine, and A. R. Parkinson, *J. Chem. Soc.*, 2204 (1961).

(9) A. L. Henne and E. G. Wiest, *J. Am. Chem. Soc.*, **62**, 2051 (1940).

(10) D. R. Stull, *Ind. Eng. Chem.*, **39**, 517 (1947).

By means of the Stock microtechnique<sup>11</sup> and a Leeds and Northrup platinum resistance thermometer, melting points were found to be: 95.4% *cis*, -119.6°; 99.6% *trans*, -93.3°; and eutectic (75% *cis*), -124.4°. From this melting point data and the assumption of a simple eutectic system with a Raoult's law solution, we calculate 2.34 kcal./mole for the heat of melting of both isomers and freezing points of -118.6° for the pure *cis* isomer and -93.2° for the pure *trans* isomer. Isomeric compositions were determined from the infrared intensities of the 990-cm.<sup>-1</sup> band ( $\alpha = 0.035$  torr<sup>-1</sup> cm.<sup>-1</sup>) of the *cis* isomer and the 890-cm.<sup>-1</sup> band ( $\alpha = 0.014$  torr<sup>-1</sup> cm.<sup>-1</sup>) of the *trans* isomer.

Fractional melting was carried out in the apparatus outlined in Figure 1. A sample was frozen on the glass beads above the 3.0-cm. diameter, medium porosity frit, and then the dewar was lowered to the position shown. The capillary tubing was warmed electrically, and the outflow from the capillary was continuously pumped through a trap held at liquid nitrogen temperature while small bursts of CO<sub>2</sub>-free, dry air were admitted into the chamber above the frit. In this way, as the sample melted, the liquid phase was continuously drawn off until about half of the sample had been removed. A micromodification with a 0.5-cm. diameter frit accommodated samples as small as 0.5 ml. Nine fractionations gave the *trans* sample of 99.6% purity. Isolation of the *cis* isomer, which was initially concentrated in the liquid phase, was more difficult as its separation was blocked by the eutectic point. Material with a composition near that of the eutectic mixture was accumulated by fractional melting and then fractionally distilled three times on the spinning-band column until a quantity of distillate with a composition in the *cis*-rich side of the eutectic was obtained. Since the *cis* isomer was concentrated in the distillate, it is presumed to have a slightly lower boiling point than the *trans*. After seven fractional meltings of the distillate, in which the *cis* isomer was concentrated in the solid phase, a small sample of 95.1% *cis* material was accepted. The eutectic composition given above was obtained by approaching the eutectic point with fractional melting from both *cis*-rich and *trans*-rich sides.

An attempt was made to obtain a useful change in the

(11) A. Stock, *Ber.*, **50**, 156 (1917).

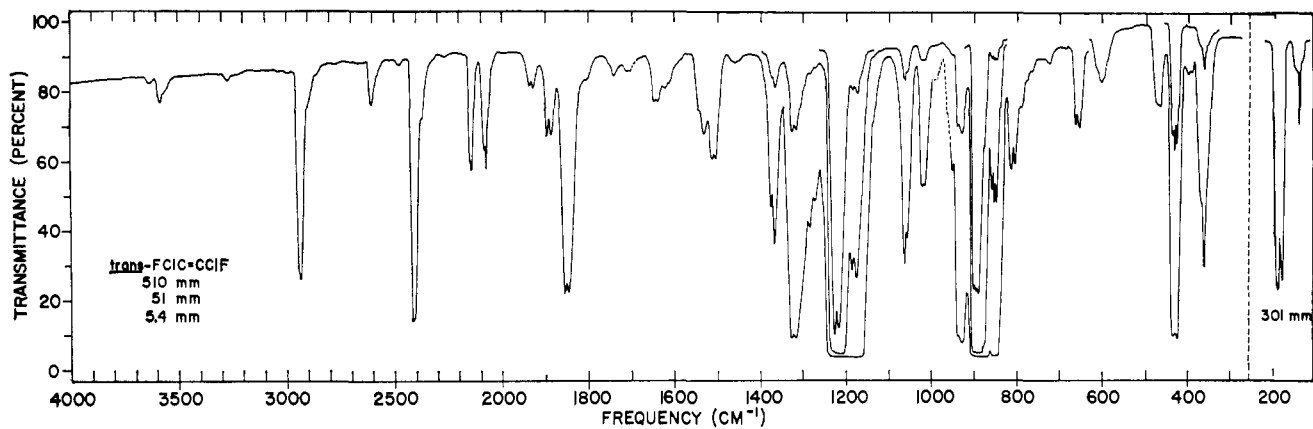


Figure 2. Gas phase infrared spectrum of *trans*-CFC1CFCl.

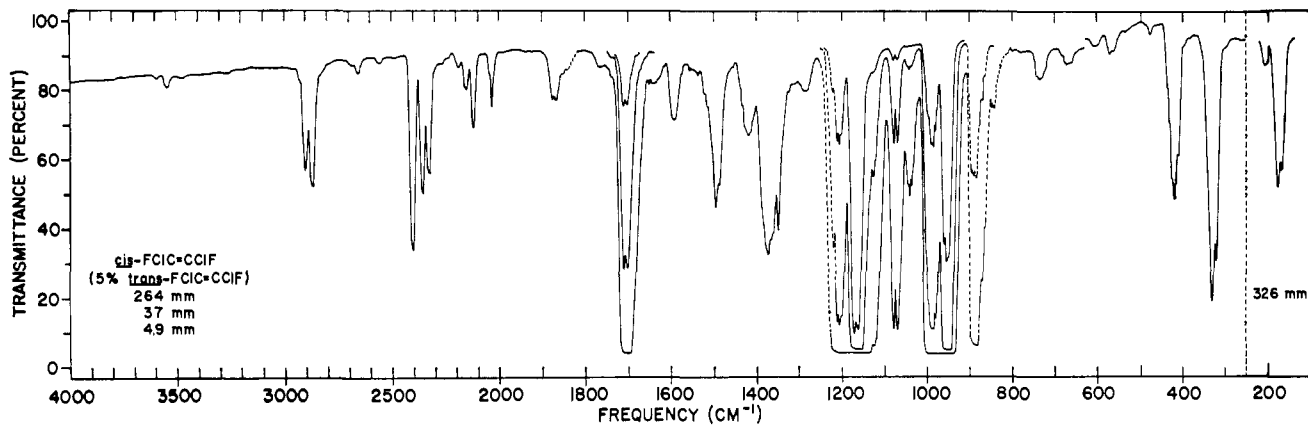


Figure 3. Gas phase infrared spectrum of *cis*-CFC1CFCl.

*cis-trans* CFC1CFCl ratio by heating the original mixture to about 400° in the presence of iodine catalyst. The *cis-trans* ratio changed only a few per cent.

Final purification of the fractionated samples made use of distillation through Ascarite to remove carbon dioxide and through phosphorus pentoxide to remove water. Purity was checked by gas chromatography on a tricresyl phosphate column and found to be greater than 99.5% CFC1CFCl for the samples used in the melting point and spectroscopic experiments.

**Spectroscopy.** Raman spectra and infrared spectra were obtained at the University of Minnesota as previously described.<sup>12</sup> The gas cell was 10 cm. in length and fitted with cesium iodide windows. The far-infrared spectra, 250 to 70  $\text{cm}^{-1}$ , were recorded on a Beckman IR-11 spectrometer at Case Institute of Technology in a 10-cm. cell equipped with  $\frac{1}{16}$ -in. thick Marlex polyethylene windows. Frequencies were measured to  $\pm 1 \text{ cm}^{-1}$  for well-defined bands.

The gas phase infrared spectrum of *trans*-CFC1CFCl is presented in Figure 2, and that of *cis*-CFC1CFCl in Figure 3. Pressures are given with the spectra, the higher pressures being approximate owing to solubility of the olefins in stopcock grease. Details of the liquid phase Raman spectrum and gas and solid phase infrared spectra are compiled in Tables II and III for the *trans* isomer and in Tables IV and V for the *cis* isomer. For the Raman spectrum of the *cis* isomer, a 23-mmole

(12) C. J. Bjork, N. C. Craig, R. A. Mitsch, and J. Overend, *J. Am. Chem. Soc.*, **87**, 1186 (1965).

sample which contained about 11% of the *trans* isomer was used.

Fluorine-19 n.m.r. spectra were measured on a Varian DP-60 spectrometer at 56.4 Mc./sec. by Dr. William Schwabacher at the University of Minnesota. These spectra of the nearly pure isomers fully confirmed the observations of Tiers and Lauterbur<sup>6</sup> on two mixtures that had *cis-trans* ratios of 57:43 and 32:68, respectively, and gave an independent value of 95% for the purity of our *cis* sample.

## Results and Discussion

**Assignment of Isomeric Configurations.** A preliminary comparison of the infrared and Raman spectra of the two CFC1CFCl isomers with the predictions of Table I leaves little doubt about the assignment of isomeric configurations. The gas phase infrared spectrum of the isomer which has been assigned the *trans* configuration (Figure 2) has only six principal infrared bands which can reasonably be identified as the six infrared-active fundamentals. (The medium intensity bands at 1179 and 852  $\text{cm}^{-1}$  are doubtlessly components of Fermi resonance doublets since each has the same band shape as its intense neighbor.) Two bands with type C shape are expected and are found at 357 and 132  $\text{cm}^{-1}$ . Furthermore, the Raman spectrum of this isomer (Table II) contains six intense bands, four of which are at frequencies distinctly different from those of the infrared-active fundamentals and five of which are polarized. In contrast the gas phase infrared spectrum

**Table II.** Raman Spectrum and Assignments for *trans*-CFCICFCl

Frequency, cm. <sup>-1</sup>	Intensity	Depol.	Assignment		Species
			Frequency, cm. <sup>-1</sup>		
2366	w	...	2372	2ν <sub>2</sub>	A <sub>g</sub>
2341	vw	...	2343	ν <sub>1</sub> + ν <sub>3</sub>	A <sub>g</sub>
1815	w	...	1819	ν <sub>2</sub> + ν <sub>3</sub>	A <sub>g</sub>
1764	w	Pol.	1788	2ν <sub>10</sub>	A <sub>g</sub>
1710	vs	Pol.	ν <sub>1</sub>	Fund.	a <sub>g</sub>
1700	w	...	1704	<i>cis</i> -CFCICFCl, impurity	
1680	w	...	1709	ν <sub>2</sub> + ν <sub>8</sub>	B <sub>g</sub>
1186	m	Pol.	ν <sub>2</sub>	Fund.	a <sub>g</sub>
1048	w	Pol.	1060	ν <sub>3</sub> + ν <sub>4</sub>	A <sub>g</sub>
725	w	Pol.		Unidentified, impurity	
633	s	Pol.	ν <sub>3</sub>	Fund.	a <sub>g</sub>
523	s	Depol.	ν <sub>3</sub>	Fund.	b <sub>g</sub>
427	s	Pol.	ν <sub>4</sub>	Fund.	a <sub>g</sub>
289	vs	Pol.	ν <sub>5</sub>	Fund.	a <sub>g</sub>

**Table III.** Infrared Spectra and Assignments for *trans*-CFCICFCl<sup>a</sup>

Gas phase			Solid phase		Assignment		Species
Frequency, cm. <sup>-1</sup>	Intensity	Band shape <sup>b</sup>	Frequency, cm. <sup>-1</sup>	Intensity	Frequency, cm. <sup>-1</sup>		
2929	m	A/B	2907	w	2928	ν <sub>1</sub> + ν <sub>9</sub>	B <sub>u</sub>
2404	m	B	2373	w	2404	ν <sub>2</sub> + ν <sub>9</sub>	B <sub>u</sub>
2137	m		2137	w	2136	ν <sub>1</sub> + ν <sub>11</sub>	B <sub>u</sub>
2082	w				2080	ν <sub>2</sub> + ν <sub>10</sub>	B <sub>u</sub>
2069	m	C			2067	ν <sub>1</sub> + ν <sub>8</sub>	A <sub>u</sub>
1890	w	B	1891	w	1888	ν <sub>1</sub> + ν <sub>12</sub>	B <sub>u</sub>
1849	m	B	1830	w	1851	ν <sub>3</sub> + ν <sub>9</sub>	B <sub>u</sub>
1708	vw				1709	<i>cis</i> -CFCICFCl, impurity	
1535	w	B			1543	ν <sub>2</sub> + ν <sub>6</sub>	A <sub>u</sub>
					1527	ν <sub>3</sub> + ν <sub>10</sub>	B <sub>u</sub>
1507	m	B			1507	ν <sub>6</sub> + ν <sub>9</sub>	B <sub>u</sub>
1370	m	B	1362	w	1364	ν <sub>2</sub> + ν <sub>12</sub>	B <sub>u</sub>
1319	m	B	1309	w	1321	ν <sub>4</sub> + ν <sub>10</sub>	B <sub>u</sub>
1276	m	B	1279	w	1280	2ν <sub>4</sub> + ν <sub>11</sub>	B <sub>u</sub>
1218	vs	B	1192	vs	ν <sub>9</sub>	Fund.	b <sub>u</sub>
			1183	s			
1179	m	B	1170	s	1183	ν <sub>5</sub> + ν <sub>10</sub>	B <sub>u</sub>
			1166	s			
1061	m	A	1059	w	1059	ν <sub>3</sub> + ν <sub>11</sub>	B <sub>u</sub>
1018	w	B			1008	ν <sub>2</sub> - ν <sub>12</sub>	B <sub>u</sub>
990	vw				990	<i>cis</i> -CFCICFCl, impurity	
958	w	A	956	vw	958	<i>cis</i> -CFCICFCl, impurity	
932	m	A/B	908	s	944	ν <sub>5</sub> + ν <sub>7</sub> + ν <sub>8</sub>	B <sub>u</sub>
894	vs	A	896	vs	ν <sub>10</sub>	Fund.	b <sub>u</sub>
880	m	A	883	vs	880	ν <sub>6</sub> + ν <sub>3</sub>	B <sub>u</sub>
			878	m	884	2ν <sub>5</sub> + ν <sub>12</sub>	B <sub>u</sub>
			876	m			
			870	m	882	2ν <sub>6</sub> + ν <sub>12</sub>	B <sub>u</sub>
			868	m			
852	m	A	853	m	853	ν <sub>4</sub> + ν <sub>11</sub>	B <sub>u</sub>
843	m	C	844	w	846	2ν <sub>6</sub> + ν <sub>7</sub>	A <sub>u</sub>
			843	w			
808	w	B			811	ν <sub>3</sub> + ν <sub>12</sub>	B <sub>u</sub>
725	vw					Unidentified, impurity	
657	w	B			655	ν <sub>7</sub> + ν <sub>8</sub>	B <sub>u</sub>
467	w	A/B			467	ν <sub>5</sub> + ν <sub>10</sub>	B <sub>u</sub>
426	m	A	426	m	ν <sub>11</sub>	Fund.	b <sub>u</sub>
			422	m	Isotope splitting in solid		
359	m	C	367	m	ν <sub>6</sub>	Fund.	a <sub>u</sub>
357							
178	m	B			ν <sub>12</sub>	Fund.	b <sub>u</sub>
132	w	C			ν <sub>7</sub>	Fund.	a <sub>u</sub>

<sup>a</sup> Although most of the weak bands seen in Figure 2 have been omitted from this table, satisfactory assignments have been found for each of them. <sup>b</sup> Designation of a band shape as A or B is approximate for this C<sub>2h</sub> molecule.

of the other isomer (Figure 3) contains at least seven prominent bands including a band at 1709 cm.<sup>-1</sup> for the CC stretch which is expected in the infrared only for the *cis* isomer. The seven well-defined bands in the Raman spectrum (Table IV) are coincident with

infrared bands. The detailed analysis of the spectra below give strong confirmation to these preliminary assignments of configuration. In addition, the assignments are consistent with the general observations of larger fluorine-fluorine coupling constants for *trans*

**Table IV.** Raman Spectrum and Assignments for *cis*-CFCICFCl

Frequency, cm. <sup>-1</sup>	Intensity	Depol.	Assignment		Species
			Frequency, cm. <sup>-1</sup>		
1704	vs	Pol.	$\nu_1$	Fund.	a <sub>1</sub>
1672	vw	...	1688	$\nu_2 + \nu_6 + \nu_7$	A <sub>1</sub>
~1203 <sup>9</sup>	vw	...	$\nu_8$	Fund.	b <sub>1</sub>
1186	w	Pol.	1186	<i>trans</i> -CFCICFCl, impurity	
1154	m	Pol.	$\nu_2$	Fund.	a <sub>1</sub>
			Fermi resonance with $2 \times \nu_8$		
1126	vw	...	1159	$\nu_5 + \nu_9'$	B <sub>1</sub>
			1140	$\nu_7 + \nu_9'$	B <sub>2</sub>
1070	w	Pol.?	1130	$2\nu_8 = \nu_2'$	A <sub>1</sub>
			Fermi resonance with $\nu_2$		
953	vw	...	$\nu_9$	Fund.	b <sub>1</sub>
			Fermi resonance with $\nu_9'$		
676	w	Pol.?	683	$\nu_7 + \nu_{12}$	B <sub>1</sub>
633	w	...	633	<i>trans</i> -CFCICFCl, impurity	
566	s	Pol.	$\nu_8$	Fund.	a <sub>1</sub>
562	m	...			
534	s	Depol.	$\nu_{12}$	Fund.	b <sub>2</sub>
~523	w	...	523	<i>trans</i> -CFCICFCl, impurity	
427	m	Depol.	$\nu_{10}$	Fund.	b <sub>1</sub>
~410?	w	...	$\nu_{11}$	Fund.	b <sub>1</sub>
339	w	...	$\nu_6$	Fund.	a <sub>2</sub>
328	m	Pol.	$\nu_4$	Fund.	a <sub>1</sub>
289	w	...	289	<i>trans</i> -CFCICFCl, impurity	
170	s	Pol.	$\nu_5$	Fund.	a <sub>1</sub>

configurations<sup>6</sup> and of higher melting points for *trans* isomers.

It is now clear that Sullivan<sup>3</sup> did not fully separate *cis*- and *trans*-CFCICFCl. It also seems unlikely that a significant degree of separation was achieved by Locke, *et al.*<sup>2</sup> Examination of the spectrum which Sullivan gave for the *cis* isomer shows it to be the spectrum of an approximately 75–20–5 mixture of the *cis*, *trans*, and *asym* isomers, and that which he gave for the *trans* isomer to be a spectrum of an approximately 40–60 mixture of *cis* and *trans* isomers. It is then likely that the melting point which he reported for the *cis* isomer of  $-128.7^\circ$  was a measurement of the temperature of the ternary eutectic point. The  $-105.5^\circ$  melting point which he reported for the *trans* isomer is very close to the  $-106^\circ$  melting point calculated for a 40–60 *cis*–*trans* mixture from a *trans* melting point of  $-93.2^\circ$  and a heat of melting of 2.34 kcal./mole. If this heat of melting is used along with the reported melting point of  $-115.5^\circ$  for CF<sub>2</sub>CCl<sub>2</sub>,<sup>9</sup> one calculates for the ternary eutectic a temperature of  $-133^\circ$  and a composition of 45% *cis*, 15% *trans*, and 40% *asym*.<sup>13</sup> Locke, *et al.*, reported a melting point of  $-130.5^\circ$  for the *cis* isomer, which may well have been another measurement of the ternary eutectic point, and  $-110.3^\circ$  for the *trans* isomer. This latter value and that of  $-112^\circ$  reported for CFCICFCl by Booth, *et al.*,<sup>14</sup> can now be seen to be melting points of nearly equimolar mixtures of *cis* and *trans* isomers. Thus, the new melting point data provide a reasonable explanation of a number of previously divergent observations.

*trans*-CFCICFCl Vibrational Assignment. With the predictions of Table I in hand, the assignment of the

(13) Fractional melting in the presence of a third, easily removed component such as CF<sub>2</sub>CCl<sub>2</sub> does not provide a convenient access to the *cis*-rich side of the binary eutectic point. Whenever  $\Delta H_m(\textit{cis}) = \Delta H_m(\textit{trans})$  and the solution is ideal, one can easily show that the *cis*–*trans* composition of the precipitated solid remains constant from the binary eutectic point to the ternary eutectic point.

(14) H. S. Booth, P. E. Burchfield, E. M. Bixby, and J. B. McKelvey, *J. Am. Chem. Soc.*, **55**, 2231 (1933).

vibrational fundamentals for *trans*-CFCICFCl is straightforward. From the gas phase infrared spectrum the two prominent bands with type C shape, 357 and 132 cm.<sup>-1</sup>, are immediately recognized as the a<sub>u</sub> fundamentals expected at 358 and 140 cm.<sup>-1</sup>. The four remaining prominent bands in the infrared with type A/B shape, 1218, 894, 426, and 178 cm.<sup>-1</sup>, are assigned as the b<sub>u</sub> fundamentals expected at 1235, 878, 431, and 184 cm.<sup>-1</sup>. In the Raman spectrum, five of the intense bands are polarized, and one is depolarized. As a consequence, the a<sub>g</sub> fundamentals are assigned as 1710, 1186, 633, 427, and 289 cm.<sup>-1</sup>, which compare quite favorably with the calculated frequencies of 1731, 1207, 644, 413, and 299 cm.<sup>-1</sup>. The depolarized band at 523 cm.<sup>-1</sup> is then the single b<sub>g</sub> fundamental which was predicted at 514 cm.<sup>-1</sup>. With this assignment of the fundamentals, the weaker bands in the spectra were satisfactorily assigned, mostly as binary combinations. These results are summarized in Tables II and III.

The assignment of the solid phase infrared spectrum of the *trans* isomer, which is also included in Table III, is fully consistent with the assignment of the gas phase spectrum. It is of particular value in the analysis of the *cis* spectrum where the *trans* is present as a 5% impurity.

In Table VI, the fundamental vibrations of *trans*-CFCICFCl are summarized. This assignment is in good agreement with that of Mann and Plyler when account is taken of the fact that they worked unknowingly with an equimolar *cis*–*trans* mixture.<sup>4</sup> They were not able to pinpoint the highest frequency b<sub>u</sub> mode which falls in the crowded 1200-cm.<sup>-1</sup> region and also were not in a position to observe the lower frequency a<sub>u</sub> mode at 132 cm.<sup>-1</sup>. For the remaining *trans* fundamentals only the assignment of the higher frequency a<sub>u</sub> mode is changed significantly, from 333 to 357 cm.<sup>-1</sup>.

*cis*-CFCICFCl Vibrational Assignment. The assignment of fundamentals for *cis*-CFCICFCl is not as straightforward or complete as is that for the *trans*

Table V. Infrared Spectra and Assignments for *cis*-CFCICFCl<sup>a</sup>

Gas phase			Solid phase		Assignment		Species
Frequency, cm. <sup>-1</sup>	Intensity	Band shape	Frequency, cm. <sup>-1</sup>	Intensity	Frequency, cm. <sup>-1</sup>		
2908	m		2887	vw	2918	$\nu_1 + \nu_8$	B <sub>1</sub>
2875	m		2850	vw	2877	$\nu_1 + \nu_2$	A <sub>1</sub>
2410	m		2381	w	2418	$2\nu_8$	A <sub>1</sub>
2364	m		2330	vw	2377	$\nu_2 + \nu_8$	B <sub>1</sub>
2324	m		2302	vw	2336	$2\nu_2$	A <sub>1</sub>
2126	w				2140	$\nu_1 + \nu_{10}$	B <sub>1</sub>
					2124	$\nu_1 + \nu_{11}$	B <sub>1</sub>
					2126	$\nu_2 + \nu_9$	B <sub>1</sub>
2040	w	C	2047	vw	2028	$\nu_2 + \nu_4 + \nu_{12}$	B <sub>2</sub>
1875	w	B	1873	vw	1878	$\nu_1 + \nu_5$	A <sub>1</sub>
1849	w	B			1849	<i>trans</i> -CFCICFCl, impurity	
1709	s	B	1706	m	$\nu_1$	Fund.	a <sub>1</sub>
1596	w				1599	$\nu_2 + \nu_{10}$	B <sub>1</sub>
					1583	$\nu_2 + \nu_{11}$	B <sub>1</sub>
1493	m	B	1479	vw	1508	$\nu_2' + \nu_{10}$	B <sub>1</sub>
					1492	$\nu_2' + \nu_{11}$	B <sub>1</sub>
					1495	$\nu_2 + \nu_4$	A <sub>1</sub>
1421	w		1435	vw	1421	$\nu_9' + \nu_{10}$	A <sub>1</sub>
					1405	$\nu_9' + \nu_{11}$	A <sub>1</sub>
1385	m		1381	w	1389	$\nu_9 + \nu_{10}$	A <sub>1</sub>
					1373	$\nu_9 + \nu_{11}$	A <sub>1</sub>
1368	m		1362	vw	1378	$\nu_5 + \nu_8$	B <sub>1</sub>
1352	m	C	1358	vw	1359	$\nu_7 + \nu_8$	B <sub>2</sub>
1320	w	B			1319	<i>trans</i> -CFCICFCl, impurity	
1285	w				1285	$\nu_4 + \nu_9$	B <sub>1</sub>
1219	s	B	1194	m	1218	<i>trans</i> -CFCICFCl, impurity	
			1183	m			
1209	s	A	1209	m	$\nu_8$	Fund.	b <sub>1</sub>
			1171	m	1170	<i>trans</i> -CFCICFCl, impurity	
1168	vs	B	1144	vs	$\nu_2$	Fund.	a <sub>1</sub>
						Fermi resonance with $2\nu_8$	
1139	m	A	1131	m	1159	$\nu_5 + \nu_9'$	B <sub>1</sub>
			1125	m			
1077	m	B	1072	m	1130	$2\nu_3 = \nu_2'$	A <sub>1</sub>
						Fermi resonance with $\nu_2$	
1045	m	A	1053	vw	1066	$2\nu_{12}$	A <sub>1</sub>
1000	s	A	1003	m	996	$\nu_3 + \nu_{10}$	B <sub>1</sub>
			997	m		Fermi resonance with $\nu_9$	
						(990 = $\nu_9'$ )	
990	s	A	988	m	980	$\nu_3 + \nu_{11}$	B <sub>1</sub>
			983	m		Fermi resonance with $\nu_9$	
958	vs	A	955	vs	$\nu_9$	Fund.	b <sub>1</sub>
894	s	A	894	w	894	<i>trans</i> -CFCICFCl, impurity	
872	m		884	w	883	$\nu_6 + \nu_{12}$	B <sub>1</sub>
852	w	A			852	<i>trans</i> -CFCICFCl, impurity	
740	w	A			758	$\nu_4 + \nu_{10}$	B <sub>1</sub>
					742	$\nu_4 + \nu_{11}$	B <sub>1</sub>
664	w	C			683	$\nu_7 + \nu_{12}$	B <sub>1</sub>
604	w	B			600	$\nu_5 + \nu_{10}$	B <sub>1</sub>
					584	$\nu_5 + \nu_{11}$	B <sub>1</sub>
565	w	B			$\nu_8$	Fund.	a <sub>1</sub>
533	vw	C			$\nu_{12}$	Fund.	b <sub>2</sub>
431	m		435	w	$\nu_{10}$	Fund.	b <sub>1</sub>
			432	vw			
426	m		426	vw	426	<i>trans</i> -CFCICFCl, impurity	
			422	vw	422		
415	m	A	417	w	$\nu_{11}$	Fund.	b <sub>1</sub>
			415	w			
357	w	C	368	vww	357	<i>trans</i> -CFCICFCl, impurity	
			352	m	$\nu_8$	Fund.	a <sub>2</sub>
			349	m			
327	m	B	331	m	$\nu_4$	Fund.	a <sub>2</sub>
205	w				206	$\nu_{12} - \nu_4$	B <sub>2</sub>
169	m	B			$\nu_3$	Fund.	a <sub>1</sub>

<sup>a</sup> Although most of the weak bands seen in Figure 3 have been omitted from this table, satisfactory assignments have been found for each of them.

isomer. Overlap of several fundamentals is the principal difficulty. As a consequence the solid phase infrared spectrum is of significant help. With little hesitation we can assign the five totally symmetric fundamentals to the transitions observed as type B

bands in the gas phase infrared spectrum (Figure 3) and as intense and polarized bands in the Raman spectrum. The a<sub>1</sub> fundamentals are then 1709, 1168, 565, 327, and 169 cm.<sup>-1</sup> which compare very well with the calculated values of 1729, 1140, 565, 324, and 183

**Table VI.** Summary of Assignments of Vibrational Fundamentals for *cis*- and *trans*-CFCICFCl (Frequencies in cm.<sup>-1</sup>)

<i>cis</i> -CFCICFCl			<i>trans</i> -CFCICFCl			
a <sub>1</sub>	ν <sub>1</sub>	1709	a <sub>g</sub>	ν <sub>1</sub>	1710 <sup>d</sup>	
	ν <sub>2</sub>	1168 <sup>a</sup>		ν <sub>2</sub>	1186 <sup>d</sup>	
	ν <sub>3</sub>	565		ν <sub>3</sub>	633 <sup>d</sup>	
	ν <sub>4</sub>	327		ν <sub>4</sub>	427 <sup>d</sup>	
	ν <sub>5</sub>	169		ν <sub>5</sub>	289 <sup>d</sup>	
a <sub>2</sub>	ν <sub>6</sub>	351 <sup>b</sup>	a <sub>u</sub>	ν <sub>6</sub>	357	
	ν <sub>7</sub>	(150) <sup>c</sup>		ν <sub>7</sub>	132	
b <sub>1</sub>	ν <sub>8</sub>	1209	b <sub>g</sub>	ν <sub>8</sub>	523 <sup>d</sup>	
	ν <sub>9</sub>	958 <sup>a</sup>		b <sub>u</sub>	ν <sub>9</sub>	1218
	ν <sub>10</sub>	431			ν <sub>10</sub>	894
	ν <sub>11</sub>	415			ν <sub>11</sub>	426
b <sub>2</sub>	ν <sub>12</sub>	533	ν <sub>12</sub>	178		

<sup>a</sup> Perturbed by Fermi resonance. <sup>b</sup> Solid phase infrared. <sup>c</sup> Zero-order calculation, ref. 4. <sup>d</sup> Liquid phase Raman.

cm.<sup>-1</sup>. The ascription of a type B shape to the 565-cm.<sup>-1</sup> band was based on a careful examination of the gas phase spectrum with 720-mm. pressure of an 89% *cis*-CFCICFCl sample and with ordinate expansion of the spectrum. The 1168-cm.<sup>-1</sup> band appears to occur at a somewhat higher frequency than expected owing to Fermi resonance between the fundamental and the first overtone of ν<sub>3</sub> which is expected at 1130 cm.<sup>-1</sup> but is found with substantial intensity and the required type B shape at 1077 cm.<sup>-1</sup>. In the Raman spectrum, the 565-cm.<sup>-1</sup> band shows evidence of isotope splitting in that a second band of somewhat lower intensity was found at 561 cm.<sup>-1</sup>. Cl<sup>35</sup>Cl<sup>35</sup>-Cl<sup>35</sup>Cl<sup>37</sup> splitting for the fundamental was calculated to be 3.8 cm.<sup>-1</sup>.

In the gas phase infrared spectrum in Figure 3, no significant absorption is seen in the 518-cm.<sup>-1</sup> region where a type C band is expected for the b<sub>2</sub> fundamental. However, under the more extreme conditions described in the paragraph above, a very weak band which appeared to be of type C shape was brought out at 533 cm.<sup>-1</sup>. The assignment of this band to the b<sub>2</sub> fundamental is established by the strong, depolarized Raman band observed at 534 cm.<sup>-1</sup>. This fundamental was not observed in the solid phase infrared spectrum with moderate sample thickness.

For the four fundamentals of b<sub>1</sub> symmetry only three candidates are immediately apparent in the gas phase infrared spectrum once it is recognized that type A bands at 1000, 990, and 958 cm.<sup>-1</sup> are probably part of another Fermi resonance multiplet, ν<sub>3</sub> + ν<sub>10</sub> = 996 cm.<sup>-1</sup> and ν<sub>3</sub> + ν<sub>11</sub> = 980 cm.<sup>-1</sup>. In fact, one clue to the location of the fourth fundamental comes from the rather obvious overlap of two bands of comparable intensity at 995 cm.<sup>-1</sup> which can be most reasonably derived from a pair of fundamentals overlapped in the 420-cm.<sup>-1</sup> region. The combination band at 1500 cm.<sup>-1</sup> (ν<sub>2</sub> + ν<sub>10</sub> and ν<sub>2</sub> + ν<sub>11</sub>) and to a lesser degree that at 740 cm.<sup>-1</sup> (ν<sub>4</sub> + ν<sub>10</sub> and ν<sub>4</sub> + ν<sub>11</sub>), which was more readily seen at the higher pressure, also have a shape similar to that seen in the 420-cm.<sup>-1</sup> region. In the Raman spectrum, a weak band appears to be present at 410 cm.<sup>-1</sup> on the shoulder of the medium intensity band at 427 cm.<sup>-1</sup>. In addition to the zero-order calculations which predicted b<sub>1</sub> fundamentals at 434 and 411 cm.<sup>-1</sup>, the strongest evidence for two fundamentals in this region comes from the infrared spec-

trum of the solid. Here are found two bands, each a doublet, at 435 and 432 cm.<sup>-1</sup> and at 417 and 415 cm.<sup>-1</sup>. Cl<sup>35</sup>Cl<sup>35</sup>-Cl<sup>35</sup>Cl<sup>37</sup> isotope splittings were calculated as 0.8 and 3.7 cm.<sup>-1</sup> for the fundamentals of higher and lower frequency in this region. Only the intensity ratio of the lower frequency doublet, in which the lower frequency member is about two-thirds as intense, is consistent with isotope splitting. The b<sub>1</sub> fundamentals are finally assigned with considerable confidence as 1209, 958, 431, and 415 cm.<sup>-1</sup>. Calculated values for the two higher frequencies were 1260 and 969 cm.<sup>-1</sup>.

The Raman spectrum of *cis*-CFCICFCl was examined with much care in the regions of 349 and 150 cm.<sup>-1</sup>, the frequencies which were calculated for the Raman-active, infrared-inactive a<sub>2</sub> fundamentals. The medium intensity band at 328 cm.<sup>-1</sup> dominates the higher frequency region, and the strong 170-cm.<sup>-1</sup> band the lower. The 11% *trans* impurity does not, however, interfere in this region because the corresponding out-of-plane modes for this isomer have a<sub>u</sub> symmetry. A weak Raman band appears to be present as a shoulder at 339 cm.<sup>-1</sup>. This observation finds some support in the 352- and 349-cm.<sup>-1</sup> doublet which appeared with significant intensity in the solid phase infrared spectrum. It is quite possible that the a<sub>2</sub> modes lead to infrared-active modes in the crystal lattice. We have therefore tentatively assigned one of the a<sub>2</sub> fundamentals at 351 cm.<sup>-1</sup>. No significant Raman band was found in the 150-cm.<sup>-1</sup> region. In addition to the calculated value of 150 cm.<sup>-1</sup> for the lower frequency a<sub>2</sub> mode, evidence for this fundamental comes from two of the weaker bands that are most readily explained with a fundamental at 150 cm.<sup>-1</sup> or somewhat lower. One which is at 1352 cm.<sup>-1</sup> and which appears to have the expected type C shape is assigned as ν<sub>7</sub> + ν<sub>8</sub> = 1359 cm.<sup>-1</sup> (B<sub>2</sub>). The other is at 664 cm.<sup>-1</sup> and can be assigned as ν<sub>7</sub> + ν<sub>12</sub> = 683 cm.<sup>-1</sup> (B<sub>1</sub>). The zero-order calculated value for ν<sub>7</sub> is given in Table VI, which summarizes the assignment for *cis*-CFCICFCl.

Tables IV and V include satisfactory assignments for nearly all of the weak bands in the *cis*-CFCICFCl spectra. Most of these assignments are binary combinations.

*Normal Coordinate Calculations.* The zero-order calculations of Mann, *et al.*, with Urey-Bradley force constants transferred from C<sub>2</sub>F<sub>4</sub> and C<sub>2</sub>F<sub>4</sub><sup>7</sup> were repeated for the planar modes by means of the Minnesota normal coordinate programs.<sup>1</sup> The same geometric parameters were used. Agreement was good with only one frequency differing by as much as 10 cm.<sup>-1</sup>. Cl<sup>35</sup>Cl<sup>35</sup> and Cl<sup>35</sup>Cl<sup>37</sup> isotopic modifications were treated separately to obtain estimates of the isotopic splittings. Since the isotopic splittings are useful in confirming some of the assignments, they are included in Table I along with the fundamental frequencies for the naturally occurring isotopic mixture of molecules.

At an early stage in the work, we attempted refinements of the force constants for the planar modes by treating the two isomers together in an overlay and also individually. At that point the solid phase infrared spectra and far-infrared spectra had not been obtained. Eight planar fundamentals had been assigned for the *trans* and seven for the *cis* isomer. Most of these

calculations were directed at an exploration of the possibility that  $\nu_{10}$  or  $\nu_{11}$  of the *cis* isomer was to be found at a significantly different frequency from that predicted by the zero-order calculations. It seems, however, that a splitting of less than  $60 \text{ cm.}^{-1}$  is to be expected between this pair of frequencies even though the fundamentals are members of the same symmetry class. This result provided further support for the assignments discussed above for  $\nu_{10}$  and  $\nu_{11}$ .

Diagrams of the atom displacements in the normal coordinates for the planar modes, as derived from the zero-order calculations, are given in ref. 7.

*cis-trans Stability.* Although *cis*-CFHCFH<sup>15</sup> and *cis*-CCIHCCI<sup>16</sup> have been found to be relatively more stable than the corresponding *trans* isomers, equilibrium data are not as yet available for the CF-CICFCl isomerization. The one qualitative attempt,

(15) N. C. Craig and E. A. Entemann, *J. Am. Chem. Soc.*, **83**, 3047 (1961).

(16) R. E. Wood and D. P. Stevenson, *ibid.*, **63**, 1650 (1941).

mentioned above, to obtain a significant change in a mixture of nearly equal amount of *cis-trans* isomers produced little change. Our calculation of statistical thermodynamic functions for both isomers gave results little different from those previously reported by Mann and Plyler.<sup>4</sup> For the *cis* to *trans* reaction  $\Delta S^\circ$  is  $0.20 \text{ cal./mole } ^\circ\text{K.}$  throughout the temperature range 200 to  $1500^\circ\text{K.}$  We must therefore tentatively conclude that *cis*- and *trans*-CFCICFCl are about equally stable and the enthalpy change for this isomerization is practically zero.

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## Perturbation of Singlet-Triplet Transition Energies<sup>1</sup>

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Contribution from the Department of Chemistry of the University of Washington, Seattle, Washington. Received April 5, 1965

*The first singlet-triplet transition energies for various substituted butadienes have been measured. A red shift found consistently going with 1- or 1,4-substitution but not consistently with 2- or 2,3-substitution is taken as evidence of hyperconjugation. A major conflicting possibility for explaining spectral shifts is internal dispersion forces. The dispersion force effect here is minimized because the transition studied has almost zero transition moment. A valence bond theory of perturbation of  $\pi$ -electron systems is developed and used to explain the results. A formula for free valence or residual affinity can be adapted from another, complementary, expression which automatically appears in the theory. It is judged more approximate to emphasize the complementary expression, which is called fixed valence. The fixed valence for a site is the sum of the Dirac-Penney bond orders of all bonds in the unperturbed molecule involving that site. The perturbation energy for radical attack is found to be inversely proportional to the fixed valence.*

### Introduction

Hyperconjugation in the original sense<sup>3,4</sup> is almost certainly to be reckoned with, as can be inferred from the magnitudes of relevant overlap integrals or from

(1) This research was supported in part by the Directorate of Chemical Sciences, U. S. Air Force Office of Scientific Research.

(2) Department of Chemistry, University of Oregon, Eugene, Ore.

(3) R. S. Mulliken, C. A. Rieke, and W. A. Brown, *J. Am. Chem. Soc.*, **63**, 41 (1941).

(4) See also G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 149.

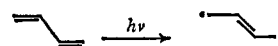
wave functions deduced from certain e.s.r. results. Thus to look for a direct energetic effect attributable to hyperconjugation may be somewhat redundant, but certainly not entirely so. Much of the supposed experimental evidence for hyperconjugation has been questioned: small effects can so easily have several plausible causes.

Evidence from spectral shifts would seem to be pertinent. The characteristic dye-like ions



have absorptions which shift markedly as the nitrogen atoms are alkylated. This could be caused by hyperconjugation, but also by changes in the effective ionization potential of nitrogen on alkylation (which changes are partly explicable through hyperconjugation),<sup>5</sup> or by internal dispersion forces; so an examination of spectral shifts for dyes may not be especially fruitful.

Here we shall be looking for hyperconjugation by examining spectral shifts<sup>6</sup> for a singlet-triplet transition: the first singlet-triplet transition in substituted butadienes. The transition may be represented



In the excited state there are electrons anti-paired but essentially non-interacting at the 1- and 4-positions. Thus changing hydrogen for methyl in the 1-position,

(5) M. Goeppert-Mayer and K. J. McCallum, *Rev. Mod. Phys.*, **14**, 248 (1942), explain spectral shifts in the Wurster's salts on this basis.

(6) Measurements were made by the Evans technique: D. F. Evans, *J. Chem. Soc.*, 1735 (1960).