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Carbon Monofluoride. Evidence for a Structure Containing an Infinite Array of Cyclohexane Boats

Sir:

Poly(carbon monofluoride, $(\text{CF}_x)_n$, has recently been a subject of interest in both basic^{1,2} and applied^{3,4} research. Many of its unique properties arise from its lamellar structure of weakly coupled nongraphitic sp^3 -carbon fluorine sheets. For no compelling reason, the geometry of these layers has been assumed to be an infinite array of trans-linked cyclohexane chairs.^{5,6} We have found that such an assignment is inconsistent with the results of nuclear magnetic resonance second moment studies and that the most plausible structure compatible with these and other experimental measurements is the infinite array of cis-trans-linked cyclohexane boats⁷ illustrated in Figure 1.

The materials investigated were Fluorographites CF_x (x

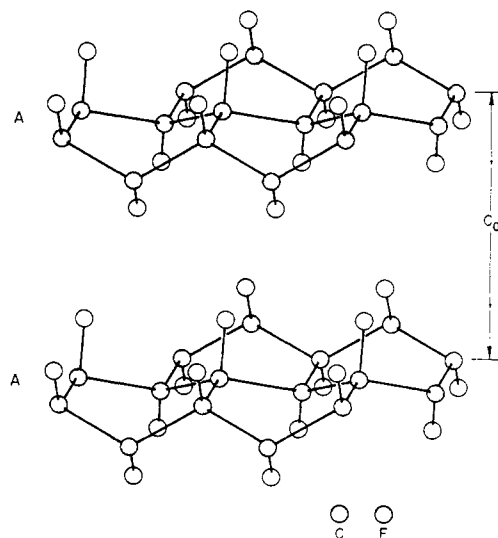


Figure 1. Structure of poly(carbon monofluoride) composed of an infinite array of cis-trans-linked cyclohexane boats.

$= 1, 1.1$) obtained from Ozark-Mahoning. Carbon combustion analyses yielded formulas by difference of $\text{CF}_{1.06}$ and $\text{CF}_{1.15}$, respectively. The infrared spectrum (1070 (m), 1215 (s), 1348 cm^{-1} (m)) is analogous to that obtained by previous workers.^{1,2,6,8} Powder X-ray diffraction of $\text{CF}_{1.06}$ calibrated against silicon showed lines at 6.16, 2.05, and 1.54 Å assignable as (00 l) reflections of a lattice with $c_0 = 6.16$ Å, as well as lines at 2.21 and 2.13 Å. Rudorff^{5,6} has shown the c_0 of CF_x to be a function of fluorine content. Recent workers have reported d values of¹ 5.80, 2.89, 2.22, and 1.29 Å ($c_0 = 5.8$ Å) and⁹ 6.0, 2.23, and 1.30 ($c_0 = 6.0$ Å).

Structural investigations employing the nuclear magnetic resonance absorption mode second moment afford precise values of internuclear magnetic moment separations when a relatively complete knowledge of compound geometry already exists.^{10–14} As CF is available only as a polycrystalline powder, no studies of the angular dependence of the second moment can be made, and evaluation by means of the Van Vleck^{10–14} formula (eq 1) leads to determination of only one parameter from knowledge of the experimentally obtained polycrystalline second moment.

Table I. Theoretical Evaluation of the Second-Moment Formula (eq 1) for Infinite Boat and Chair Structures^a

Boat model	Second moment (G ²)	Chair model	Second moment (G ²)	
			Distorted tetrahedron	Tetrahedron
	0.0088		0.0038	0.0039
	0.0538		0.0132	0.0138
	0.4669		0.0618	0.0631
	20.5082		1.2544	1.3644
	0.5527		7.5003	7.9898
	0.0538		0.7749	0.7496
	0.0094		0.0618	0.0631
			0.0112	0.0113

^a Because all fluorine atoms are magnetically equivalent in either the chair or the boat form, the double sum of eq 1 reduces to a single sum, representing the interactions of one "test" fluorine nucleus with all others in the lattice. The second-moment values in the above are for interactions of the circled test fluorine with each of the nearest 1600 fluorine nuclei in the indicated fluorine plane. The sum of these contributions for the tetrahedral boat structure is 21.7 G². For the infinite chair structure, we have calculated second moments arising from not only a tetrahedral carbon array but also a distorted tetrahedral array which will allow indexing of the 2.22-Å diffraction line.⁶ The values are 10.3 and 9.7 G², respectively.

$$\langle \Delta H^2 \rangle = (3/5) \hbar^2 \gamma^2 I(I+1) N \sum_j \sum_k (1/r_{jk})^6 \quad (1)$$

in which r_{jk} is the separation distance between dipoles j and k of magnetogyric ratio γ and spin I .

In the present case, chemical and physical arguments suggest reasonable models for the CF structure to be infinite arrays of either cyclohexane boats or chairs. This assumption made, one can calculate theoretical ^{19}F second moments for each structure and compare them with the experimentally measured quantity.

As is illustrated in Table I, the experimental second moment¹⁵ of $24.2 \pm 1.3 \text{ G}^2$ is consistent only with the boat model of CF. Second-moment values for the chair model are approximately 50% of the measured quantity.

The relatively large difference in second-moment values for the two structures arises from the 1,4 flagpole interaction found only in the boat, in which fluorines separated by 1.63 Å contribute 16.9 G² to the theoretical value. Since all fluorines have magnetically equivalent environments, this significant contribution is unaffected by averaging over the complete fluorine array. Only for a case of multiple fluorine environments, as in a hybrid boat-chair structure, would its impact diminish.

If CF does indeed exist in the boat rather than the chair modification, thorough investigation of the X-ray diffraction pattern should reveal the existence of an orthorhombic unit cell with approximate unit cell constants¹⁶ $a_0 = 2.51$, $b_0 = 5.13$, and $c_0 = 6.16 \text{ Å}$ rather than the previously assumed hexagonal cell¹⁶ of $a_0 = 2.51$ and $c_0 = 6.16 \text{ Å}$. Significantly, lines found for CF after tetrahedral anvil pressing² at 2.57, 1.72, and 1.29 Å, are assignable as (020), (030), and (040) reflections in the orthorhombic cell.¹⁷ As interconversion of chair and boat forms involves C-F bond rupture, it is reasonable to assume that the boat structure was present both before and after pressing.

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- A Varian 4200 spectrometer interfaced to a PDP 8/e minicomputer through a PAR 129 lock-in amplifier was used for data collection. Double integration using the trapezoidal rule gave a second moment of $24.2 \pm 1.3 \text{ G}^2$ for CF_{1.06} at 8 MHz. Assuming a Gaussian line shape model, we may calculate the second moment directly from the measured line width. For five runs in the frequency range 3.76–16 MHz, we obtain second-moment values of $18.0 \pm 0.7 \text{ G}^2$ for CF_{1.06} and $20.8 \pm 1.6 \text{ G}^2$ for CF_{1.15}.
- We assume a carbon-carbon bond length of 1.54 Å, a carbon-fluorine length of 1.4 Å, tetrahedral coordination about carbon atoms, and an AA stacking of layers. With these assumptions, the value of a_0 must be adjusted to assign the 2.22 Å line in either the orthorhombic or hexagonal system. The indexing of (00l) reflections is the same in either the orthorhombic or hexagonal system, and, as mentioned,⁵ c_0 is a function of fluorine composition.
- Furthermore, if we adjust a_0 to be 2.46 Å (which does not affect (0k0) reflections), we may index the lines² at 2.23, 1.86, and 1.64 Å as (110), (102), and (031) reflections in an orthorhombic cell. The remaining line² at 3.24 Å is not easily indexed into either a hexagonal or an orthorhombic system within the constraints of AA stacking.
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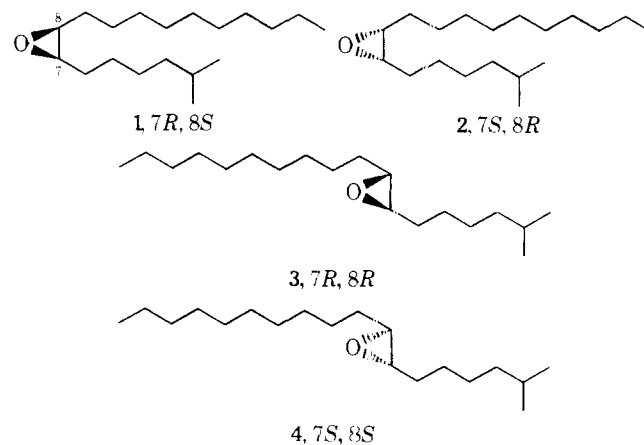
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Synthesis and Activity of Optically Active Disparlure

Sir:

The plain structure of disparlure, the sex attractant emitted by the female gypsy moth (*Porthetria dispar* (L.)), has been established as *cis*-7,8-epoxy-2-methyloctadecane.¹ The natural pheromone is supposed to be optically active, with its chiral centers at C₇ and C₈. Its absolute stereochemistry, however, remained obscure, because of the small magnitude of the expected optical rotation and the extremely low yield of the pheromone from the insects. This communication describes the synthesis of both enantiomers of disparlure and its trans analog and also their activity on the male moth, in hopes of determination of the absolute stereochemistry of the natural pheromone.



(S)-(+)-Glutamic acid, $[\alpha]^{23\text{D}} +30.9^\circ$ (c 1.0, 6 N HCl), was deaminated with nitrous acid in 1 N HCl-acetic acid-water (2:3:4) to give a lactone acid (6)² (80%). As the deamination reaction proceeds with retention of configuration at the chiral center,³ 6 should have the S configuration (the methyl ester of 6, $[\alpha]^{12\text{D}} +14.6^\circ$ (c 1.7, MeOH)). 6 was converted with oxalyl chloride in benzene to the acid chloride (7), which was condensed with dicycliccadmium to yield a lactone ketone (8) (34% overall yield from 6). Reduction of 8 with NaBH₄ in methanol afforded a diastereomeric mixture of a lactone alcohol (9 and 10) (81%). Each diastereomer was isolated in a completely pure state by preparative tlc (silica gel, ethyl acetate-*n*-hexane) followed by repeated recrystallization (ethyl acetate-petroleum ether). 9 was identified as 5-hydroxypentadecan-4-olide with a 4S,5S configuration⁴ by the following properties: mp 66.0°; $[\alpha]^{20\text{D}} +29.2^\circ$ (c 1.2, CHCl₃); mass m/e 256 (M⁺); nmr (CDCl₃) δ 4.46 (1 H, m), 3.60 (1 H, bm), 2.92 (bs, OH), 2.58 (2 H, m), 2.24 (2 H, m), 0.89 (3 H, a virtually coupling triplet). Data for 10 (mp 63.5°; $[\alpha]^{20\text{D}} +14.8^\circ$ (c 1.2, CHCl₃); mass m/e 256 (M⁺); δ 4.48 (1 H, m), 3.96 (1 H, bm), 2.60 (2 H, m, and 1 H, OH exchangeable with