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The Gauche, Ortho, and Anti Conformers of Perfluoro-*n*-butane: Matrix-Isolation IR Spectra

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We report the IR spectra of three distinct (racemic) conformers of perfluoro-*n*-butane, recorded under conditions of matrix isolation, and assigned by comparison with HF/6-31G* calculations. We propose to call them gauche ($g_\pm$), ortho ($o_\pm$), and anti ($a_\pm$).[1]

Textbook[2] notions of saturated chain conformational analysis assume the general existence of two and only two conformers in a saturated X_4Y_{10} four-atom chain: gauche at about ±60° dihedral angle (racemic), and anti, either exactly at 180° (achiral), as in *n*-butane, or merely close to 180° (racemic), as in helical polymers. Over the years, some of the many semiempirical calculations performed for saturated chains predicted the existence of a larger number of conformational minima for rotation around a single bond, not only for permethylated and perfluorinated chains but also for parent *n*-alkanes and *n*-oligosilanes.[3] In general, these results have not been taken very seriously. Very recent *ab initio* results for Si_4Me_{10},[4] C_4F_{10},[5] at least one other type of X_4Y_{10} chain,[6,7] and poly(tetrafluoroethylene),[8] which predict the existence of three racemic conformers at about 55°, 90°, and 165°, cannot be dismissed as easily. Also, it has been pointed out[5] that the splitting of the "ordinary" gauche minimum at 60° into two at 55° and 90°, presumably due primarily to 1,4 substituent interactions, would be analogous to the splitting of the "ordinary" anti minimum at 180° into two at ±165°, presumably due to 1,3 substituent interactions.

Matrix isolation of room-temperature or hot vapors with excess inert gas has been long known to permit the trapping of conformer mixtures in high-viscosity media,[9,10] permitting their leisurely spectroscopic observation under conditions where they do not interconvert, and allowing studies of their interconversion upon annealing. Our efforts to observe the three predicted[4] conformers of Si_4Me_{10}, whose gauche and ortho forms are calculated to have nearly identical vibrational spectra, have not been successful so far, although the spectra of the anti and the twisted (perhaps gauche overlapped with ortho) conformers have been clearly distinguished.[11,12] Since the gauche, ortho, and anti conformers of C_4F_{10} are calculated to have quite different IR spectra (Figure 1), they offer an easier initial target. A direct observation of three distinct conformers of any one of the X_4Y_{10} chains would provide strong support for all the *ab initio* predictions for the conformers of these chains.

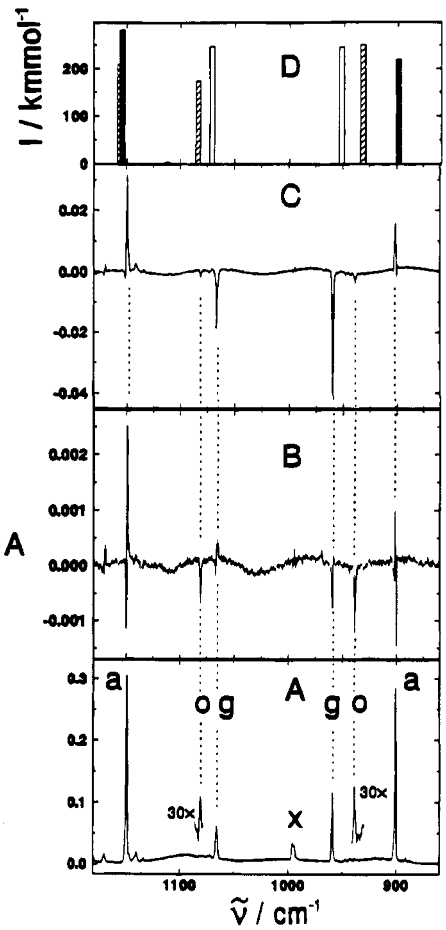

Figure 1. IR spectra of the ortho (*o*, **1**), gauche (*g*, **2**), and anti (*a*, **3**) conformers of *n*-C_4F_{10}: the observed FTIR spectrum of the deposited (12 K) conformer mixture in N_2 matrix (oven at 873 K) before annealing (A); the observed computer-produced difference spectra after annealing to 14 K (B) and 18 K (C); and the calculated spectra (D, HF/6-31G*, computed frequency scaled by 0.90; *o*, hatched; *g*, white; and *a*, black bars) are shown. An impurity peak labeled X is not affected by annealing.

A 1500:1 mixture of N_2 and C_4F_{10} (>97%, Indofine Chemical Co.) was deposited through an 873 K oven onto a CsI window held at 12 K, and a series of IR spectra were recorded as the sample was annealed. Disregarding minor changes in peak shapes, attributable to the usual site effects, the spectra revealed three independent sets of peaks clearly associated with three different species, **1**−**3**. In contrast, under similar conditions *n*-butane shows only two sets of peaks, attributed to the gauche and anti conformers.[10] In our case, a temperature increase of just a few kelvins caused the peaks of **1** to disappear gradually, while the percentage change of the much stronger peaks of **2** and **3** was much smaller. At higher temperatures, the peaks of **2** gradually disappeared as well, and those of **3** increased. Figure 1 shows the spectral region in which the differences

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(1) "Ortho" stands for orthogonal. We believe that these names and labels are simpler and more in keeping with organic stereochemical nomenclature than the $g^{\pm}_{\pm}$ and $t_\pm$ labels used in ref 5.

(2) Eliel, E. L. *Stereochemistry of Organic Compounds*; Wiley: Chichester, U.K., 1994.

(3) E.g.: Morokuma, K. *J. Chem. Phys.* **1971**, *54*, 962. Welsh, W. J.; Johnson, W. D. *Macromolecules* **1990**, *23*, 1882.

(4) Michl, J.; Albinsson, B.; Plitt, H.; Raymond, M.-K.; Teramae, H.; Veas, C. Second International Topical Conference on Optical Probes of Conjugated Polymers and Fullerenes, Salt Lake City, UT, Feb 15−19, 1994. Teramae, H.; Michl, J. *Mol. Cryst. Liq. Cryst.* **1994**, *256*, 149.

(5) Smith, G. D.; Jaffe, R. L.; Yoon, D. Y. *Macromolecules* **1994**, *27*, 3166.

(6) C_4Me_{10}: Teramae, H.; Neumann, F.; Downing, J. W.; Michl, J. Unpublished results. We are now trying to determine computationally just how general the three-conformer situation is.

(7) The ortho conformation was found in *ab initio* computations on various occasions before, but the authors did not realize at the time that it was distinct from the gauche conformation. $(CF_2)_n$: Otto, P.; Ladik, J.; Förner, W. *Chem. Phys.* **1985**, *95*, 365. Si_4Me_{10} and Si_5Me_{12}: Plitt, H. S.; Downing, J. W.; Raymond, M. K.; Balaji, V.; Michl, J. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1653. See also ref 11.

(8) Teramae, H. Private communication (band structure calculation at HF/3-21G level, rigid rotor approximation starting with an optimized anti conformation, minima at 51°, 90°, and 160°).

(9) Huber-Wälchli, P. *Ber. Bunsen-Ges. Phys. Chem.* **1978**, *82*, 10. Squillacote, M. E.; Sheridan, R. S.; Chapman, O. L.; Anet, F. A. L. *J. Am. Chem. Soc.* **1979**, *101*, 3657. See also: Arnold, B. R.; Balaji, V.; Downing, J. W.; Radziszewski, J. G.; Fisher, J. J.; Michl, J. *J. Am. Chem. Soc.* **1991**, *113*, 2910 and references therein.

(10) Rasanen, M.; Bondybey, V. E. *Chem. Phys. Lett.* **1984**, *111*, 515.

(11) Plitt, H. S.; Michl, J. *Chem. Phys. Lett.* **1992**, *198*, 400.

(12) Albinsson, B.; Teramae, H.; Downing, J. W.; Michl, J., unpublished results.

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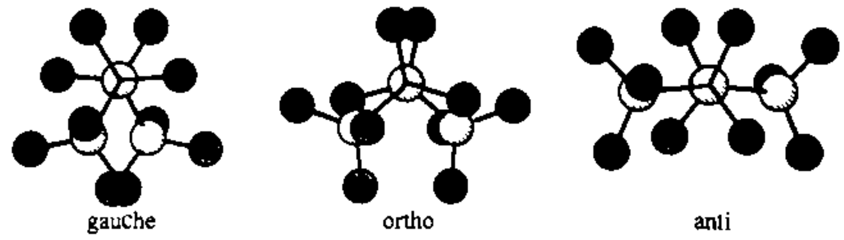

Figure 2. Fully optimized MP2/6-31G* geometries of the gauche, ortho, and anti conformers of n-C_4F_{10} viewed along the C_2C_3 bond. CCCC dihedral angles: 54.2° (*g*), 94.8° (*o*), and 165.5° (*a*).

among the three species are the largest. Comparison with the calculated IR spectra, also shown in Figure 1, leaves no doubt that **1** is the ortho, **2** is the gauche, and **3** is the anti conformer. Their calculated[5,13] relative energies are indeed in the order **1** > **2** > **3**, and it is reasonable that a reduction of matrix viscosity upon annealing should at first permit only the small dihedral angle change from 90° to 55° before permitting a change from either one to 165°.[14] The calculated molecular geometries are shown in Figure 2.

The presently reported observations lend strong support to the recent *ab initio* predictions[4-6] of the existence of three racemic conformers in certain saturated X_4Y_{10} chains, at least some of which are not severely sterically hindered. The simpler gauche, anti situation known from the parent n-alkanes and n-oligosilanes is not as general as is often assumed.

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[13] Our results for C_4F_{10} are similar to those of ref 5. At the fully optimized frozen-core MP2/6-31G* level, the *o* conformer is 1.63 kcal/mol and the *g* conformer 0.68 kcal/mol above the *a* conformer.

[14] Since the disappearance of the ortho form upon annealing is so extremely facile, it is unlikely that its trapped abundance in the matrix is representative of its true abundance in the vapor phase at 873 K.