# Fluorocarbon sulfides
# 4. The slow conformational isomerization of perfluorodithianes [1]

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## Abstract

From low-temperature $^{19}$F spectra the inversion of octafluoro-1,4-dithiane is found to have $\Delta H^{\ddagger} = 8.2$ kcal/mol, $\Delta G^{\ddagger}(25°C) = 10.7$ kcal/mol, and $\Delta S^{\ddagger} = -8.4$ e.u., much like perfluorocyclohexane. The geminal coupling, $^2J_{AB}$, is 231 Hz. Perfluoro-1,2-dithiane, previously reported in error, is conformationally stiff at ordinary temperatures, having $\Delta G^{\ddagger} = 14.5$ kcal/mol. Its geminal couplings, $^2J_{AB}$, are 236 and 268 Hz. © 1998 Elsevier Science S.A. All rights reserved.

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## 1. Introduction

In a previous paper, the kinetic parameters for the slow conformational isomerization of perfluorocyclohexane had been deduced by means of NMR spectroscopy [1]. The studies have now been extended to two perfluorodithianes. One of these molecules, octafluoro-1,4-dithiane [2–4], resembles perfluorocyclohexane in showing, at ordinary temperatures, a single $^{19}$F line [4]; it is thus particularly suitable for kinetic measurements.

## 2. Results and discussion

At low temperatures the 1,4-$C_4F_8S_2$ line broadens and separates, eventually becoming a wide AB pattern similar to that of perfluorocyclohexane.[2] From the virtual constancy of the shifts (Table 1) it is highly probable that a single form greatly predominates at all temperatures studied; only one is present at low temperatures, most probably the 'chair' form rather than the 'symmetrical boat' having sulfurs at prow and stern.

It is unlikely that both forms would subject the fluorine nuclei to the same (average) magnetic shielding; therefore, a progressive shift in the peak-center position should be observed in the event that increasing temperature produces significantly increasing quantities of the second form.

In 1,4-$C_4F_8S_2$, the low-temperature AB shielding difference is 14.9 ppm, as compared to 18.2 ppm for perfluorocyclohexane [1]. For the rate calculations, observed line widths were decreased by 0.6 Hz to allow for the estimated instrumental resolution; the correction was, however, virtually negligible below +50.5°C. The resulting rate constants and the calculated free energies of activation, $\Delta G^{\ddagger}$, are presented in Table 1, plus that from the −67°C AB pattern. A good linear plot of $R \ln k$ against $1/T$ resulted, from which there was obtained by linear regression $\Delta H^{\ddagger} = 8.5 \pm 0.6$ kcal/mol ($r^2 = 0.997$) and, taking the measured $\Delta G^{\ddagger}(25°C)$, 10.80 kcal/mol, $\Delta S^{\ddagger} = -7.7 \pm 2.0$ e.u. The data was recalculated[3] by non-linear least squares fitted to the Eyring equation, obtaining the improved result $\Delta H^{\ddagger} = 8.2 \pm 0.6$ kcal/mol and $\Delta S^{\ddagger} = -8.4 \pm 2.2$ e.u.; $\Delta G^{\ddagger}(25°C)$ becomes $10.7 \pm 0.1$ kcal/mol, error values being $2\sigma$. These quantities do not differ greatly from those for perfluorocyclohexane [1] ($8.8 \pm 0.3$ kcal/mol and $-8.4 \pm 0.7$ e.u.) despite the substantial differences in bond lengths and angles from replacement of two $CF_2$ groups by large heteroatoms. The AB coupling constant for the $CF_2S$ group, 231 Hz, while smaller than for the $CF_2$

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[1] Presented (poster) at the 15th International Symposium on Fluorine Chemistry, UBC, Vancouver BC Canada, August 2–7, 1997, Abstracts, p. P(1)16.

[2] Rate constants have been recalculated with deduction of 0.6 Hz from line widths; and from AB line widths $W_1 = 39.7 \pm 0.6$ and $W_0 = 48.7 \pm 1.6$ Hz at −60°C (unpublished) k = 68/s (improved method) and $\Delta G^{\ddagger} = 10.5_4$ kcal/mol. From that, $\Delta G^{\ddagger}(25°C) = 11.30$ kcal/mol, $\Delta H^{\ddagger} = 8.8$ kcal/mol, and $\Delta S^{\ddagger} = -8.4$ e.u. (see Ref. [1]).

[3] A Referee, taking exception, has kindly furnished this recalculation.

Table 1
Octafluoro-1,4-dithiane: NMR spectral data at 40 MHz and kinetic parameters

| $T$ (°C) | $\delta$ ( = $-\phi^*$) [a] (ppm) | $W_{1/2}$ [b] (Hz) | $k$ [c] $\times 10^{-4}$ (s$^{-1}$) | $\Delta G$ [d] (kcal/mol) |
|---|---|---|---|---|
| + 50.5 | − 91.041 ± 0.003 | 2.45 ± 0.002 | 30.13 ± 0.20 | 10.8$_8$ |
| + 26.8 [e] | ( − 91.08 ± 0.01) [e] | 7.15 ± 0.12 | 8.54 ± 0.13 | 10.7$_9$ |
| + 21.5 | − 91.07 ± 0.01$_5$ | 10.16 ± 0.08 | 5.83 ± 0.04 | 10.8$_1$ |
| 0.0 | − 91.16 ± 0.01 | 23.4 ± 0.2 | 2.45 ± 0.02 | 10.4$_5$ |
| − 11.0 | − 91.17 ± 0.01$_5$ | 53.5 ± 0.3 | 1.067 ± 0.005 | 10.4$_4$ |
| − 20.0 | − 91.21 ± 0.02 | 83.0 ± 0.2 | 0.692 ± 0.004 | 10.2$_9$ |
| − 67. | (AB center [f]) | 45.4 ± 0.4 [g] | | |
| | − 91.17$_5$ ± 0.01$_3$ | 64.1 ± 1.0 [h] | 0.0111 [i] | 9.9$_8$ |
| − 93. | − 91.15 ± 0.01 | (AB center [j]) | ($\delta_A$ = − 83.70 ± 0.01, $\delta_B$ = 98.59 ± 0.01) | |

[a] At 20 vol% (1.28 M) conc. in $CCl_3F$; see Ref. [4].
[b] Observed line width at half-maximal amplitude; for $CCl_3F$ 1.28 ± 0.02 at 50.5°C.
[c] First-order rate constant for conformational isomerization.
[d] From Eyring's equation; see Refs. [1,5].
[e] At 5 vol% conc. in $CCl_3F$.
[f] $^2J_{AB}$ = 230.3 ± 1.0 Hz; $\delta_A$ = − 83.67 ± 0.03; $\delta_B$ = − 98.67 ± 0.03 ppm.
[g] For the strong inner components of the AB pattern.
[h] For the weak outer components of the AB pattern.
[i] Using $W_{1/2}$(corr.) = 35.3 Hz, from the observed $W_I$ and $W_O$ by the improved method.
[j] $^2J_{AB}$ = 232.0 ± 0.8 Hz.

in perfluorocyclohexane (284 Hz) [1], is very much larger than that for the isoelectronic $CF_2Cl$ group (175 Hz in $CF_3CFClCF_2Cl$ [6]).

The isomeric octafluoro-1,2-dithiane has been reported [7], albeit mistakenly. Isolated in very small yield by g.c., a fraction was 'identified' by NMR and mass spectroscopy. The unusually high shielding, − 111.4 $\delta$, for the cyclic $CF_2SS$ group differed drastically from the − 84 to − 92 $\delta$ range previously given for other $C-CF_2S$ and $C-CF_2SS$ structures [4] and further supported in the same paper [7]. The structure claimed is incorrect.

In the present work, octafluoro-1,2-dithiane has been isolated in ca. 80% purity as a small higher-boiling fraction in the reaction of 1,4-diiodoperfluorobutane with sulfur [8]. Although it could not then be identified, later NMR spectroscopy verified the structure. Carbon–fluorine analyses, corrected for the most probable impurity 1,4-$C_4F_8I_2$ (from the NMR spectrum) are in agreement. The NMR spectral data are presented in Table 2. The first-order rate constant should be uninfluenced by impurities.

In sharp contrast to its 1,4-isomer, and to perfluorocyclohexane, the octafluoro-1,2-dithiane molecule is conformationally stiff even at room temperature, and fully rigid at − 64°C. It is noteworthy that its geminal AB coupling constant for $CF_2S$, 236 Hz, differs little from that for its 1,4-isomer, 231 Hz. One may surmise therefrom that the bond angles, and hybridization, are very similar. The sizable decrease in flexibility must thus be attributed largely to resistance of the disulfide structure to assuming a cis-coplanar conformation in the transition state. Rigid space-filling molecular models of it and of $CF_3SSCF_3$ suggest significant steric interference. Computations yield a barrier height of 14.9 kcal/mol for the eclipsed form of the latter [9].

Although a full kinetic investigation of octafluoro-1,2-dithiane was not done, the geometric mean of the + 25°C line widths for the cyclohexane-like $C-CF_2-C$ AB-type system, corrected by subtraction of the corresponding − 64°C widths for the fully-rigid system, yields the rate constant for inversion $k$(25°C) = 121.9/s. From this value for $k$, using the relation

$$\Delta G^{\ddagger} = 47.21T + RT \ln (T) - RT \ln (k) \qquad (T \text{ in K}),$$

one finds $\Delta G^{\ddagger}$(25°C) = 14.6 kcal/mol (failure to correct yields 14.2 kcal/mol). An improved treatment, not using − 64°C data (see Section 3), gives 14.5 kcal/mol. If instead the partial collapse of the AB pattern is employed [1,5,10], there is calculated $k$(25°C) = 475/s and $\Delta G^{\ddagger}$ = 14 kcal/mol, in good agreement; a weighted average value of 14.5( ± 0.5; 2σ) kcal/mol is proposed. Notably, this $\Delta G^{\ddagger}$ is appreciably higher than for its 1,4-isomer, 10.7 kcal/mol, or for perfluorocyclohexane [1] (11.3 kcal/mol). The $CF_2S$ AB pattern was too poorly resolved for analysis.

## 3. Experimental details

The 40 MHz NMR equipment used for the kinetic studies, and the mathematical methods employed, have been described [1,4,5,10,11]. For the detection of impurities, the greatly improved sensitivity of the 470 MHz (for $^{19}$F) Varian UNITY 500 spectrometer was essential. Chemical shifts, $\delta$, are here defined as − $\phi^*$ [11], and infinite-dilution shifts, $\delta^\circ$, as − $\phi^\circ$; the latter (unlike the former) provide unambiguous, highly-reproducible characterization of molecular species.

Table 2
Octafluoro-1,2-dithiane: NMR spectral data at 40 MHz and kinetic parameters

| $T$ (°C) | $CCF_2C$ [a] peaks | $W_{1/2}$ [b] (Hz) | Corr. [c] $W_{1/2}$ | $\delta$ [d] $(CCF_2C)$ (ppm) | $CF_2S$ [a] peaks | $W_{1/2}$ [b] (Hz) | $\delta$ [d] $(CF_2S)$ (ppm) | $k$ [e] (s$^{-1}$) | $\Delta G^{\ddagger}$ (kcal/mol) |
|---|---|---|---|---|---|---|---|---|---|
| +25 | −119.4 | 105. | | | − | | | | |
| | | | 41.0 | −122.6$_5$ | | | −99.1 [l] | | |
| | −124.9 | 59. | | | −100.3$_3$ | 30. | | | |
| | | | | (−127.9$_3$) [g] | | | (−100.8$_7$) [g] | | |
| | −129.8 | 65. | | | −101.4 | 36. | | | |
| | | | 36.6 | −132.1$_2$ | | | −102.7 [l] | | |
| | −136.5 | 105. | | | − | | | 122. [h] | 14.6 [h] |
| | | | | | | | | 149. [i] | 14.5 [i] |
| −64 | −118.6 | 35. | | | −94.2 | 34. | | 475. [j] | 14. [i] |
| | | | | −122.9$_8$ | | | −98.6$_9$ | | |
| | −125.3 | 35. | | | −100.1 | 31. | | | |
| | | | | (−127.9$_0$) [k] | | | (−100.7$_5$) [l] | | |
| | −130.5 | 43. | | | −101.4 | 23. | | | |
| | | | | −132.8$_2$ | | | −102.8$_1$ | | |
| | −137.2 | 44. | | | −107.3 | 26. | | | |

[a] AB system peak positions in ppm at 40 MHz.
[b] Observed full line widths at half-maximal amplitude.
[c] Calculated as the geometric mean of widths reduced by the −64° line widths.
[d] From AB analysis; $\delta = -\phi^*$; see Ref. [4]. Remeasurement, extrapolated to infinite dilution at 470 MHz, gave $\delta° = -132.07$, $-122.51$, $-102.72$, and $-98.84$.
[e] First-order rate constant for conformational isomerization.
[f] From AB analysis using $^2J_{AB} = 236$ Hz, measured at −64°C.
[g] Center of the AB pattern.
[h] From the average of corrected [c] line widths.
[i] From $W_{1/2}$(corr.) = 47.3 Hz, calculated by the improved method.
[j] From the equation for early stages of collapse of an AB system; see Ref. [5].
[k] Center of the AB pattern; $^2J_{AB} = 268$ Hz.
[l] Center of the AB pattern; $^2J_{AB} = 236$ Hz.

The 1,4-$C_4F_8S_2$ was the sample previously studied [4]. Its isomer, 1,2-$C_4F_8S_2$, was found in two higher-boiling fractions from the reported preparation of $C_4F_8S$ [8]. The first of these, 0.3 g, b.p. 92°C, had $n_D^{25}$ 1.3621. The amount being insufficient for elemental analysis, an additional 1.0 g of less-pure product was collected by reducing the pressure, and had $n_D^{25}$ 1.3724. This was the sample later used for all of the NMR work. The likely volatile and higher-boiling impurities are unreacted 1,4-$C_4F_8I_2$, b.p. 150°C, $n_D^{25}$ 1.4278, and the NMR spectrum has peaks at $\delta° = -58.71$ and $-112.58$ signifying its presence, together with comparable quantities of a $C_4F_8$ component which might be the cyclic trisulfide 1,2,3-$(CF_2)_4S_3$ from the similarity of its AB-type patterns for C-$CF_2$S at $\delta° -92.56$ and $-97.93$ ($^2J_{AB} = 205$ Hz) and for C-$CF_2$-C at $\delta° -117.63$ and $-121.58$ ($^2J_{AB} = 245$ Hz) to those of 1,2-$C_4F_8S_2$; an unidentified triplet ($J = 14$ Hz) was at $\delta° -75.15$. Among weaker peaks are two at $\delta° -86.99$ and $-131.91$ for $(CF_2)_4S$. Analysis: calculated for $C_4F_8S_2$: C, 18.20%; F, 57.57%; calculated for 87 mol% $C_4F_8S_2$ and 13 mol% $C_4F_8I_2$: C, 17.21%; F, 54.44%; found: C, 17.5%; F, 54.8%. The mixture ratio chosen is in fair agreement with NMR relative intensities; the calculated analytical values would improve slightly upon dilution by small amounts of sulfur-bearing $C_4F_8$ impurities.

An improved treatment of the slow-exchange AB case when additionally broadened by unresolved multiplets regards the latter as roughly normal distributions, independent from the kinetic broadening, which arguably should obey normal-vector subtraction from the observed widths, rather than scalar (Lorentzian) subtraction, to find the kinetically-broadened line widths. These corrected widths are required to be in the ratio $R = \Delta_I/\Delta_O$ of the inner and outer line spacings; their geometric mean is the kinetic line width,
$$W_{1/2}(\text{corr.}) = [(W_I^2 - M^2)^{1/2}(W_O^2 - M^2)^{1/2}]^{1/2} = k/\pi,$$
where $M^2 = (W_I^2 - R^2 W_O^2)/(1 - R^2)$.

## Acknowledgements

## References

[1] G.V.D. Tiers, Proc. Chem. Soc. (1960) 389.
[2] C.G. Krespan, U.S. Patent 2,931,803 (1960).

[3] C.G. Krespan, C.M. Langkammerer, J. Org. Chem. 27 (1962) 3584.
[4] G.V.D. Tiers, J. Phys. Chem. 66 (1962) 764.
[5] R.K. Harris, N. Sheppard, Proc. Chem. Soc. (1961) 418.
[6] A. DeMarco, G. Gatti, J. Magn. Reson. 6 (1972) 200.
[7] R. James, D.J. Rowsell, Chem. Commun. (1969) 1274.

[8] G.V.D. Tiers, J. Org. Chem. 26 (1961) 2538.
[9] J. Stevens, High-level computation, to be submitted.
[10] J.A. Pople, W.G. Schneider, H.J. Bernstein, High Resolution Nuclear Magnetic Resonance, McGraw-Hill, New York, 1959, p. 224.
[11] G. Filipovich, G.V.D. Tiers, J. Phys. Chem. 63 (1959) 761.