

## Short Communications

### Electron-diffraction Study of Gaseous Tetrafluoro-1,3-dithietane

ZUZANA SMITH and RAGNHILD SEIP

Department of Chemistry, University of Oslo,  
Oslo 3, Norway

The geometry and the low-frequency ring-puckering motion in four-membered rings depend on the relative magnitude of the two opposing forces, the bond angle strain and the torsional strain. It has been reported that all cyclobutane rings unconstrained by adjacent rings are puckered in the gas phase.<sup>1</sup> Harris and Yang,<sup>2</sup> however, interpreted vibrational spectra of perfluorocyclobutane in terms of a planar molecule with  $D_{4h}$  symmetry, even though electron-diffraction studies find the ring puckered.<sup>3</sup> In a spectroscopic work by Durig *et al.*<sup>4</sup> the authors concluded that tetrafluoro-1,3-dithietane belongs to the  $D_{2h}$  symmetry group, while a related molecule, trimethylene sulfide, was found to be puckered<sup>5,6</sup> with a puckering angle of  $26^\circ$ . This study was undertaken in order to determine the structural parameters of tetrafluoro-1,3-dithietane by the electron-diffraction method.

**Experimental.** A sample of tetrafluoro-1,3-dithietane was purchased from PCR, Incorporated, and purified by distillation. The diffraction diagrams were recorded with a Balzers Eldigraph KD-G2,<sup>7,8</sup> at a nozzle temperature of about  $25^\circ\text{C}$ . Five plates exposed at a camera distance of 500.12 mm and four at 250.12 mm were used in the structural analysis. The electron wavelengths were  $0.05865\text{ \AA}$  and  $0.05857\text{ \AA}$  for the two camera distances as calibrated with the diffraction patterns of gaseous benzene. The intensity data spanned the range of  $s = 1.625 - 15.50\text{ \AA}^{-1}$  and  $5.0 - 28.75\text{ \AA}^{-1}$ . The data processing and the structural analysis were carried out in the usual way.<sup>9</sup> The elastic scattering factors were calculated by the partial wave method<sup>10</sup> based upon analytical HF potentials,<sup>11</sup> and the inelastic scattering factors used were those of Tavard *et al.*<sup>12</sup> The modification function  $s/(|f_S'|/|f_F'|)$  was applied. The average modified molecular intensities<sup>9</sup> for each camera distance are shown in Fig. 1, and the radial distribution function calculated from the composite molecular intensity is shown in Fig. 2.

**Structural analysis.** A preliminary set of amplitudes of vibration ( $u$ ) and the correction

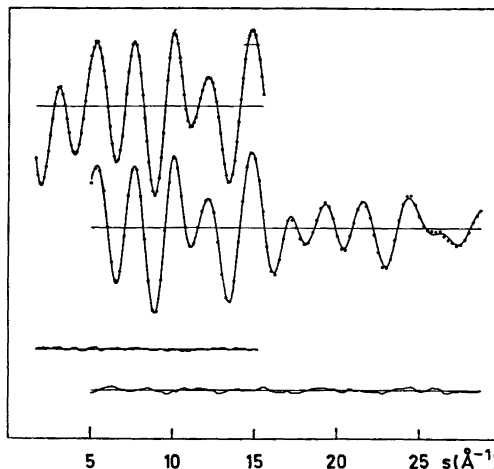


Fig. 1. The experimental intensity data (circles) for tetrafluoro-1,3-dithietane from the 50 cm ( $\Delta s = 0.125\text{ \AA}$ ) and the 25 cm ( $\Delta s = 0.25\text{ \AA}$ ) camera distances. The solid line corresponds to the calculated molecular intensities, while the lower curves represent the difference between the experimental and the calculated intensities.

coefficients ( $K$ ) were calculated by normal coordinate analysis<sup>13</sup> using the experimental data of Durig *et al.*<sup>4</sup> Due to some discrepancies in fitting the experimental frequencies, more extensive analysis will be necessary.

The least-squares refinements were carried out under the assumption that the FCF planes bisect the corresponding SCS angles and are perpendicular to the corresponding SCS plane. As one can see from Table 1, the puckering angle ( $\alpha$ ) C1S2C3—C3S4C1, is highly correlated with the CSC angle and with the amplitudes of vibrations  $u(\text{C1F7})$  and  $u(\text{F5F7})$ . When angle  $\alpha$  was kept at  $0^\circ$  the values shown in Table 2 were found. When all four parameters were varied simultaneously, least-squares refinement converged to the following values of these parameters:  $\alpha = 5.4(18)^\circ$ ,  $\angle \text{CSC} = 82.7(2)^\circ$ ,  $u(\text{C1F7}) = 0.083(9)\text{ \AA}$  and  $u(\text{F5F7}) = 0.141(43)\text{ \AA}$ , while the other parameters were not significantly influenced. The agreement is nearly identical for  $\alpha$  values in the range  $0 - 6^\circ$ ; with further increase in the angle the agreement becomes quickly worse. Study of the refined

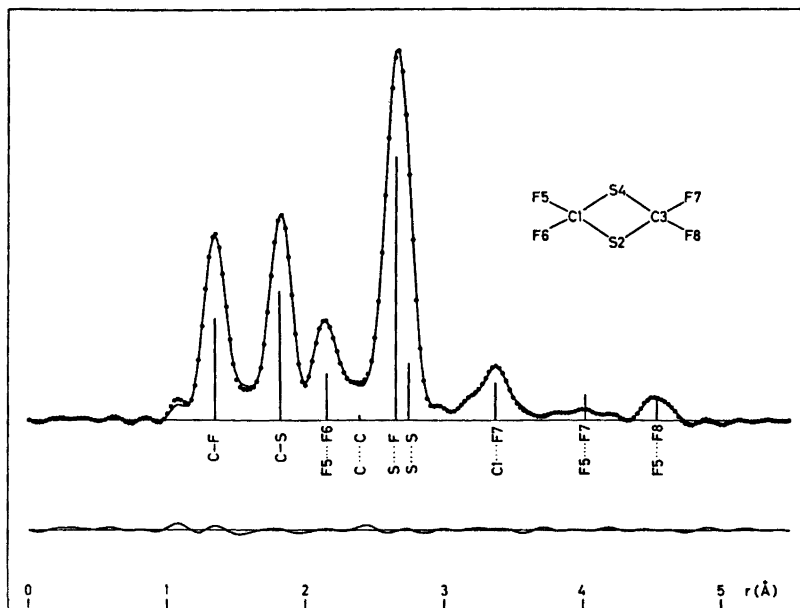


Fig. 2. Experimental (circles) and calculated (solid line) radial distribution curves for tetrafluoro-1,3-dithietane. The lower curve represents the difference between the experimental and calculated curves. The positions and approximate areas are indicated. Damping constant was  $0.001 \text{ \AA}^2$ .

Table 1. Correlation coefficients,  $\rho_{ij}$ , greater than 0.5, obtained when all parameters were varied and a diagonal weight matrix was used.

i	j	$\rho_{ij}$
$r(\text{CS})$	$\angle \text{FCF}$	0.62
$\angle \text{CSC}$	$\alpha$	0.81
$\angle \text{CSC}$	$u(\text{C1F7})$	-0.74
$\angle \text{CSC}$	$u(\text{SF})$	0.53
$\angle \text{CSC}$	$u(\text{F5F7})$	-0.79
$\alpha$	$u(\text{C1F7})$	-0.89
$\alpha$	$u(\text{F5F7})$	-0.96
$u(\text{C1F7})$	$u(\text{F5F7})$	0.84
$u(\text{SF})$	scale (50 cm)	0.51

amplitudes of vibration indicates that the equilibrium angle is very close to zero, since the values  $u(\text{C1F7})=0.10$  and  $u(\text{F5F7})=0.21$  were obtained by normal coordinate analysis. When the amplitudes of vibration  $u(\text{CC})$  and  $u(\text{SS})$  were varied, they converged to unreasonably small values (0.040 and 0.048, respectively), therefore the calculated values were assumed.

The C-S bond distance and the CSC angle in thietane ( $1.847(2) \text{ \AA}$  and  $77.0(5)^\circ$ , respectively) were compared with corresponding parameters in analogous molecules,<sup>15</sup> and it was

Table 2. Structural parameters<sup>a</sup> for tetrafluoro-1,3-dithietane.

Parameter	$r_a$ (Å)	$u$ (Å)
C-S	1.820(2)	0.049(2)
C-F	1.344(2)	0.049(2)
$\angle \text{CSC}(\circ)^b$	82.7(2)	
$\angle \text{FCF}(\circ)^b$	106.5(2)	
$\alpha(\circ)$	0.0	
C...C	2.402(5)	0.069
S...S	2.728(4)	0.056
F5...F6	2.154(4)	0.053(4)
C...F	3.376(5)	0.091(4)
S...F	2.656(3)	0.070(1)
F5...F7	3.991(6)	0.179(14)
F5...F8	4.538(6)	0.082(5)

<sup>a</sup> Results from geometrically consistent  $r_a$ -refinements. The standard deviations given in parentheses include correction for data correlation.<sup>13</sup> The deviations for distance parameters are corrected for systematic uncertainties according to  $\sigma = [\sigma_{\text{LS}}^2 + (0.001r)^2]^{1/2}$ . The asymmetry constants used were (in  $10^{-6} \text{ \AA}^3$ ):  $k(\text{C-S})=2.0$ ,  $k(\text{C-F})=2.0$ , and zero for non-bonded distances. <sup>b</sup> When refinement is carried out on the  $r_a$ -structure,  $\angle \text{CSC}=82.4(2)^\circ$  and  $\angle \text{FCF}=106.6(2)^\circ$ .

concluded that the C-S bond lengths in four-membered rings are clearly longer than in other environments. The C-S bond distance in tetrafluoro-1,3-dithietane, 1.820(2) Å, is shorter than that in thietane; however, the CSC angle is larger, 82.7(2)°. The corresponding parameters are 1.804(3) Å and 97.0(19)° in 4-thiacyclohexanone.<sup>16</sup>

The ED-data are consistent with  $D_{2h}$  symmetry for tetrafluoro-1,3-dithietane, a result which is in agreement with vibrational<sup>4</sup> and NMR<sup>17</sup> spectroscopy.

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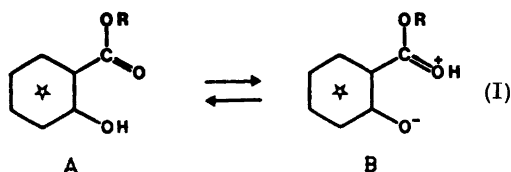
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## Hydrogen Bonding Effects on the Fluorescence of Methyl Salicylate

KJELL SANDROS

Department of Physical Chemistry, Chalmers University of Technology, Fack, S-402 20 Göteborg, Sweden

Some twenty years ago Weller<sup>1</sup> found that salicylic acid and methyl salicylate in methanol solution have unstructured fluorescence spectra both with a Stokes' shift about 5000  $\text{cm}^{-1}$  greater than that of the corresponding methoxy compound, *o*-methoxy benzoic acid and its methyl ester. An additional weak fluorescence component with a Stokes' shift similar to that of the corresponding methoxy compound appeared in hydrocarbon solutions. The ratio between the intensities of the short and long wavelength components of the methyl salicylate fluorescence decreased as the temperature was reduced. Partial quenching of the fluorescence with carbon disulfide did not affect the intensity ratio. Weller interpreted the fluorescence properties of salicylic acid and methyl salicylate as a result of the following, at room temperature fully established, protolytic equilibrium in the excited state:



where R denotes H or  $\text{CH}_3$ . The short and long wavelength fluorescence components should emanate from A and B, respectively. This interpretation was supported by the fact that phenolic groups are much more acidic in the lowest excited singlet state than in the ground state, while excitation makes aromatic carbonyl and carboxyl groups much more basic. Excitation of intramolecularly hydrogen-bonded salicylic acid or methyl salicylate molecules would thus favour an intramolecular proton transfer. From the measurements on methyl salicylate in methylcyclohexane, Weller calculated the  $\Delta H$  values for the proton transfer as  $-1.0 \text{ kcal mol}^{-1}$  and  $13.5 \text{ kcal mol}^{-1}$  in the excited and ground states, respectively.\*

A preliminary new study of the methyl salicylate fluorescence has revealed some unexpected effects of solvent and excitation wavelength, which indicate that the hitherto accepted reaction mechanism should be modified. As seen from Fig. 1, the ratio between the intensities of the short and long wavelength

\* 1 kcal = 4.184 kJ.