

distances are 2.557 (3) and 1.75 (3) Å and the O(1)—H(1)—N(1) angle is 147 (3)°. In addition, there are three polar H atoms on the thiosemicarbazone fragment, one on N(2) and the other two on N(3) that participate in the hydrogen-bond scheme. The distances and angles are: N(2)...S(1) 3.406 (2), H(2)...S(1) 2.56 (1) Å; 167 (1)° (2-x, 1-y, 1-z); N(3)...O(1) 3.064 (3), H(3A)...O(1) 2.24 (1) Å; 151 (1)° (2.5-x, 0.5+y, 1.5-z); N(3)...S(1) 3.408 (2), H(3B)...S(1) 2.75 (1) Å; 142 (1)° (2.5-x, -0.5+y, 1.5-z). Similar intramolecular hydrogen bonds have been observed in some thiosemicarbazides and thiosemicarbazones (Andreotti, Domiano, Fava Gasparri, Nardelli & Sgarabotto, 1970; Restivo & Palenik, 1970; Nandi, Chaudhuri, Mazumdar & Ghosh, 1984).

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Structure of *sym*-C₂F₄Br₂

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Abstract. The structure of 1,2-dibromo-1,1,2,2-tetrafluoroethane is shown to be stable down to low temperatures. $M_r = 259.84$, monoclinic, $P2_1/c$, $Z = 2$. At $T = 100$ K, $a = 5.963$ (5), $b = 6.252$ (5), $c = 8.656$ (8) Å, $\beta = 114.64$ (5)°, $V = 293.3$ (4) Å³, $D_x = 2.94$ Mg m⁻³. At $T = 4.2$ K, $a = 5.934$ (5), $b = 6.190$ (5), $c = 8.460$ (8) Å, $\beta = 114.36$ (5)°, $V = 283.1$ (4) Å³, $D_x = 3.05$ Mg m⁻³. The technique of powder neutron diffraction ($\lambda = 2.2018$ Å) followed by constrained refinement was used, achieving R factors

for the two temperatures of 15.4% and 13.4%. Refinements result in a structure close to that obtained by packing calculations. The structure is not that of a plastic crystal but has features very similar to the disordered structure of 1,2-dichloroethane.

Introduction. Some substituted ethanes have interesting phase transitions, and we undertook the present study to investigate the phase structure of 1,2-dibromo-1,1,2,2-tetrafluoroethane (*sym*-C₂F₄Br₂). Spectroscopic and acoustic studies on the internal rotation in the liquid material (Crook, Park & Wyn-Jones, 1969) have shown that, owing to the repulsion of the large Br

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atoms, the greatest stability is achieved when they are farthest apart as in the *trans* form, though some *gauche* form exists at higher temperatures (Gloekler & Sage, 1941; Kagarise & Daasch, 1955). The large potential barriers which exist hinder rotation between the *trans* and *gauche* forms, and so we expect to find a structure with *trans* molecules.

The possibility of rotational or orientational disorder of the molecules arose from the evidence of such disorder in 1,2-dichloroethane (Milberg & Lipscomb, 1951; Reed & Lipscomb, 1953). In this material the disorder is uniaxial about the Cl...Cl axis, and this disappears as the temperature is lowered to below 177 K.

Our studies are sufficient to show that no similar behaviour takes place in sym-C₂F₄Br₂. This is in agreement with our differential thermal analysis measurements throughout the solid phase down to liquid nitrogen temperatures, and the diffraction work extends this result down to 4.2 K.

Experimental. A powdered sample of sym-C₂F₄Br₂ was prepared by freezing the liquid in a vanadium can packed with quartz wool (Baharie & Pawley, 1977). This method inhibits the growth of large crystallites but does not produce powder samples of the quality obtained by cryo-grinding. The presence of some small but significant crystallites causes the data to be poor, but the refinement techniques are capable of extracting the information required for this study.

This sample was used at 100 K and 4.2 K for recording neutron diffraction scans on the PANDA diffractometer at AERE Harwell, Oxfordshire, England. The sample was continuously rotated in a beam of neutrons of wavelength $\lambda = 2.2018 \text{ \AA}$. Diffraction data were recorded at intervals of 0.1° in 2θ from 6 to 85° (100 K scan) and from 14 to 95° (4.2 K scan), using three independent ¹⁰BF₃ detectors.

Structure solution. The angular positions of the Bragg reflections were measured and used in the triangulation method (Ito, 1949), readily giving a monoclinic unit cell at both temperatures. Systematic absences suggested the ubiquitous space group *P*2₁/*c*, and the structure was then solved by packing methods, assuming the molecules to be in the *trans* conformation.

Refinements. Constrained refinements were performed with the program *EDINP* (Pawley, Mackenzie & Dietrich, 1977; Pawley, 1980), and it became clear that the quality of the data was insufficient for the removal of all constraints. The full constraint first applied was of a molecule with fixed bond lengths, arranged tetrahedrally. This molecule was placed in the unit cell using Euler angles; these were the refinement structure variables. The definition of Euler angles is as given by Goldstein (1959), related to orthogonal crystal axes along *x*, *y* and *z*^{*}, as used in the review of constraint procedures by Pawley (1972).

Table 1. Details of the constrained refinements of sym-C₂F₄Br₂

The *R* factors contain contributions from all points in the scan. Only the newly varied parameters are presented in the second refinements. The errors are resolution normalized.

Temperature (K)	4.2	100
Scan details ($2\theta^\circ$)	6 (0.1) 85	14 (0.1) 95
First refinement, molecule fully constrained		
Scale factor	2.09 (15)	3.07 (20)
Scan zero correction ($^\circ$)	-0.23 (3)	-0.22 (2)
Peak shape parameters (deg) ² <i>u</i>	0.47 (35)	0.44 (35)
<i>v</i>	-0.42 (33)	-0.33 (32)
<i>w</i>	0.20 (7)	0.17 (7)
Unit-cell axes (\AA)	5.934 (5)	5.963 (5)
angle ($^\circ$)	6.190 (5)	6.252 (5)
<i>c</i>	8.460 (8)	8.656 (8)
β	114.36 (5)	114.64 (5)
Unit-cell volumes (\AA^3)	283.1 (4)	293.3 (4)
Euler angles (rad)	ϕ 2.59 (2)	2.60 (2)
	θ -1.02 (3)	-1.10 (3)
	ψ 2.26 (3)	2.27 (3)
Overall temperature factor	2.7 (8)	3.0 (8)
Bond lengths fixed (\AA)	C—C 1.541	1.541
	C—F 1.344	1.344
	C—Br 1.920	1.920
<i>R</i> factor (inclusive)	15.4%	13.4%
Second refinement, molecule bonds refined		
Bond lengths varied (\AA)	C—C 1.73 (5)	1.65 (5)
	C—F 1.36 (2)	1.36 (2)
	C—Br 1.77 (3)	1.84 (3)
<i>R</i> factor (inclusive)	15.7%	13.1%

The results of refinements using a fixed flat background function are given in Table 1. Unit weights were used throughout. The errors presented in Table 1 are calculated using for the number of observations the number of points in the total diffraction scan divided by the mean peak full-width at half maximum.

The first constraint to be relaxed was that of fixed bond lengths. The result obtained on varying the three bond lengths but still keeping tetrahedral bond angles is set out at the foot of Table 1. The bonds remained physically reasonable, giving not so much a measurement of bond lengths but an indication that the refinement is reliable.

Although the *R* factor could be considerably reduced (to around 9% for both scans) by removing all the constraints and replacing the overall isotropic temperature factor by individual anisotropic parameters, many of the parameters took on values which were physically unacceptable. Therefore we do not present these later refinements, which just serve to emphasize the value of constrained refinements with 'noisy' data.

Plots of the observed (points) and calculated (curve) diffraction scans are shown in Fig. 1, along with the difference (observed — calculated).*

* Lists of observed and calculated data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44868 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

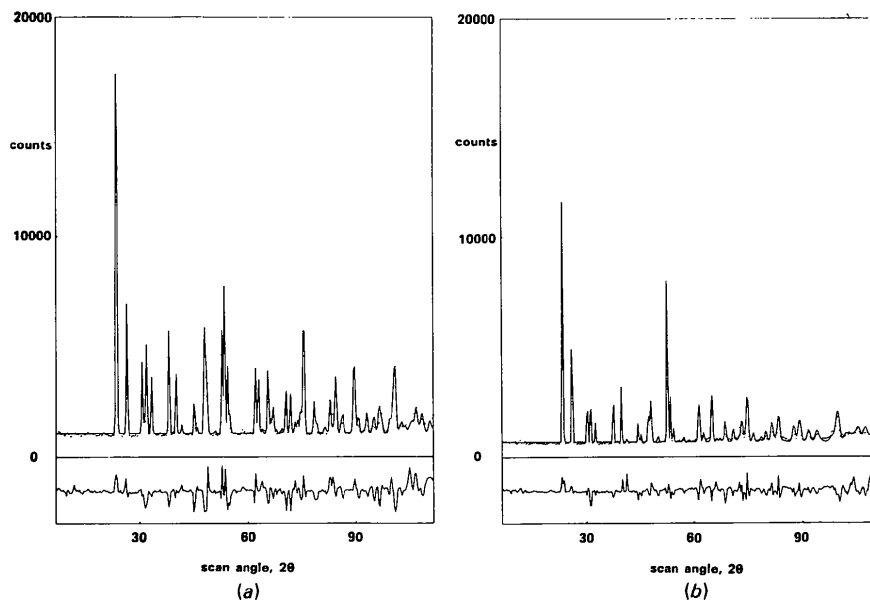


Fig. 1. Observed counts (points) and calculated values (curve) for (a) 4.2 K and (b) 100 K data. The lower curve is the difference (observed—calculated). These scans are simplified by reducing to a common range, 6.9 to 111.6°, with a step of 0.3°.

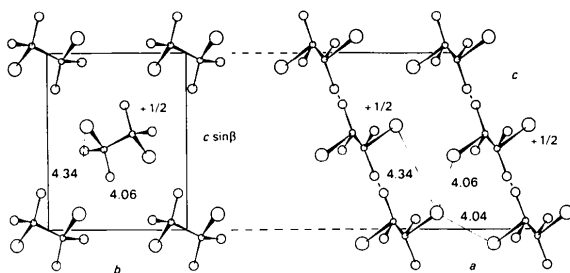


Fig. 2. Structure projections down (a) the a axis and (b) the b axis using the data of Table 2. The shortest Br—Br distances are indicated.

Discussion. The reliability of the refinement result is well demonstrated by a calculation of packing distances. Using the constrained bond lengths of Table 1 and adjusting the Euler angles we can find those values which maximize the minimum intermolecular atom-to-atom distance. For a minimum of 3.25 Å the Euler angles in radians are $\varphi = 2.55$, $\theta = -1.09$, $\psi = 2.13$ for the 4.2 K cell. This is in excellent agreement with the refinement values of Table 1; equally good agreement is obtained with the 100 K cell.

The atomic positions in Å relative to the orthogonal axes (along x , y , z^*) as given in Table 2 for the 4.2 K structure have been used to construct the projections of Fig. 2. The minimum separation between any pair of Br atoms is 4.04 Å; this and some other similar Br—Br distances are shown in Fig. 2. The requirement to maximize the Br—Br separations is a dominant feature of this structure.

The rather low quality of the data is thought to derive from the persistence in the sample of rather large

Table 2. Orthogonal coordinates (Å) for the fully constrained refinement parameters of Table 1

	Temperature 4.2 K			Temperature 100 K		
	x	y	z	x	y	z
C	0.2565	0.6393	-0.3453	0.2826	0.6223	-0.3557
F	-0.7446	1.5312	-0.4373	-0.7033	1.5156	-0.5466
F	0.7007	0.3357	-1.5769	0.7986	0.2637	-1.5437
Br	1.6913	1.3916	0.6851	1.6583	1.4094	0.7281

crystallites, disturbing the intensity values but not of course affecting their positions and thus the unit-cell determination.

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