The Structure of Triflupromazine, a Phenothiazine 'Tranquilizer' Drug Molecule

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The crystal structure of triflupromazine (trade name 'Vesprin'), a very potent tranquilizer drug molecule, has been determined by X-ray diffraction using three-dimensional manual-diffractometer data with Mo $K\alpha$ radiation. The crystals are monoclinic (space group $P2_1/c$) with $a=11\cdot187$ (3), $b=11\cdot899$ (2), $c=30\cdot082$ (5) Å, $\beta=108\cdot71$ (1)°, $d_m=1\cdot37$ g cm^{-3} and $Z=8$. 1103 observed $[I>2\sigma(I)]$ reflections were used in the isotropic full-matrix least-squares refinement to give a final residual $R=0\cdot11$. For the two crystallographically independent molecules the average C–S bond distance is $1\cdot74$ (2) Å, the average C–S–C bond angle is $97\cdot2$ (7)°, and the two dihedral angles between C$_6$SN units of the butterfly tricyclic system are $134\cdot4$ (5) and $141\cdot0$ (5)°.

Introduction

Triflupromazine, or 10-[3-(dimethylamino)propyl]-2-(trifluoromethyl)phenothiazine hydrochloride (trade name 'Vesprin'), is one of the most potent 'tranquilizer' drug molecules; small amounts of Vesprin produce the same effect as a much larger dosage of the more common chlorpromazine (Domino, 1965). The structure determination of triflupromazine was undertaken to allow comparison with those of previously reported phenothiazine drug molecules in order to gain information about a suspected relationship between drug potency and the butterfly angle of the phenothiazine ring system.

Experimental

A sample of triflupromazine, kindly supplied by Smith, Kline and French laboratories, was recrystallized from hexane to give colorless rhombohedral crystals. Crystal data and data-reduction details are given in Table 1. The unit-cell parameters were obtained from the least-squares fitting of 27 carefully centered reflections. The crystal used for data collection measured $0\cdot30 \times 0\cdot25 \times 0\cdot30$ mm (all $\pm0\cdot01$ mm) in the [11$\bar{1}$], [001], and [110] directions. It was mounted with the a axis nearly parallel to the φ axis of the manually operated GE XRD-5

diffractometer. The Mo $K\alpha$ X-rays were filtered with 1 mil Zr. The range of calculated transmission coefficients is 0·94 to 0·96, and the correction was ignored. Four reflections measured periodically during the 14 day data collection indicated crystal and electronic stability.

Neutral-atom scattering factors were used for C, H, N, F and S, and chloride ion factors were used for Cl (*International Tables for X-ray Crystallography*, 1974);

Table 1. *Crystal data for triflupromazine hydrochloride*

Formula: $C_{18}H_{19}SN_2F_3 \cdot HCl$ F.W. 388·9
Crystal system: monoclinic
$a=11\cdot187$ (3), $b=11\cdot899$ (2), $c=30\cdot082$ (5) Å, $\beta=108\cdot71$ (1)°,
    $V=3793$ Å^3 at 22°C.
$D_m=1\cdot37$ (1) g cm^{-3} (suspension in n-butyl bromide–carbon tetrachloride mixture)
$D_c=1\cdot37$ g cm^{-3} for $Z=8$
μ $(\lambda=0\cdot71069$ Å$)=3\cdot5$ cm^{-1}
Space group: $P2_1/c$. Absences: $h0l$ for l odd, $0k0$ for k odd.
θ-2θ scan of 2° in 2θ at 2° min^{-1}, 10 s stationary backgrounds.
3596 unique data measured $(2\theta<40°)$; 1103 with $I>2\sigma(I)$.
$\sigma(I)=(S+9B+0\cdot0016\ I^2)^{1/2}$ where $S=$ scan count, $B=B_1+B_2$
    (sum of background counts) and $I=S-3B$.
If $|B_1-B_2|>2\sigma(I)$ (above), $\sigma(I)=1\cdot5|B_1-B_2|$.
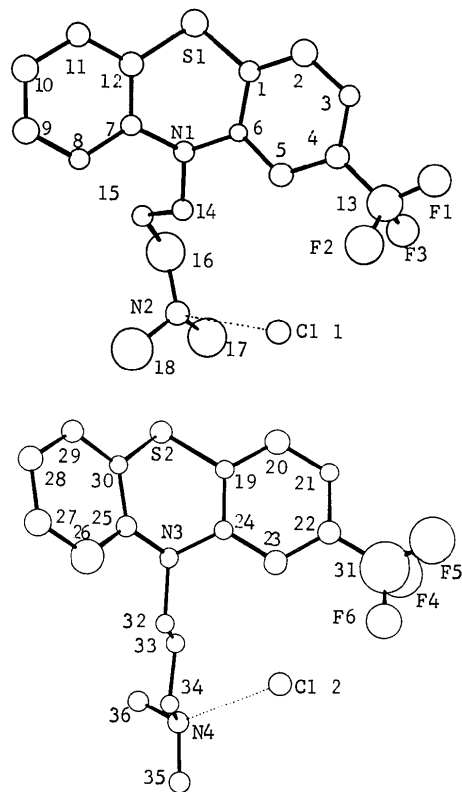

Fig. 1. Atom numbering scheme employed, and comparison of the two crystallographically independent molecules. Atoms with numbers only are carbon atoms. The ellipsoids include 30% probability.

anomalous dispersion corrections were made for S and Cl⁻ (Cromer, 1965). All calculations were performed with an IBM 360/50 computer at the University of Arkansas Computing Center.

Structure determination and refinement

Trial positional parameters for the four heavy atoms of the two crystallographically independent molecules

Table 2. *Final atomic positional and thermal parameters for triflupromazine*

Positional parameters are given as fractions of cell edges. The numbers in parentheses are the standard deviations of the last specified digit of the preceding parameter. Positional parameters for Cl and S atoms are $\times 10^4$, for other atoms $\times 10^3$. Hydrogen atom positions were calculated as described in the text, and included with $B = 5\cdot0$.

	x	y	z	$B(\text{Å}^2)$
Cl(1)	3446 (8)	917 (7)	2760 (3)	4·4 (2)
Cl(2)	7970 (7)	355 (7)	2341 (3)	4·0 (2)
S(1)	2157 (8)	3049 (7)	4929 (3)	4·7 (2)
S(2)	134 (8)	5211 (7)	915 (3)	3·7 (2)
F(1)	478 (2)	760 (2)	432 (1)	7·5 (6)
F(2)	488 (2)	647 (2)	382 (1)	8·5 (6)
F(3)	317 (2)	735 (2)	370 (1)	7·8 (6)
F(4)	97 (3)	−20 (3)	131 (1)	16·0 (1)
F(5)	73 (3)	−25 (3)	64 (1)	13·7 (9)
F(6)	250 (2)	2 (2)	109 (1)	8·8 (6)
N(1)	206 (2)	315 (2)	394 (1)	2·7 (5)
N(2)	7 (2)	346 (2)	239 (1)	4·5 (7)
N(3)	272 (2)	424 (2)	127 (1)	2·5 (5)
N(4)	532 (2)	276 (2)	283 (1)	3·6 (6)
C(1)	275 (2)	417 (2)	469 (1)	3·2 (6)
C(2)	330 (3)	511 (2)	494 (1)	4·7 (7)
C(3)	372 (2)	599 (2)	472 (1)	2·7 (5)
C(4)	359 (3)	592 (3)	425 (1)	3·2 (5)
C(5)	304 (3)	497 (3)	399 (1)	4·0 (6)
C(6)	262 (3)	410 (2)	421 (1)	2·5 (5)
C(7)	247 (3)	209 (3)	415 (1)	3·1 (5)
C(8)	275 (2)	121 (2)	389 (1)	2·9 (5)
C(9)	317 (3)	19 (3)	411 (1)	4·5 (7)
C(10)	331 (3)	4 (2)	458 (1)	4·2 (6)
C(11)	303 (2)	92 (2)	484 (1)	4·1 (6)
C(12)	261 (3)	195 (3)	462 (1)	3·7 (5)
C(13)	405 (3)	686 (3)	401 (1)	8·6 (7)
C(14)	160 (3)	326 (3)	343 (1)	3·6 (7)
C(15)	45 (3)	253 (2)	318 (1)	2·9 (6)
C(16)	−53 (5)	309 (4)	276 (2)	12·0 (2)
C(17)	−93 (5)	415 (5)	206 (2)	14·0 (2)
C(18)	50 (5)	263 (5)	214 (2)	14·0 (2)
C(19)	52 (2)	381 (2)	90 (1)	2·6 (5)
C(20)	−46 (3)	304 (2)	75 (1)	4·0 (6)
C(21)	−21 (3)	189 (2)	79 (1)	2·6 (5)
C(22)	103 (3)	151 (2)	98 (1)	3·6 (6)
C(23)	202 (3)	228 (2)	114 (1)	3·9 (6)
C(24)	176 (2)	343 (2)	110 (1)	2·4 (5)
C(25)	265 (3)	521 (3)	100 (1)	2·2 (5)
C(26)	372 (3)	569 (3)	93 (1)	3·1 (4)
C(27)	362 (4)	670 (3)	69 (1)	3·7 (6)
C(28)	245 (3)	723 (2)	51 (1)	4·2 (6)
C(29)	138 (2)	675 (2)	58 (1)	6·5 (7)
C(30)	148 (2)	575 (2)	82 (1)	2·9 (5)
C(31)	131 (4)	27 (4)	102 (2)	17·0 (2)
C(32)	399 (2)	387 (2)	157 (1)	2·4 (6)
C(33)	393 (3)	347 (2)	206 (1)	2·7 (7)
C(34)	528 (3)	316 (2)	233 (1)	2·8 (7)
C(35)	663 (3)	230 (2)	308 (1)	3·4 (7)
C(36)	501 (3)	368 (3)	309 (1)	4·1 (8)

Table 2 (cont.)

	x	y	z		x	y	z
H(C2)	339	516	527	H(C21)	−88	136	68
H(C3)	410	664	490	H(C23)	286	202	127
H(C5)	295	492	367	H(C29)	59	712	454
H(C8)	266	132	357	H(C28)	238	792	342
H(C9)	336	−41	394	H(C27)	435	702	64
H(C10)	359	−66	473	H(C26)	451	533	105
H(C11)	312	195	516	H(C32)	455	448	162
H(C14)	224	309	328	H(C32)	427	327	142
H(C14)	131	401	333	H(C33)	359	404	221
H(C15)	78	185	306	H(C33)	338	281	202
H(C15)	13	224	342	H(C34)	578	383	236
H(C16)	−79	369	293	H(C34)	557	261	217
H(C16)	−118	254	267	H(C35)	733	291	311
H(C17)	−100	397	173	H(C35)	663	162	335
H(C17)	−188	395	215	H(C35)	684	165	287
H(C17)	−65	490	215	H(C36)	450	428	290
H(C18)	18	190	214	H(C36)	588	415	326
H(C18)	75	270	189	H(C36)	493	335	340
H(C18)	155	268	230	H(N4)	440	200	285
H(C20)	−130	329	62	H(N2)	80	380	245

Table 3. *Selected bond distances (Å) and angles (°) in triflupromazine*

S(1)—C(1)	1·746 (8)	C(12)-S(1)—C(1)	97·9 (4)
S(1)—C(12)	1·766 (8)	C(19)-S(2)—C(30)	96·5 (4)
S(2)—C(19)	1·729 (8)	C(6)—N(1)—C(7)	115 (1)
S(2)—C(30)	1·738 (8)	C(24)-N(3)—C(25)	117 (1)
N(1)—C(6)	1·47 (2)	C(6)—N(1)—C(14)	119 (2)
N(1)—C(7)	1·42 (2)	C(7)—N(1)—C(14)	121 (2)
N(1)—C(14)	1·46 (4)	N(1)—C(14)-C(15)	115 (2)
N(3)—C(24)	1·40 (2)	C(14)-C(15)-C(16)	115 (3)
N(3)—C(25)	1·41 (2)	C(15)-C(16)-N(2)	111 (4)
N(3)—C(32)	1·48 (3)	C(16)-N(2)—C(17)	104 (3)
N(2)ᵃ–Cl(1)	3·07 (3)	C(16)-N(2)—C(18)	119 (4)
N(4)—Cl(2)	3·00 (3)	C(17)-N(2)—C(18)	110 (4)
C(14)-C(15)	1·53 (4)	C(24)-N(3)—C(32)	120 (2)
C(15)-C(16)	1·53 (6)	C(25)-N(3)—C(32)	117 (2)
N(2)-C(16)	1·53 (6)	N(3)—C(32)-C(33)	110 (2)
N(2)—C(17)	1·47 (7)	C(32)-C(33)-C(34)	105 (2)
N(2)—C(18)	1·42 (6)	C(33)-C(34)-N(4)	109 (2)
C(32)-C(33)	1·55 (4)	C(34)-N(4)—C(35)	108 (2)
C(33)-C(34)	1·52 (4)	C(34)-N(4)—C(36)	111 (2)
N(4)—C(34)	1·56 (4)	C(35)-N(4)—C(36)	112 (2)
N(4)—C(35)	1·45 (4)	F(1)—C(13)-F(2)	100 (1)
N(4)—C(36)	1·52 (4)	F(1)—C(13)-C(3)	112 (1)
C(13)-F(1)	1·34 (2)	F(2)—C(13)-F(3)	109 (1)
C(13)-F(2)	1·31 (2)	F(4)—C(31)-F(5)	104 (2)
C(13)-F(3)	1·27 (3)	F(4)—C(31)-F(6)	109 (2)
C(31)-F(4)	1·18 (3)	F(5)—C(31)-F(6)	103 (2)
C(31)-F(5)	1·29 (3)	S(1)—C(1)—C(6)	117·0 (3)
C(31)-F(6)	1·32 (2)	S(1)—C(12)-C(7)	118·8 (3)
		S(2)—C(19)-C(24)	121·7 (3)
		S(2)—C(30)-C(25)	121·5 (3)
		N(1)—C(6)—C(1)	121·8 (9)
		N(1)—C(7)—C(12)	119·1 (9)
		N(3)—C(24)-C(19)	118·1 (9)
		N(3)—C(25)-C(30)	118·1 (9)

Weighted averages and r.m.s. deviations (c = chain, r = ring)

C –S	1·74 (2)	C –S—C	97·2 (7)
C_r–N_r	1·42 (3)	C_r–N_r–C_r	116 (1)
C_c–N_r	1·47 (1)	C_r–N_r–C_c	119 (2)
C_c–N_c	1·49 (5)	C_c–N_c–C_c	111 (5)
C –F	1·28 (6)	F—C—F	106 (5)
C_c–C_c	1·53 (1)	C_c–C_c–C_c	110 (5)
		S—C—C(central ring)	120 (2)
		N–C—C(central ring)	119 (2)

were obtained from analysis of a sharpened Patterson map, and the remaining non-hydrogen atoms were located by Fourier methods. Because of the size of the structure (200 parameters) and the limited number of data (1100 reflections) the phenyl rings were constrained as rigid groups (C–C = 1·395 within the ring and 1·505 to the CF_3 carbon, C–H = 0·95 Å, and C angles of 120°) and all atoms were refined with isotropic thermal factors in the full-matrix least-squares refinement.

The function minimized in the least-squares program was $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma(F)$. The hydrogen atoms, which were included for structure-factor calculations but not refined, were put in calculated positions except for the methyl and ammonium hydrogen atoms which were located on difference maps. The final refinement consisted of 147 parameters and 1066 reflections, and gave $R = 0·108$ and $R_w = 0·118$. There were 37 reflections of the 'observed' data and 16 reflections of the 'unobserved' data which were given zero

weight in the refinement due to recording or setting errors in the manual data collection; these errors were verified by qualitative film data. With the exception
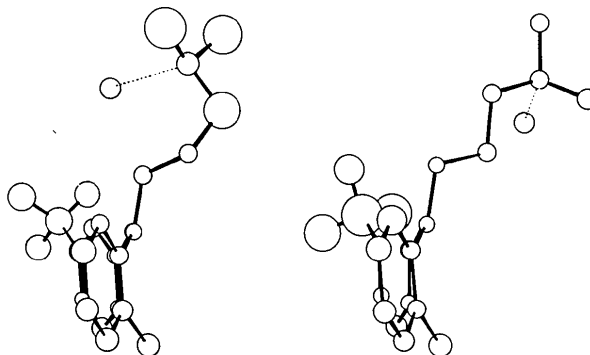

Fig. 2. View for comparison of the alkyl chain orientations of the two independent molecules. The ellipsoids include 30% probability.

Table 4. *Atom displacements from best planes in triflupromazine*

Each atom included in the calculation of a plane was weighted by $1/\sigma_\perp$, where $\sigma_\perp$ is the positional uncertainty component perpendicular to the plane. Asterisks indicate atoms not included in the calculation of the best plane.

Plane 1		Plane 2		Plane 3		Plane 4	
S(1)	−0·002 (8)	S(1)	0·007 (8)	S(2)	0·01 (1)	S(2)	0·002(9)
N(1)	0·00 (2)	N(1)	−0·02 (2)	N(3)	−0·01 (2)	N(3)	0·02 (2)
C(1)	0·02 (3)	C(7)	−0·01 (3)	C(19)	−0·10 (3)	C(25)	−0·03 (2)
C(2)	0·01 (3)	C(8)	0·03 (3)	C(20)	−0·07 (3)	C(26)	0·00 (3)
C(3)	−0·00 (3)	C(9)	0·03 (3)	C(21)	0·02 (3)	C(27)	0·02 (3)
C(4)	−0·01 (3)	C(10)	0·00 (3)	C(22)	0·07 (3)	C(28)	0·02 (3)
C(5)	−0·01 (3)	C(11)	−0·04 (3)	C(23)	0·04 (3)	C(29)	−0·01 (4)
C(6)	0·01 (3)	C(12)	−0·05 (3)	C(24)	−0·04 (3)	C(30)	−0·04 (3)
C(13)*	−0·03 (3)	C(14)*	0·35 (3)	C(31)*	0·16 (3)	C(32)*	0·41 (3)
C(14)*	−0·41 (3)			C(32)*	0·35 (3)		
$\chi^2 = 0·7$		$\chi^2 = 3·5$		$\chi^2 = 8·6$		$\chi^2 = 1·8$	

Table 5. *Best planes and dihedral angles of phenothiazine drug molecules*

Column three gives the dihedral angles between the best planes of the two C_6SN groups, and column four gives the angles between the two C_6 phenylene planes: positive values indicate a displacement on the outside of the fold. Where e.s.d.'s are given the weighting was proportional to $\sigma_\perp$, where $\sigma_\perp$ is the positional uncertainty perpendicular to the plane. In the other cases unit weights were used for all atoms due to the lack of e.s.d.'s for the atom positions. All of the values were calculated from published atom positions, using the methods described by Waser, Marsh & Cordes (1973).

R_1	R_2	C_6SN-C_6SN	C_6-C_6	S displacement	N displacement	Reference
$CH_2CH(CH_3)N(CH_3)_3SO_4CH_3$	H	134·6°	136·6°	0·19, 0·08 Å	−0·04, 0·09 Å	(Cam & Marsau, 1970)
$CH_2CH(CH_3)N(C_2H_5)_2HCl$	H	137·3	138·8	0·13, 0·04	0·02, 0·04	(Calas & Marsau, 1969)
$(CH_2)_2N(C_2H_5)_2HCl$	H	134·6	135·8	0·03, 0·03	−0·02, −0·01	(Marsau, 1971)
$CH_2CH(CH_3)N(C_2H_5)_2HCl$	H	137·2	138·2	0·02, 0·11	0·03, 0·00	(Marsau & Calas, 1971)
$CH_2CH(CH_3)N(CH_3)_2HBr$	H	140·7	142·6	0·15, 0·06	−0·03, 0·15	(Busetta & Marsau, 1968)
$CH_2CH(CH_3)N(CH_3)_2HCl$	H	130·7	130·7	−0·02, 0·07	0·00, −0·04	(Escobar, Marsau & Clastre, 1968)
$(CH_2)_3(CH_3)_2HCl$	Cl	137·1	137·8	0·07, 0·08	0·01, −0·04	(Dorignac-Calas & Marsau, 1972)
$(CH_2)_3(CH_3)_2$	Cl	137·4 (1)	139·2 (3)	0·133 (2), 0·018 (2)	0·006 (5), 0·055 (5)	(McDowell, 1969)
$(CH_2)_3(N_2C_3H)CH_3$	SC_2H_5	137·5 (3)	139·1 (5)	0·143 (4), −0·007 (4)	0·05 (4), −0·01 (1)	(McDowell, 1970)
$(CH_2)_3N(CH_3)_2HX$	OCH_3	154·7	157·4	0·22, 0·18	−0·01, 0·02	(Marsau & Gauthier, 1972)
$(CH_2)_3(CH_3)HCl$	CF_3	134·4 (5)	136 (1)	0·038 (9), 0·103 (9)	0·00 (2), 0·01 (2)	(This report)
		141·0 (5)	145 (1)	0·22 (1), 0·065 (9)	0·07 (2), 0·09 (2)	

of these erroneous readings, all but 7 of the approximately 2500 'unobserved' reflections had $F_{calc} > F_{max} + 3\sigma(F)$. The standard deviation of an observation of unit weight was 1·60, and no $\Delta F/\sigma$ values were greater than 5·3. The relatively high value for the latter is
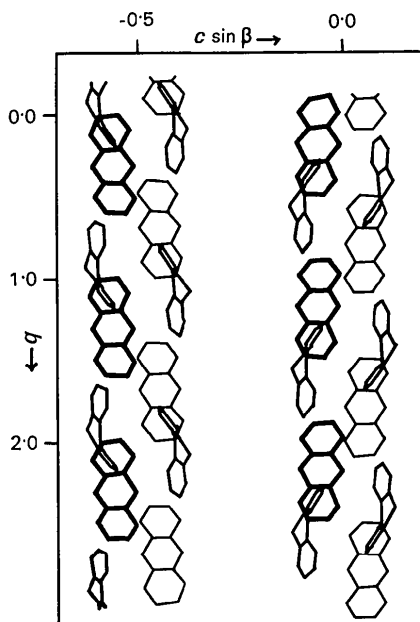

Fig. 3. Columnar packing of the heterocyclic rings. The rings that are mainly parallel to the plane of the figure are folded away from the column axis. The other independent set of molecules is approximately perpendicular to the plane of the drawing; these molecules are folded toward the column axis.
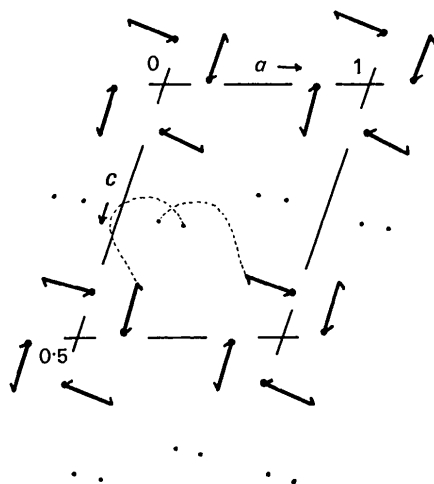
Fig. 4. Schematic view parallel to the column formed by the heterocyclic rings. Heavy lines indicate S···N lines, the heavy dots on the end of the lines show the S position, and the barbs indicate the direction of folds of the butterfly portion of the molecule. The isolated dots are chloride ions; the dotted lines show the general orientation of the two independent alkyl chains.

attributed largely to the lack of anisotropic thermal treatments caused by the relative paucity of data for this size of unit cell. The isotropic restriction is probably most severe for the S and F atoms, which showed characteristic anisotropic features on the final difference map.

The final positional and thermal parameters for the two molecules are given in Table 2.* Table 3 gives some of the intramolecular bond distances and angles, and Table 4 summarizes the best planes within the molecules. Figs. 1 and 2 are *ORTEP* drawings of the two molecules in comparable orientations, and Figs. 3–5 display the molecular packing in the unit cell.

Discussion of the structures

None of the exocyclic C–C, N–C, and C–F bond distances in Table 3, or the angles between these bonds, have unusual values. Within the central ring system, the C–S distances of 1·738(8)–1·766(8) Å, the N–C distances of 1·40(2)–1·47(2) Å, the CSC angles of 96·5(4)–97·9(4)° and the CNC angles of 115(1)–119 (1)° are all within the range of values found for the other phenothiazine structures given in Table 5. The relatively high thermal motion found for the CF_3 groups is apparently not unusual for that group (Cotton & Norman, 1972; Mague, 1970).

The main purpose of this study was to determine the effect of the highly electronegative CF_3 group on the dihedral angle of the tricyclic system (the butterfly angle of fold at the S···N line). The 7·4° difference in this angle between the two crystallographically independent molecules in this crystal is unexpected, since previous studies have shown a constant angle of fold for similar molecular systems even when very different lattice packing was involved (Malmstrom & Cordes, 1973). The reason for the difference in the butterfly angles in the two molecules of the present structure apparently lies in the general packing of the molecules rather than in any specific intermolecular contact. Indeed, the three intermolecular distances involving the ring portion of the molecules that are significantly shorter than van der Waals contacts [F(6)–H(C36) at 2·43 Å, H(C35)–C(25) at 2·56 Å, and H(C35)–C(39) at 2·51 Å, where in each case the second atom is at $1-x, -0·5+y, 0·5+z$ with respect to the positions given in Table 1] would all tend to fold the ring which in fact has the larger dihedral angle. The more dominant factor appears to be related to the overall packing. As Figs. 3 and 4 show, the tricyclic parts of the molecules form helical cylinders parallel to **b**. The ring systems are arranged such that the molecule with
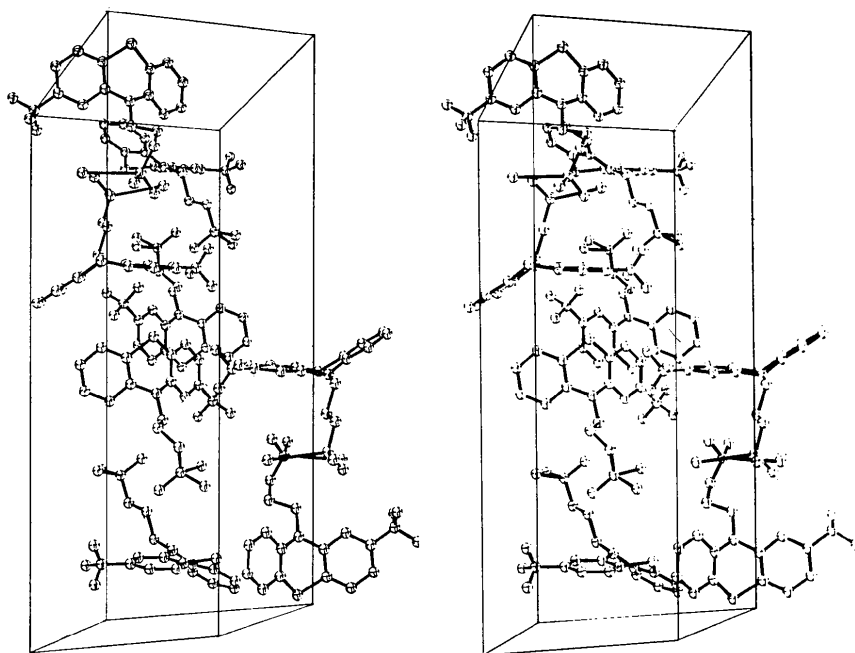

Fig. 5. Stereo *ORTEP* drawing of the crystal packing. All atom spheres have been made the same size for viewing convenience. The origin of the cell is the upper left rear corner. The + a direction is from the drawing plane toward the viewer, the + b direction is left to right on the page, and the + c direction is from top to bottom.

the 141·0° fold has the inside of the fold directed toward the center of the column, an orientation which would resist further folding. The molecule with the 134·4° fold has the back of the fold directed toward the center of the column, an orientation less restrictive for a smaller angle. Figs. 2 and 4 also show that the two independent alkyl chains have somewhat different orientations in the crystal; the torsion angles about C(14)–C(15) and C(15)–C(16) are 37·9 (9) and 56·71 (3)°, respectively, as compared with the corresponding C(32)–C(33) and C(33)–C(34) angles of 1·3 (9) and 178·73 (3)°. Although the charged part of the structure is near the CF_3 end of both molecules, both chloride ions are more nearly in the plane of the S(1) molecule. Fig. 4 shows the cation columns and the chloride ions form a layered structure parallel to the *ab* plane.

The only reported structure of a phenothiazine drug molecule with a butterfly angle significantly different from the others is that of the methoxy molecule, as shown in Table 5; it is somewhat surprising that the highly electronegative CF_3 groups at the R_2 position do not result in a more planar molecule.

References

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