## The Crystal and Molecular Structure of 2-Formylthiophene Thiosemicarbazone

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The compound 2-formylthiophene thiosemicarbazone,  $C_6H_7N_3S_2$ , forms pale yellow, lath-like, monoclinic crystals with cell dimensions of a=13.580, b=5.839, c=24.024 Å and  $\beta=117.69^\circ$ . The space group is  $P2_1/c$ ; there are 8 molecules per unit cell and hence two per asymmetric unit. The four sulphur atoms were located using the symbolic addition method and the light atoms from Fourier syntheses. The structure was refined by least-squares methods to an *R* index of 0.052 for the 2848 observed reflecions measured with a diffractometer.

The thiophene rings are planar but slightly distorted from *mm* symmetry, presumably due to a resonance interaction with the thiosemicarbazone side chain. The bond distances in the side chain are similar to those of other thiosemicarbazones. The planarities of the two molecules in the asymmetric unit are different. This difference can be related to different hydrogen bonding schemes for the molecules.

#### Introduction

The relationship between metal ions and cancer is intriguing and controversial. French & Freedlander (1958) suggested that one common property of some antitumor agents was their ability to function as chelating agents. Subsequently, French & Blanz (1966) prepared a large number of thiosemicarbazones and found that all the tumor inhibitors were potentially capable of acting as a tridentate N-N-S type ligand. A crystal structure study of bis-(1-formylisoquinolinethiosemicarbazonato)nickel(II) monohydrate by Mathew & Palenik (1969) confirmed the ability of the ligand to act as a tridentate chelate. The related compound 2-formylthiophenethiosemicarbazone(2FTTSC) shows no tumor inhibition although the possibility of an S-N-S type chelate exists. A knowledge of the conformation and bond distances of an inactive thiosemicarbazone is essential for a final explanation of the requirements for biological activity; thus, the crystal structure determination of 2FTTSC was undertaken.

## Experimental

A sample of 2FTTSC was kindly supplied by F. A. French and slow evaporation of an ethanol solution produced pale yellow, lath-like crystals elongated along **b**.A crystal was cleaved to give a parallelepiped of dimensions  $0.18 \times 0.15 \times 0.15$  mm which was mounted with the [010] direction parallel to the  $\varphi$  axis of a General Electric single-crystal orienter. The unit-cell dimensions were obtained from a least-squares fit of twenty  $2\theta$  values measured using a narrow beam (0.7° takeoff angle) of Cu  $K\beta$  ( $\lambda = 1.39217$  Å) radiation.  $C_6H_7N_3S_2$ , mol. wt. 185·3, monoclinic  $a=13\cdot580$  (6),  $b=5\cdot839$  (4),  $c=24\cdot024$  (9) Å,  $\beta=117\cdot69$  (4)°,  $D_m=1\cdot450$  g.cm<sup>3</sup>,  $D_c=1\cdot459$  g.cm<sup>3</sup>, Z=8, space group  $P2_1/c$  ( $C_{2h}^5$ ), from systematic absences (hol with l odd and 0k0 with k odd).

Alternate setting: a=13.580, b=5.839, c=21.410 Å,  $\beta=96.48^{\circ}$ , space group  $P2_1/n$ .

A take-off angle of  $3.7^{\circ}$ , which produces a wide beam, was used in measuring intensities. A 0.7 mil Ni foil was placed in front of the counter window. Each reflexion was counted for 20 sec with the crystal and counter stationary. All the reflexions for which  $2\theta \le 135^{\circ}$  (Cu radiation,  $\lambda = 1.54051$  Å) in a unique quadrant were measured first and then the entire hemisphere was surveyed, a total of 10260 intensity measurements. A small correction (maximum 4%) was applied to correct for a slight decline in the intensities of the 4 standard reflexions which were measured after every 100 reflexions. After averaging equivalent reflexions, a total of 3038 unique intensities was obtained of which the 2848 greater than 1.30 times the background counts were considered to be observed and were used in the structure analysis. No absorption correction was applied.

## Structure determination and refinement

The structure was solved by the symbolic addition procedure (Karle & Karle, 1966) using the computer programs FAME-MAGIC-LINK-SYMPL of Dewar, Stone & Fleischer (1966). The computed distribution of E values is compared with the theoretical values in Table 1. Seven large E's were assigned symbols and after 5 iterations, a total of 445 reflexions had their signs determined in terms of the seven symbols. After

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choosing the signs of three reflexions to define the origin, the most consistent set of signs was used to calculate an *E*-map.

Table 2. The final positional parameters ( $\times 10^{5}$ ) of non-hydrogen atoms with their e.s.d.s. in parentheses

	$x(\sigma_x)$	$y(\sigma_y)$	$z(\sigma_z)$
S(A1)	- 19957 (7)	22313 (16)	25049 (4)
S(A2)	15001 (6)	82623 (15)	50929 (4)
N(A1)	-2263(18)	39008 (44)	37693 (11)
N(A2)	6236 (19)	49158 (45)	42801 (11)
N(A3)	-6228(20)	73542 (49)	43452 (13)
C(A1)	-7639 (23)	9383 (48)	30134 (13)
C(A2)	- 6364 (27)	-11452 (55)	27772 (15)
C(A3)	-15573 (31)	- 16227 (66)	21805 (17)
C(A4)	- 23403 (29)	290 (75)	19800 (16)
C(A5)	171 (23)	20266 (52)	35832 (13)
C(A6)	4134 (21)	67723 (49)	45377 (12)
S(B1)	48318 (6)	14481 (13)	16580 (3)
S(B2)	66400 (5)	90277(12)	1396 (3)
N(B1)	52877 (17)	53045 (38)	9547(10)
N(B2)	55016 (17)	70554 (38)	6404 (10)
N(B3)	68839 (19)	48522 (40)	6250 (12)
C(B1)	41450(21)	40132 (45)	13960 (11)
C(B2)	33286 (24)	42634 (54)	15725 (13)
C(B3)	32618 (26)	23579 (67)	19160 (15)
C(B4)	40194 (28)	7287 (59)	19999 (14)
C(B5)	44451 (21)	56570 (46)	10545 (11)
C(B6)	63289 (20)	68171 (42)	4848 (11)
2(20)			

## Discussion

There are two molecules in the asymmetric unit; hence, we have two determinations of the dimensions of 2FTTSC. The atomic numbering, average bond distances and average bond angles are given in Fig. 1. The individual bond distances and angles together with their estimated standard deviations are given in Table 6. Excluding the bonds C(1)-C(2) and C(6)-N(3), the differences in bond lengths in the two molecules average 0.006 Å, with none of the differences being statistically significant. However, following the criteria of Cruickshank & Robertson (1953), the difference between the C(1)–C(2) bonds of 0.020 Å ( $t_0 = 3.1$ ) is significant and the difference between the C(6)-N(3) bonds of 0.021  $(t_0=3.7)$  is highly significant. The difference in the C(6)-N(3) bonds may be related to hydrogen bonding (see below).

Both thiophene rings are planar (see Table 7) but the side chains are bent out of the planes of the rings. A survey of bond distances in thiophene rings has been given by Rychnovsky & Britton (1968). However, only two of the compounds reported there contain asymmetrically substituted thiophene rings. The two C-S distances in the thiophene ring of 2FTTSC are significantly different  $(t_0 = 3.0)$ . The lengthening of the C(1)-S(1) bond relative to the C(4)-S(1) bond is easily explained in terms of the double-bond character in the C(1)-C(5) bond. The difference in the C(1)-C(2)compared to the C(3)-C(4) bond also reflects the double-bond character in the C(1)-C(5) bond. A similar effect was observed by Bartlett, Schreiber & Palenik (1969) in bis-(4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedionato)copper(II) where the C-S bond lengths were found to be 1.691 and 1.710 Å.

# Table 1. Statistical data for the symbolic addition procedure

A. Statistical averages	for normali	zed structure	factors,	$E_{i}$
	$\langle  E  \rangle$	$\langle  E^2-1  \rangle$	$\langle  E ^2 \rangle$	
Experimental	0.814	0.933	1.000	
Theoretical: centric	0.798	0.968	1.000	
acentric	0.886	0.736	1.000	

B. Distribution of structure factors.

		Theoretical			
	Experimental	Centric	Acentric		
E  > 1	32.4%	32.0%	37.0%		
E  > 2	4.2	5.0	1.8		
E  > 3	0.2	0.3	0.01		

The *E*-map contained four large peaks which were assigned to the four sulphur atoms. A Fourier synthesis phased on the four sulphur atoms was calculated and used in conjunction with the *E*-map to locate the remaining light atoms. In retrospect, both molecules could have been found in the first *E*-map. Structure factors were calculated using all the atoms except the hydrogens to give an R index, the usual residual, of 0.22.

Five full-matrix least-squares cycles using individual isotropic thermal parameters reduced R to 0.12, and four additional cycles using anisotropic thermal parameters dropped R to 0.069. The positions of all the hydrogen atoms were located in a difference Fourier synthesis. Three cycles of block-diagonal  $(6 \times 6 \text{ and }$  $3 \times 3$ ) least-squares calculations were computed in which all heavy atoms were assigned anisotropic thermal parameters and the hydrogen atoms had isotropic thermal parameters. Two reflexions, 204 and 114, which were apparently affected by extinction were not included in the final cycles. At this point the shifts were less than 0.3 of a standard deviation, and with R at 0.052, the refinement was considered completed. The weighting scheme used in all the calculations was:

$$\begin{aligned} & \forall w = |F_o|/4F_{\min} \text{ if } |F_o| < 4F_{\min} \\ & \forall w = 1 \text{ if } 4F_{\min} \le |F_o| \le 6F_{\min} \\ & \forall w = 6F_{\min}/|F_o| \text{ if } |F_o| > 6F_{\min} \end{aligned}$$

where  $F_{\min}$  was 1.7 (on the same scale as Table 5). The quality  $\sum w(|F_o| - |F_c|)^2$  was minimized in the least-squares calculations. The scattering factors for all atoms were taken from *International Tables for X-ray Crystallography* (1962).

The final atomic parameters along with their estimated standard deviations are given in Tables 2, 3 and 4. The observed and calculated structure amplitudes are listed in Table 5.

A comparison of the bond distances in the side chain with the corresponding values in other thiosemicarbazones and in thiosemicarbazide is presented in Table 8. The bond distances in thiosemicarbazones show a lengthening of the C(6)-N(2) and a shortening of the N(1)-N(2) and C(6)-N(3) bonds compared to thiosemicarbazide. The decrease in the N(1)-N(2) bond length was discussed by Restivo & Palenik (1970) who attributed the effect to an interaction between the ring and the side chain. A structural study of acetone thiosemicarbazone currently in progress may resolve the question. The distances in 2FTTSC and KTS [2-keto-3-ethoxybutyraldehydebis(thiosemicarbazone), Gabe, Taylor, Glusker, Minkin & Patterson (1969)] are in excellent agreement but both sets of values differ from the distances in 4FPYTSC (4-formylpyridine thiosemicarbazone). The C(1)-C(5) distances in 2FTTSC and 4 FPYTSC are significantly different ( $t_0 = 6.0$ ) suggesting less interaction between the ring and side chain in 4 FPYTSC compared to 2 FTTSC. The significantly shorter C-S bond ( $t_0 = 4.4$ ) in 4FPYTSC supports this conclusion. The C-S bonds in all three compounds are shorter than in the thiosemicarbazonato ligand reported by Mathew & Palenik. The changes in the bond lengths resulting from the formation of the metal complex suggest that the thiosemicarbazones are a highly delocalized system, in agreement with previous observations.

An ORTEP drawing of the two molecules is given in Fig. 2. The thermal ellipsoids are surprisingly isotropic, a fact which is presumably related to the hydrogen bonding. The conformation of the side chain is the same in both molecules with the S atom *trans* to N(1). The same conformation was found in 4FPYTSC, KTS and thiosemicarbazide. However, in the formation of metal complexes where the thiosemicarbazone acts as a bidentate chelate, the S and N atoms must be *cis*. Therefore, a change in conformation about the

Table 3. Final thermal parameters with their e.s.d.s. in parentheses

The temperature factor is of the form exp  $\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)\}$ .

	$\beta_{11}  imes 10^5$	$\beta_{22} \times 10^4$	$\beta_{33} \times 10^5$	$\beta_{12} \times 10^4$	$\beta_{13} \times 10^5$	$\beta_{23} \times 10^4$
S(A1)	679 (6)	368 (3)	231 (2)	8 (2)	226 (5)	-51(1)
S(A2)	489 (5)	363 (3)	238 (2)	-33(2)	284 (5)	-79(1)
N(AI)	493 (15)	314 (8)	179 (5)	-16(5)	224 (15)	-35(3)
N(A2)	460 (15)	337 (9)	213 (6)	1 (6)	193 (15)	-58(4)
N(A3)	547 (17)	363 (10)	268 (7)	4 (7)	290 (17)	-68(4)
C(A1)	621 (20)	257 (9)	204 (6)	- 33 (6)	387 (19)	-23(4)
C(A2)	770 (23)	309 (10)	249 (7)	-29(8)	501 (23)	-40(4)
C(A3)	1000 (30)	398 (12)	283 (9)	-110(9)	670 (28)	- 95 (6)
C(A4)	803 (26)	499 (15)	242 (8)	- 85 (10)	374 (24)	- 85 (6)
C(A5)	633 (20)	290 (9)	185 (6)	-1(7)	329 (18)	- 16 (4)
C(A6)	487 (17)	294 (9)	181 (6)	5 (6)	293 (17)	- 17 (4)
S(B1)	732 (5)	247 (2)	200 (2)	28 (2)	349 (5)	14 (1)
S(B2)	495 (4)	225 (2)	200 (2)	-17(1)	290 (4)	22 (1)
N(B1)	541 (15)	221 (6)	163 (5)	-35(5)	257 (14)	3 (3)
N( <i>B</i> 2)	502 (15)	224 (7)	193 (5)	- 19 (5)	333 (14)	5 (3)
N( <i>B</i> 3)	621 (17)	224 (7)	246 (6)	18 (6)	377 (17)	17 (3)
C(B1)	507 (17)	244 (8)	137 (5)	-31(6)	198 (16)	-9 (3)
C(B2)	576 (19)	346 (11)	188 (6)	-4(7)	306 (18)	12 (4)
C(B3)	698 (23)	455 (13)	202 (7)	- 51 (9)	374 (21)	30 (5)
C(B4)	901 (27)	336 (11)	191 (7)	- 66 (9)	306 (22)	28 (4)
C(B5)	527 (18)	245 (8)	153 (5)	-37 (6)	267 (16)	-11(3)
C(B6)	461 (16)	207 (7)	135 (5)	-36(5)	162 (15)	-10(3)

Table 4. Parameters of the hydrogen atoms and their estimated standard deviations

	Bonded to	$x(\sigma_x) \times 10^3$	$y(\sigma_y) \times 10^3$	$z(\sigma_z) \times 10^3$	B (Å2)
H(A1)	N(A2)	134 (3)	439 (7)	442 (2)	3.8 (4)
H(A2)	N(A3)	-80(3)	854 (7)	450 (2)	4.1 (4)
H(A3)	N(A3)	-117(3)	630 (7)	409 (2)	4.6 (4)
H(A4)	C(A2)	-4(3)	-202(7)	299 (2)	3.3 (5)
H(A5)	C(A3)	-166(3)	-302(7)	196 (2)	3.4 (5)
H(A6)	C(A4)	-310(3)	13 (7)	157 (2)	4.1 (4)
H(A7)	C(A5)	70 (3)	125 (7)	380 (2)	3.5 (5)
H( <i>B</i> 1)	N( <i>B</i> 2)	508 (3)	837 (7)	51 (2)	2.7 (6)
H( <i>B</i> 2)	N(B3)	663 (3)	371 (6)	75 (2)	2.9 (6)
H(B3)	N(B3)	734 (3)	451 (7)	44 (2)	3.9 (4)
H( <i>B</i> 4)	C(B2)	289 (3)	574 (7)	150 (2)	3.2 (5)
H(B5)	C(B3)	268 (3)	221 (8)	206 (2)	4.5 (4)
H( <i>B</i> 6)	C(B4)	407 (3)	-70 (8)	216 (2)	4.3 (4)
H( <i>B</i> 7)	C(B5)	396 (3)	703 (7)	89 (2)	2.9 (6)

# Table 5. Observed and calculated structure amplitudes

The three columns in each group contain the values, reading from left to right of l,  $10F_o$  and  $10F_c$ . A negative  $F_o$  indicates an unobserved reflexion which was not included in the least-squares refinement.

L FN FC	L FD FC 10 154 128 12 489 -475	L FN FC 16 43 -17 14 12 77	L FO FC	L FO FC 11 271 267 12 217 -205	L FO FC 6 21 -19 7 107 103	L FO FC	1 PC FC 1 1C9 -112 2 156 150	L FO FC	L FO FC	L FO FC	L FO FC	L FC FC	L FO FC 7 285 -291
10 01 -110 12 16 -10 16 119 -134 16 16 18	14 67 -48 16 158 140 18 765 -394 20 362 398 22 18 -15	H 7, E 0 0 344 -388 2 276 281	21 128 -120 22 165 149 23 17 -32 24 28 24 25 80 -83	13 111 -105 14 453 449 15 232 -227 16 273 278	* 135 -123 10 661 6#2 11 140 147	3 248 - 244 4 75 70 5 70 69 6 206 - 208	104 47 4 301 747 4 -9 2 4 -9 2	2 980 362 3 115 109 4 175 -167 5 119 115	2 166 227 3 04 -03 4 172 -077 5 40 30	3 2C2 -147 4 74 53 5 368 -365 6 133 -138	17 127 122 18 142 -126 19 170 -160 20 147 131	24 50 47 25 25 -27 10 -4, 4+ 3	4 153 -140 10 148 149 11 180 -184 12 78 75
He -15. EF 0 4 BF 116	24 110 128 26 39 -15 28 104 108	4 212 213 4 366 764 8 165 149 10 764 296	26 67 76 He -11. Kr 1	16 312 325 19 47 -47 20 32 38 21 132 -136	12 250 750 13 84 -90 14 75 76 15 30 30 16 288 308	127 -128 8 275 272 9 123 126 10 140 -131 11 26 -25	23 12 274 265 10 275 -262	6 148 -133 7 241 -250 8 107 101 9 125 -113	6 63 69 7 295 -295 8 221 -277 9 287 276	7 215 -200 8 -9 5 9 86 -78 10 228 -215	21 46 -34 22 40 -45 23 -7 -13 24 55 55	1 437 -474 2 544 531 3 28 17	13 17 -34 14 63 43 15 227 232 16 102 -103
6 47 72 # 236 245 10 -8 -4 12 130 349	2 A17 -850 4 1500 -1912	12 172 -159 14 179 148 14 120 144	1 161 163 2 321 31A 3 223 213 4 144 -140	27 304 108 23 68 69 24 89 89 24 97 -97	17 -10 A 18 2C6 214 19 94 -91 20 114 114	12 99 -93 13 98 -49 14 -8 16 15 19 13	12 20 13 13 -9 -4 14 45 -12 15 -9 -4	11 465 457 12 167 165 13 80 -82 14 77 78	11 311 312 12 177 -185 13 215 -226 14 137 143	12 48 76 13 182 -178 14 102 -100 15 116 -116	H10, E- 3	5 154 -148 e 114 117 7 63 54 8 67 -69	18 17 -13 19 113 -107 20 23 -11 21 56 -52
16 72 75 18 15 -19 20 118 115 27 72 -P5	A 1019 -1044 10 815 -828 12 185 -15C 14 778 -821	0 461 -444 2 44 -68 4 510 -514	6 340 350 7 249 244 8 71 -67 9 25 20	26 49 62 27 35 -30 28 83 82	21 227 -236 22 187 194 23 -7 0 24 134 129	16 64 66 H- 8, R- 1	14 144 114 17 87 -81 18 83 83 19 57 -47	15 177 173 14 156 -154 17 59 46 18 47 47	15 264 27A 16 2CA -223 17, 152 159 14 17 12	16 41 103	3 47 -18 4 110 108 5 93 -#3 6 114 127	9 44 39 10 257 275 11 212 -228 17 36 -19	H= 3, K= 3 0 42 97
H+ -14. K+ 0 2 36 -49	14 245 -255 18 177 -203 20 257 -274 22 224 -230	6 375 343 8 24 -15 10 208 -188 12 250 -240	10 28 21 11 94 82 12 153 -133 13 311 294	1 50 -41 2 674 674 3 43 -41	H- 1. K- 1 0 139 -133	1 24 -17 2 547 531 3 210 -208 4 182 179	21 177 165 27 -0 -5 23 45 47 24 40 40	20 136 -143 21 160 166 22 22 16 23 134 -134	20 61 -66 21 101 -97 22 -9 5 23 78 76	1 40 42 2 2P1 -2P4 3 153 -152 4 235 233	7 140 191 8 17 -14 9 132 125 10 38 -31 11 362 -360	13 201 -212 14 -10 12 15 97 111 16 204 -223 17 284 -304	1 143 -130 2 112 102 3 406 -411 4 133 144
6 -6 9 6 -8 9 6 0 81 10 249 255 12 376 387	76 156 -155 78 18 -11	No 6. K- C	14 187 -190 15 316 302 16 283 -264 17 121 104	4 174 -181 5 267 -272 6 84 -76 7 380 -336	1 792 878 2 230 211 3 205 -188 4 744 -816	5 74 -44 6 389 396 7 83 -79 8 30 24	25 28 -10 He -11, Ke - 2	24 72 75 25 87 -82 26 67 69 27 46 47	74 RO -40'	5 113 110 e 155 -149 7 68 -57 8 56 91	12 63 -61 13 121 -113 14 105 101 15 135 -130	18 191 195 16 72 -68 20 198 -196 21 26 26	6 50 -50 7 133 -137 8 256 260 9 235 -233
14 242 244 14 245 222 18 176 170 20 53 19	2 1208 1440 4 1224 -143C 6 425 412	2 T1 59 4 34 26 6 147 135 8 49 38	14 148 176 20 85 -68 21 162 168 22 76 67	9 647 627 10 319 -298 11 92 83 12 263 263	6 753 -F17 7 211 -752 8 885 550 9 184 196	10 197 187 11 162 -159 12 -8 15 13 45 -44	> 3A 34 * 4C7 - *SC 4 104 97 * 159 -145	P= -5, E= 2 1 401 -391 7 28 -41	1 24 -79 2 51 88 3 456 -461 4 118 103	10 39 -41 11 14 -10 12 -9 4 13 46 -59	17 171 -159 18 74 -70 19 43 45 20 -9 -1	23 106 -107 24 132 -123 25 83 -80	10 70 77 11 306 -310 12 253 251 13 3C -22
24 101 117 24	10 109 110 12 204 -613 14 247 308 16 264 267	12 35 -22 H- 10. K. C	23 50 96 24 -8 12 25 65 63 26 -7 1 27 119 125	13 144 147 14 386 366 15 470 447 16 47 -47 17 -10 8	10 70 -#8 11 32 32 12 453 461 13 104 109	14 20 -15 15 43 -49 H= 9, K= 1	e 274 213 7 79 -70 # 154 140 9 441 -419	3 *38 -541 4 163 -171 5 540 -661 6 538 523	5 A14 -877 6 339 340 7 278 -246 8 767 -351	14 38 -47 He 9, EP 2	21 152 147 22 122 -112 23 27 -23 24 88 -85	H+ -3, K+ 3 1 264 -244 2 70 81	15 313 -319 16 239 229 17 107 -101 18 203 197
2 234 274 4 1e4 -193 4 -9 -17 8 30 -22	14 163 -169 20 -10 -15 27 131 131 24 242 -241	0 244 -267 2 585 -571 4 265 -252 6 42 30	N= -10, #= 1 1 101 -99	18 122 127 19 274 297 20 28 -30 21 187 183	14 267 268 16 260 264 17 141 145 18 97 -92	0 114 -111 1 142 -139 2 481 480 3 193 186	11 144 -110 12 89 85 13 163 162 14 112 -100	4 53 -48 9 803 -803 10 683 673 11 156 -164	10 94 -98 11 511 -508 17 119 121 13 140 -147	1 121 -121 1 29 -37 2 177 175 3 54 47 4 42 -47	23 40 41 He -9, K- 3 1 265 -259	5 675 -451 4 22 -28 5 377 -350 6 534 532 7 69 -87	20 152 152 He 4, Ke 3
10 -4 1 12 258 -243 14 41 80 14 174 -120 14 -9 2	76 171 116 He -2, se C 2 115 93	10 219 -229 He 11. Ke C	2 67 -62 3 173 -169 4 111 107 5 120 116 6 31 -18	22 155 -166 23 18 18 24 29 -26 25 213 209 26 28 -28	19 37 35 20 124 131 21 181 177 22 123 -112	4 31 34 5 342 344 6 186 172 7 222 213	15 207 -282 16 107 52 17 91 -46 18 253 241	17 25 -17 11 219 -214 14 63 163 15 202 -327	14 81 77 15 2 <sup>6</sup> 7 -766 16 225 232 17 391 -390	5 180 -175 6 P9 EA 7 -9 4 8 41 44	2 163 167 3 154 -152 4 A3 -90 5 21 24	8 241 .246 9 301 -726 10 173 192 11 250 262	0 215 202 1 335 -322 2 372 -382 3 166 -153
20 24 -10 72 114 -172 24 213 -726 26 47 106	4 488 -402 6 413 512 8 271 -287 10 176 180	0 239 -223 2 138 -139 4 33 -28 6 201 -194	7 100 -96 8 30 27 9 97 -93 10 128 131	27 86 87 28 33 29 He -4, Ke 1	24 65 62 H* 2, 8* 1	* 171 160 10 157 159 11 116 112 12 143 -142	21 122 -116 22 129 -127 23 54 -45	17 254 -275 18 266 248 19 133 147 20 33 -31	14 P2 Be 20 15 -18 21 15 -55 22 57 65	10 114 107 11 17 -35 17 106 115	7 133 -128 8 168 -168 9 259 -256 10 425 423	13 -10 -23 14 208 235 15 193 -202 16 22 18	5 29 -29 6 278 -279 7 375 -375 8 185 -179
H= -12, E= 0 2 +3 40 4 157 161	14 311 329 14 58 -54 18 766 496 20 95 100	H- 12. K- C	11 100 102 12 200 -1P3 13 343 -330 14 125 -120	1 93 -85 2 52 -56 3 326 -320	0 1210 1982 1 540 449 2 347 380 3 213 -192	13 -7 -17 H- 10, K- 1	74 39 14 75 107 104 76 59 49	21 144 -152 22 203 211 23 190 -140 24 50 51	21 101 -100	H= 1C, K+ 2 0 52 -48 1 155 -134	11 e9 60 12 352 355 13 23 -12 14 220 213	17 176 -188 18 252 305 19 57 -54 20 114 117	9 159 159 10 102 -96 11 108 -111 12 43 -31
6 318 344 8 196 -173 10 295 246 12 -10 8	22 274 277 24 216 216 26 118 118	2 106 107 4 52 -55 4 351 409	16 53 -47 17 146 141 18 425 -423 19 150 145	<pre>4 L20 11A 6 733 -733 7 170 -L63 8 314 309</pre>	5 458 464 6 187 189 7 221 216 8 60 57	1 60 51 2 78 - 74 3 17 -14 6 130 -123	1 84 -85	25 115 98 26 105 98 27 4C -18	1 368 -176 2 197 -197 3 280 -272	7 167 154 1 146 -119 4 39 -38 4 -9 -6	14 71 74 16 63 -66 17 -9 12 18 211 201	21 143 -140 22 134 141 23 168 162 24 16 17	13 41 41 14 164 -164 15 110 108 16 81 83
14 P3 P4 16 140 -117 19 154 -157 20 271 -246 27 91 -86	-1. E. C 2 -1C 5 4 100 -97 4 1015 -1201	He 13, Ke C 0 56 57 2 -A -17 3 50 66	20 202 -194 21 111 -109 27 100 -102 23 29 -33	9 207 -189 10 122 100 11 95 -80 12 260 265	• •0• -018 10 5• 54 11 23• -244 12 225 228	5 49 -55 6 159 -148 7 133 124 8 161 -150	4 04 01 4 114 114 6 44 -44 7 40 -44	1 297 -124 2 67 -5e 1 1e1 247	5 1+9 164 6 323 -318 7 440 -444 8 689 695	7 23 27 8 98 -91 9 125 -137 10 77 85	20 47 44 21 56 -56 22 63 52 23 145 155	H+ -2, K+ 3	18 199 -190 40 5. 80 3
24 176 -180 26 120 -125 26 -11. 84 C	8 427 455 10 13 -27 12 204 -294 14 245 351	He (4, Ee 9 0 73 82	25 45 -46 26 63 -44 27 16 -13 28 -7 -4	14 400 -475 15 305 -315 16 346 358 17 139 147	14 203 -749 15 138 -142 16 293 301 17 139 173	10 117 -120 11 42 62	9 218 211 10 -10 -4 11 148 149 12 257 -251	5 258 235 6 4CP	10 113 110 11 205 207 12 45 43 13 273 -270	H= 11, K= 2 0 79 -71 1 158 149	24 36 15 25 -7 0 He -R K 1	2 192 -195 3 29 35 4 345 310 5 19 11	0 352 342 1 412 400 2 734 244 3 111 -112
2 97 -84 4 213 -277 6 213 -374 F 201 197	14 221 -730 70 107 -113 77 66 73 74 30 -30	He -14. EF 1 11 21 27 12 123 -160	H= -9, E+ 1 1 250 239 2 170 -102	18 207 -726 19 -10 5 20 126 -133 21 93 -99 22 96 -54	18 84 -84 19 30 -25 20 27 36 21 123 -122	0 110 110 1 297 -282 2 91 80	14 101 -00 14 150 115 16 00 -43 16 25 -10	6 271 -747 10 632 62C 11 461 491 12 153 157	14 2C3 -207 15 217 -227 16 LC# 100 17 146 138	2 42 24 3 216 216 4 81 -74 5 65 61	1 144 191 2 177 -184 3 243 251 4 116 -121	7 77 -75 R 267 -283 9 243 257 10 233 -248	5 97 96 6 -10 2 7 144 149 8 99 102
10 135 -126 17 61 -56 14 46 -68 16 41 -27	26 43 P9 H0 C. K0 0 2 262 247	11 60 -40 14 10 -34 15 53 -73 16 F1 -103	3 361 354 4 146 179 5 136 129 6 225 -218	23 95 03 24 139 -143 25 96 96 26 206 -202	25 15 -11 H+ 3, x+ 1	4 81 90 5 -8 2 6 149 -151 7 -8 -6	14 115 113 16 24 -76 20 59 -59 21 90 87	14 140 187 15 1C7 1C6 14 133 -140 17 55 54	19 126 -124 20 142 136 21 184 -181 22 -7 17	7 100 115 8 21 -24 H= 12, K= 2	6 207 -201 7 341 343 8 352 -349 9 90 90	12 24 31 12 142 152 14 343 -396 15 275 299	10 47 54 11 47 36 12 5C -42 14 64 63
20 205 205 27 171 -1A7 24 54 -54 26 66 61	4 657 727 6 247 263 8 61 -57 10 75 -#2	H+ -15. K+ 1 4 65 -87 -5 -7 -17	a 32 30 a 420 300 10 349 -177 11 43 -11	He -3, Ke 1 1 519 512	1 470 440 2 12# 336 3 956 1001 4 281 -302	9 -7 -10 H= 12, K= 1	21 20 11 24 49 -57 25 164 -147 24 16 10	10 221 -242 20 74 -29 21 32 26 21 32 26	H- 2, K- 2 0 1e0 578 1 514 500	C 61 94 L 168 184 2 162 -157	10 56 50 11 85 -46 12 436 -438 13 114 -122	16 57 -55 17 132 -137 18 33 -13 19 51 -52 20 23 -18	15 53 50 14 109 -98 17 158 153
H= -1C, K= 0 2 +42 -423 4 101 -371	14 241 237 14 314 354 18 95 97 20 252 251	6 16 -19 7 -7 -11 8 -8 13 9 22 -29 10 61 -56	12 63 62 13 58 56 14 232 -220 15 99 101 16 80 -82	2 195 -185 3 613 594 4 116 -111 5 271 -260 6 1081 -1150	5 203 202 6 77 -72 7 216 209 8 434 425	0 78 FO 1 109 106 2 254 -266 3 103 114	H= -4, E= 2 1 172 155 2 202 198	23 77 -77 24 4C 43 25 143 -161 24 141 141	2 CR -91 3 250 25P 4 767 775 5 388 -379	5 145 178 H+ 13, K+ 2	15 223 216 16 44 -39 17 75 -40 14 117 -118	21 54 57 22 25 -16 23 22 -22 24 23 -24	0 163 -165 1 199 -192 2 130 125
4 131 -105 8 205 -203 10 441 -423 17 35 -39 14 537 -530	22 159 -185 24 53 44 He 1. Ke 0	11 -# 73 12 41 50 13 73 77 14 14 -24	17 122 -120 18 46 49 19 188 -182 20 201 197	7 452 454 8 378 367 5 864 818 10 605 -604	10 335 338 11 229 27A 12 149 -154 13 97 -98	5 -7 15 6 54 -65 100 134 X+ 1	3 115 105 4 255 246 5 259 265 8 247 247	1 463 472 2 197 173.	7 117 114 8 274 277 9 244 244 10 273 -265	0 -8 * 1 58 -49 2 69 -91	20 20 -16 21 210 204 22 44 -57 23 17 20	H= -1, K= 3 1 472 457 2 310 275	4 179 -190 5 76 75 6 216 219 7 167 155
14 71 -44 19 451 -459 20 221 -210 22 116 -58	0 171 -144 7 720 -165 4 1229 1418 8 73 -77	16 61 -74 17 72 -40 18 51 44 19 35 -14	22 164 -154 23 51 -52 24 145 141 25 10 -12	12 178 101 13 44 57 14 193 191 15 53 56	15 196 193 16 180 -173 17 63 63 18 -8 9	0 139 -139 1 229 -230 2 108 125 3 104 -131	4 73 77 4 215 704 10 -10 3 11 702 752	1 145 173 4 142 136 5 103 103 6 243 244 7 243 241	11 244 -286 12 247 247 13 446 473 14 175 141 15 184 176	P* -14, E* 1 5 22 -24 6 14 -21 7 106 124	24 47 -47 25 -7 4 He -7. Kr 3	3 340 -351 4 309 317 5 477 490 6 166 134 7 148 159	8 124 -115 4 85 71 10 213 208 11 114 108 12 41 42
24 172 -140 24 71 77 44 -9, 84 0	10 -9 -4 12 404 -392 14 193 186 16 276 280	20 14 -17 21 86 -111 P14, 8- 1	26 110 -106 27 56 -61 28 57 -60	16 14 -14 17 -10 8 18 24 -32 14 107 -142 20 38 36	10 -0 -14 20 -0 0 21 52 47 22 20 -27	4 41 -52 He 14, Ke 1	12 24A -740 13 643 62A 14 238 -239 14 112 106 14 223 -225	* 117 334 6 401 412 10 136 -131 11 447 417	16 163 168 17 131 172 16 75 68 16 166 165	# 126 -145 9 14 19 10 57 -65 11 14 -77	1 206 149 2 27 -27 3 60 53 4 178 179	P 543 583 5 280 288 10 349 -377 11 382 412	13 45 -62 14 91 46 15 113 109 16 12 16
7 20 19 4 73 -47 4 143 -184 8 414 -586	18 102 -44 20 -9 17 22 56 49 24 84 89	1 79 -48 2 #1 -40 3 21 -11 4 16 24	1 46 10 2 453 -499 3 526 -506	21 133 137 22 199 -211 23 97 -105 24 -9 12	H- 4, K- 1 0 673 -596 1 346 336	1 30 -42 H= -15, K= 2	17 181 178 18 203 160 16 240 247 20 28 -17	13 573 615 14 205 -214 15 278 278 16 130 137	21 141 143	17 90 100 14 35 -47 15 118 176 16 56 -47	6 31 -21 7 301 388 # 139 133 9 47 38	13 418 457 14 285 -304 15 -10 12 16 34 -35	H= 7, X= 3 0 194 -197 1 199 199
10 36 -31 12 99 90 14 178 172 16 65 80	** 2. K- C C 250 437 2 410 435	6 220 -204 7 65 -67 8 -P A 9 43 44	5 67 63 6 500 -489 7 65 -65 8 17 -17	24 -7 -10 27 26 24 Mm -2, 84 1	3 313 -303 4 680 -645 5 205 183 4 322 -314	7 108 118 8 64 -86 9 53 63 10 20 20	27 71 -74 27 105 09 24 35 -34 25 144 134	17 132 140 18 57 -46 16 451 485 20 121 -123 21 197 202	1 116 -307 2 497 488 3 313 -298 4 391 354	17 -7 0 18 31 -44 He -13, 5+ 3	10 133 -127 11 401 406 12 221 227 13 177 14 81 -80	17 157 144 18 128 -134 19 127 123 20 45 46 21 26 30	2 11C -1C7 3 66 60 4 339 -336 5 41 -30 6 261 -341
20 395 406 22 254 -211 24 234 -231 26 23 24	e 154 -605 8 713 -745 10 421 -422 12 363 -356	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	10 16 -14 11 241 226 12 4CA -186 13 64 -49	1 372 -360 2 451 -414 3 265 190 4 646 -650	7 487 474 8 7C5 -722 9 274 -274 1C 5P -48 11 41 -27	11 129 154 12 85 -90 13 143 169 14 53 -60 15 76 95	70 113 -107 77 185 189 88 -8, 84 7	27 134 -147 23 71 -72 24 11 24 25 214 706 26 72	5 22e 777 4 143 155 7 165 -16 <sup>4</sup> 8 130 -130	1 57 45 2 110 114 3 147 183 4 69 -75	15 43 48 16 412 -425 17 135 137 14 132 -141	22 168 -199 23 74 69 Me 0. x- 3	7 341 330 8 203 -199 9 43 -40 10 32 -25
2 PC A9	14 127 -121 14 403 -403 18 67 -46 70 318 -319 22 53 -93	15 -8 1 16 100 45 17 158 147 19 116 -128 19 20 53	14 256 -250 13 67 -72 16 28 18 17 302 301 18 316 -315	5 825 -852 6 1106 -1202 7 13 -29 8 760 -810 5 50 -94	12 446 -446 13 153 155 14 143 -130 15 193 101	16 77 -91 17 49 34 18 30 35 19 140 192	1 23A -233 2 113 -10A 1 128 .134 4 RA C1	1 278 -278	10 66 71 11 160 160 12 194 -197 13 117 -191	A 42 44 7 100 96 8 83 -41 9 10 -35	20 -4 2 21 81 70 22 217 -215 23 178 166	1 40 49 2 31 -2 3 33° 374 4 261 279	12 185 -187 13 90 89 14 29 32
4 101 141 4 705 449 8 120 113 70 075 479 12 244 248	0	20 50 50 21 31 -29 22 64 103 23 14 43	1º 124 130 20 97 -97 21 98 99 22 43 45	10 49 54 11 27 -19 12 316 -326 13 455 458	17 87 85 18 33 31 19 102 102 20 215 -214	He -14, En 2 1 64 -90 2 14 21	e 166 -187 7 479 -465 8 48 -46 6 26 -22	7 168 -156 4 10 -45 5 201 207 6 449 -465	14 244 -253 16 38 42 17 148 145 18 134 136	11 106 46 12 25 38 13 65 -62 14 22 -28	25 71 44 26 81 -87 He -6, 84 3	e 74 79 7 15 -14 8 212 -219 9 243 762	C 213 216 1 36 -34 2 29 -30
14 15 27 14 242 257 18 482 502 20 44 43	4 367 597 6 157 155 8 719 -218 10 200 -184	H= -13, K= 1 1 64 -70	24 56 57 25 10 -20 26 56 -46 27 49 45	15 103 102 16 190 -200 17 248 262 18 67 63	H+ 5, K+ 1 0 164 -151	3 36 -46 4 37 43 5 58 -61 6 -8 -12 7 102 -101	10 71 -40 11 61 67 12 136 127 13 42 -34 14 166 -166	7 583 -548 4 433 431 9 44 60 10 320 310 11 27 37	20 47 45 He 5, 84 2	14 14 -127 17 53 50 18 44 -51 19 47 16	1 25 -17 2 175 -180 3 122 119 5 301 112	10 164 172 11 58 -50 12 341 37C 13 82 87 14 15 -39	3 111 130 4 120 110 5 63 57 6 -9 -1
24 104 387 24 104 107 28 104 107 28 27 -26	12 411 -257 14 264 244 16 70 -66 18 44 -86 20 121 -118	2 21 21 3 117 -106 4 81 87 5 120 -174 4 238 237	2# 216 222 H= -7.K+ 1 1 369 -347	19 79 83 20 370 -389 21 144 -146 22 114 112 23 120 118	1 -11 8 2 171 165 3 151 -147 4 187 -181 5 89 80	8 10 <sup>2</sup> -111 9 -8 5 10 24 -32 11 99 -94 12 59 -46	15 149 -150 16 171 177 17 46 40 18 221 -226 19 59 -55	12 303 304 13 77 -77 14 252 -261 15 -8 9	0 425 -423 1 414 847 2 47 51 3 627 605	20 44 -53 21 45 56 44 -12, 84 3	5 48 -41 6 123 -127 7 223 725 8 107 117	15 315 332 16 75 85 17 24 -29 18 128 131	8 155 145 9 14 23 10 15 -14 11 23 -15
7 -7. X. 0 7 391 384 6 990 -876 6 93 -46	77 23 19 H+ 4, 4- C	7 169 -160 6 227 220 9 277 -222 10 46 91	2 398 177 3 104 -99 4 184 -178 5 322 -313 6 403 347	24 140 -135 25 127 127 26 63 -65	6 77 -81 7 420 -407 8 108 103 9 142 -149	13 93 -96 14 -8 -8 15 20 -18 16 21 -14	20 22 -27 21 109 109 22 66 -71 23 29 -11	17 219 213 18 206 -208 19 21 -20 20 -9 4	4 91 -86 6 253 247 7 246 260 5 344 -145	1 44 45 2 44 -42 3 89 -42 4 187 180	10 196 200 11 235 -249 12 276 282 13 73 73	20 60 56 21 137 195 22 86 81 23 55 -56	H- 9. K- 3
# 653 #27 10 254 251 12 288 -278 14 404 185 14 251 -257	2 617 -616 4 765 -353 4 710 -796 8 274 270 10 164 -164	12 2C* 145 13 36 -75 14 46 -82 15 142 -124	7 475 -451 A 278 -265 S 150 -141 10 109 112	1 120 -118 2 534 543 3 317 323	11 95 -94 12 320 -315 13 391 -377 14 120 -112	18 -8 15 19 19 -21 20 -7 10 21 -7 2	25 47 -47 74 -7 -1 71 55 40	22 11 -35 23 71 48 24 47 42 25 28 -23	10 26 24 11 21 22 12 109 -100 13 111 114	6 123 117 7 56 55 9 29 21 9 21 17	15 -10 -74 16 311 323 17 112 -117 18 107 105	No 2, Eo 3 0 485 -467 1 250 205	2 104 -100 3 246 -231 4 41 35 5 48 -68
18 18 -20 20 -10 0 22 58 56 24 310 -112	12 240 726 14 -10 -12 16 15 15 18 137 131	17 179 -172 18 68 -64 19 49 -47 20 107 101	12 34 16 13 415 -403 14 428 411 15 325 -317	5 1149 -1367 6 221 -216 7 536 -576 8 319 -341	16 157 -155 17 93 -79 18 54 -59 19 95 -94	27 -7 1 H+ -13, x= 2 1 42 41	1 445 475 1 445 475 2 377 -376 3 58 58	H1. K- 2 1 1001 1047 2 143 -117	14 44 31 15 177 169 16 144 -111 17 35 -24	10 - 4 A	19 73 -77 20 99 94 21 149 150 22 20 17 23 123 -124	2 343 325 3 121 -118 4 517 -521 5 64 -58	e 40 -48 7 35 -25 8 173 161 9 103 -101
54 135 125 H6. K- 0	20 62 62 H= 1, K= 0 0 187 -150	21 e4 -6e 22 -7 -1 23 74 -77 24 107 113 25 16 18	14 166 -149 17 193 -190 18 259 274 16 87 -96 20 55 58	• 414 -411 10 225 740 11 500 -500 12 223 -224 13 371 -379	H+ 6, K= 1 C 302 247	7 172 -168 3 40 -42 4 18 -20 5 191 189 6 337 -335	+ 126 -104 5 137 132 6 451 -432 7 331 324 8 36 -23	3 505 520 4 105 -105 5 416 421 4 103 -251 7 103	10 -7 1 H0 A, K0 2	15 34 -36 16 244 727 17 149 -136 18 53 43	24 103 97 25 18 -14 H+ -5, 8+ 3	7 341 745 8 320 -341 9 174 -177 10 143 -139	- 10, z- 3 0 54 -44
2 417 474 4 552 943 4 905 892 8 118 174 10 44 -77	2 671 -654 4 386 784 4 377 -372 8 474 430 10 395 -391	H+ -12, K- 1	21 73 -41 72 104 -102 23 23 -21 24 65 -00	14 40# 423 15 257 -258 16 103 -114 17 162 -200	2 426 409 3 -9 8 4 276 269 5 304 292	7 87 -87 8 74 -72 9 194 -180 10 95 -89	0 40 -40 10 323 -300 11 60 -66 12 111 -105	4 445 -448 4 134 14C 10 39 -34 11 171 147	1 256 244 2 247 23C 3 -9 4 4 76 -75	20 150 148 21 14 1# 22 58 40 23 126 -143	1 106 104 2 41e -414 3 264 -774 4 151 -147	12 457 -478 13 126 127 14 184 -198 15 169 -188	2 197 -182 3 140 -158 4 117 -115 5 107 -97
12 243 24C 14 241 -277 16 45 65 18 114 320	17 140 -171 14 121 -125 14 257 247 14 212 -723	3 1C8 102 4 145 140 5 176 125 6 203 201	24 28 -13 27 63 -57 28 63 -64	19 95 -98 20 95 -97 21 66 -+7 27 -9 -3	7 296 297 8 98 91 9 -10 11 10 81 74	11 110 -101 12 77 -73 13 22 -14 14 157 -151 15 239 -223	15 120 116 14 413 -410 15 405 -301 14 23 -14 17 103 -101	17 218 -250 18 179 194 14 23 -31 15 26 -27 16 146 -158	5 247 266 6 133 -129 7 159 155 8 149 -142 9 53 -54	H+ -11, X+ 1 1 30 26 2 190 -184	5 91 91 8.245 -257 7 79 -73 8 151 -142 9 255 -245	16 36 -37 17 108 -106 18 84 76 19 30 -30 20 19 -14	6 54 -59 7 145 -147 8 32 -41
76 75 -47 27 81 -44 24 58 47 26 246 -250 28 196 -194	20 75 43	7 -10 -4 # 141 125 9 141 131 10 7#1 365 11 231 225	H -6. K 1 1 110 -117 2 576 546 3 158 -159	23 61 -60 24 134 -134 25 114 -109 26 102 99	11 109 -185 12 17C 157 13 16 19 14 120 -111	16 123 115 17 188 -176 18 18 -10 19 38 -35 20 97 91	10 07 -02 10 136 -148 20 72 01 21 181 -169 22 100 -201	17 230 -275 18 103 -116 19 166 165 20 217 -223 21 50 -00	10 114 -114 11 239 226 12 68 -76 13 -8 1	3 -8 -1 4 153 -147 5 117 113 6 305 -243 7 35 -117	10 215 -216 11 69 61 12 206 -191 13 22 21	21 151 -141 22 39 33 #* 2. 1* 1	55 60 7 209 212
H4 -5, K4 0 2 405 -397	2 368 366 4 250 237 6 672 461 8 458 713	12 00 05 13 143 -141 14 285 267 15 -0 -6	4 416 385 5 20 -13 6 465 451 7 283 268	H+ 0. K+ 1 1 A+ -82 2 100 -93	16 253 234 17 -8 7 18 33 37	21 236 -235 22 78 -80 23 87 -93 24 22 36	21 221 -270 24 71 62 25 37 -35 26 71 -65	27 97 -98 23 213 -213 24 31 24 25 -7 -7	15 17 -70 16 16 -22 17 127 138	8 207 -196 9 355 -339 10 68 -58 11 295 -273	15 242 -244 16 319 -346 17 138 -165 18 24 19	D 212 206 1 318 -331 2 276 270 3 394 374	4 17 -12 5 105 -114 6 80 97
A 524 -535 E 837 P40	17 400 472 14 71 70	17 146 178	9 457 435 10 1086 1097	4 696 773 5 641 687	0 % -93	HH -12, X- 7	)7 69 -87 H1 -8, 84 }	H. B. K. 2	*** 7. E* 2 0 %* -75	17 107 100 13 114 -106 14 140 -128	19 746 -267 20 105 109 21 141 -141	4 149 159 5 272 -271 6 313 312	H== 17, K+= 3 0 27 35

Table 5 (cont.)

<pre>cut contact = """" use state of the """""""""""""""""""""""""""""""""""</pre>
1 111111111111111111111111111111111111
۲۵۰٬۰۰۰ • ۲ ۲۵۵۵٬۵۵۵٬۵۵٬۰۰۰ • ۲ ۲۵۵۵٬۵۵۵٬۵۶٬۰۰۰ • ۲ ۲۵۵۵٬۵۵۵٬۵۶٬۰۰۰ • ۲ ۲۵۶۶٬۵۵۵٬۵۰٬۰۰۰ • ۲ ۲۵۶۶٬۵۶٬۵۶٬۰۰۰ • ۲ ۲۰۰٬۶۶٬۶۶٬۶۶٬۶۶٬۶۶٬۶۶٬۶۶٬۶۶٬۶۶٬۶۶٬۶۶٬۶۶٬۶
<ul> <li>CUTAL CONTRACTOR CON</li></ul>
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Table 6. Bond lengths (Å) and angles (°)

	Molecule A	Molecule B		Molecule A	Molecule B
S(1) - C(1)	1.721 (3)	1.722 (3)	C(1)-S(1)-C(4)	92.1 (2)	91.6 (2)
C(1) - C(2)	1.387 (4)	1.367 (5)	S(1) - C(1) - C(2)	$111 \cdot 1$ (2)	111.1(2)
C(2) - C(3)	1.425(5)	1.413 (5)	S(1) - C(1) - C(5)	121.8(2)	122.7(2)
C(3) - C(4)	1.348(6)	1.346(5)	C(2) - C(1) - C(5)	127.0 (3)	126.2 (3)
C(4) - S(1)	1.707(4)	1.706 (4)	C(1) - C(2) - C(3)	111.4 (3)	$112 \cdot 2(3)$
C(1) = C(5)	1.433 (4)	1.439 (4)	C(2) - C(3) - C(4)	113.4 (4)	113.1 (3)
C(5) - N(1)	1.282(4)	1.290 (4)	C(3) - C(4) - S(1)	112.0 (3)	112.0 (3)
N(1) - N(2)	1.369 (4)	1.380 (4)	C(1) - C(5) - N(1)	121.0 (3)	120.7 (3)
N(2) - C(6)	1.343 (4)	1.346 (4)	C(5) - N(1) - N(2)	115.8 (3)	114.5 (2)
C(6) - S(2)	1.698(3)	1.691(3)	N(1) - N(2) - C(6)	119.4 (3)	119.4 (2)
C(6) - N(3)	1.306 (4)	1.327(4)	N(2)-C(6)-S(2)	118.8 (2)	119.2 (2)
N(2) - H(1)	0.92(5)	0.92 (4)	N(2)-C(6)-N(3)	118.1 (3)	117.9 (2)
N(3) - H(2)	0.88(4)	0.86(4)	N(3)-C(6)-S(2)	123.0 (2)	122.9 (2)
N(3) - H(3)	0.94(4)	0.93 (5)	N(1)-N(2)-H(1)	119 (3)	123 (3)
C(2) - H(4)	0.89 (4)	1.01 (4)	C(6) - N(2) - H(1)	121 (3)	118 (3)
C(3) - H(5)	0.95 (4)	1.00 (5)	C(6) - N(3) - H(2)	122 (3)	119 (3)
C(4) - H(6)	1.05 (4)	0.91 (4)	C(6) - N(3) - H(3)	117 (3)	119 (3)
C(5) - H(7)	0.94 (4)	1.00 (4)	H(2)-N(3)-H(3)	120 (4)	117 (4)
-(-)(-)			C(1) - C(2) - H(4)	121 (3)	121 (3)
			C(3) - C(2) - H(4)	127 (3)	126 (3)
			C(2) - C(3) - H(5)	124 (3)	123 (3)
			C(4) - C(3) - H(5)	122 (3)	124 (3)
			C(3) - C(4) - H(6)	130 (3)	128 (3)
				440 (0)	100 (0)

S(1) - C(4) - H(6)

C(1)-C(5)-H(7)N(1)-C(5)-H(7)

C(6)-N(2) bond, which has a large amount of doublebond character, must take place if metal complexes are formed.

Although each 2FTTSC molecule has three hydrogen atoms capable of forming hydrogen bonds, only two form intermolecular hydrogen bonds. The pertinent distances and angles for the contacts involving all three hydrogen atoms are tabulated in Table 9. The intermolecular hydrogen bonds are shown as dotted lines in Fig. 3, which illustrates the molecular packing. The two N···S distances of 3.360 and 3.348 Å are close to the mean N···S distance for

118 (3)

115 (3)

124 (3)

128 (3) 120 (3)

117 (3)

122 (3)



Fig.1. The atomic numbering, average bond distances and average bond angles in 2-formylthiophene thiosemicarbazone.

N-H...S hydrogen bonds quoted by Srinivasan & Chacko (1967); the other two  $N \cdots S$  distances of 3.484 and 3.489 Å are longer. The two shorter and presumably stronger N-H····S bonds involve hydrogen atoms from the A molecule. A consideration of various least-squares planes through the two molecules which are given in Table 7 indicates that the A molecule is much less planar than the B molecule. Apparently the A molecule is twisted as a result of the two stronger N-H $\cdots$ S hydrogen bonds. The shortening of the C(6)-N(3) bond distance in the A molecule may be a result of the N-H...S hydrogen bonds.

The molecular packing can be viewed as chains of dimer-like molecules held together by two N-H $\cdots$ S hydrogen bonds. There are only five intermolecular contacts less than 3.5 Å. These are 3.355 Å between C(B6) and N(B1) (in molecule 1-x, 1-y, -z), 3.439 Å between N(B3) and N(B2) (in molecule 1-x, 1-y, -z), 3.454 Å between C(B3) and N(A3) (in molecule

 $-x, y-\frac{1}{2}, \frac{1}{2}-z$ , 3.454 Å between C(A3) and C(A5)  $(-x, \frac{1}{2}+y, \frac{1}{2}-z)$  and 3.475 Å between C(B2) and N(A3) (in molecule -x,  $y-\frac{1}{2}$ ,  $\frac{1}{2}-z$ ). Therefore, all the contacts between the chains are normal van der Waals contacts.

We wish to thank Fred French and Erwin Blanz Jr for the sample of 2-formylthiophene thiosemicarbazone



Fig.2. An ORTEP drawing showing the conformation and thermal ellipsoids in the two independent molecules.

Table	7.	Least-squares	planes
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Planes and deviations	from plane ( $\dot{A} \times 10^3$ )
II	III

	I		]	II		111		IV	
	A	В	· A	В	A	В	A	В	
S(1)	1*	0*			529	22	216*	3*	
S(2)	548	406	+1*	3*	132	30	362*	100*	
N(1)	- 14	126			0*	0*	- 63*	-11*	
N(2)	212	193	+1*	3*	0*	0*	51*	-4*	
N(3)	-537	150	+1*	3*	-415	-173	- 392*	- 53*	
$\mathbf{C}(1)$	1*	1*			150	45	- 62*	-47*	
$\mathbf{C}(2)$	1*	3*			90	151	-169*	-9*	
$\mathbf{C}(3)$	Ō*	- 3*			363	203	-15*	45*	
C(4)	0*	2*			613	150	195*	62*	
C	69	32			0*	0*	-95*	78*	
Č(6)	29	228	-2*	-9*	- 119	-66	26*	-3*	
			Parame	eters of the	plane†				
<i>4</i> × 104	7618	2904	4055	2584	6044	2189	6455	2674	
$R \times 10^4$	4267	4397	5722	3575	5167	4342	5421	4092	
C × 104	-4534	8499	-7129	8975	6065	8738	5380	87 <b>2</b> 4	
D(Å)	- 6.007	4.738	-6.443	4.438	- 6.415	4.458	- 5.931	4.686	

\* Deviations of atoms which were used to define the plane.

† Equation of the plane in the form: Deviation  $(\hat{A}) = AX + BY + CZ + D$  with X, Y, Z the coordinates of the atom in  $\hat{A}$  with respect to a, b, c\*.

	C(1)-C(5)	C(5)-N(1)	N(1)-N(2)	N(2)-C(6)	C(6)-S	C(6)-N(3)	Reference
2-Formylthiophene	1·433 (4)	1·282 (4)	1·369 (4)	1·343 (4)	1·698 (3)	1·306 (4)	1
thiosemicarbazone	1·439 (4)	1·290 (4)	1·380 (3)	1·346 (4)	1·691 (3)	1·327 (4)	
4-Formylpyridine	1·467 (3)	1·275 (3)	1·365 (3)	1·354 (3)	1·678 (2)	1·329 (3)	2
thiosemicarbazone	1·447 (6)	1·285 (6)	1·371 (6)	1·351 (6)	1·692 (4)	1·310 (6)	
2-Keto-3-ethoxybutyral-	1·447	1·294	1·371	1·359	1·687	1·305	3
dehyde bis(thiosemi-	1·445	1·284	1·379	1·351	1·689	1·314	
carbazone)	1·445	1·290	1·365	1·352	1·682	1·311	
Bis(isoquinoline-1- carboxaldehyde thio- semicarbazonato) nic- kel(II) monohydrate thiosemicarbazide	1·446 (12) 1·457	1·295 (9) 1·279	1·356 (8) 1·357 1·399 (6)	1·328 (9) 1·331 1·337 (6)	1·735 (7) 1·719 1·685 (5)	1·350 (9) 1·345 1·316 (6)	4 5
References: (1) Present (4) Mathe	t study; w & Palenik (	1969);	(2) Rest (5) Dom	ivo & Palenik (1 iino, Gasparri, N	970); ( Nardelli & Sgara	3) Gabe <i>et al.</i> ( abotto (1969).	(1969);

Table 8.	Comparison	of	' bond	distances	(Å)	of	`various i	hiosemicarl	bazones
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Table 9. Hydrogen bonds and close contacts

Bond			D-H	$\mathbf{H} \cdots \mathbf{A}$	$D \cdots A$	$D-H\cdots A$ angle
$D-\mathrm{H}\cdots A^*$	Position	of A	(Å)	(Å)	(Å)	(°)
$N(A2)-H(A1)\cdots S(B2)$	$1 - x  v - \frac{1}{2}$	$\frac{1}{2}-z$	0.92	2.45	3.348 (3)	165
$N(B2)-H(B1)\cdots S(B2)$	1-x $2-y$	z - z	0.92	2.61	3.484 (3)	159
$N(A3)-H(A2)\cdots S(A2)$	-x $2-y$	1-z	0.88	2.49	3.360 (3)	174
$N(B3)-H(B3)\cdots S(A2)$	$1-x$ $y-\frac{1}{2}$	$\frac{1}{2}-z$	0.93	2.55	3.489 (3)	175
B. Close contacts						
$N(B3)-H(B2)\cdots N(B1)$	x v	, z	0.86	2.29	2.644 (4)	104
$N(A3)-H(A3)\cdots N(A1)$	x v	, Z	0.94	2.26	2.639 (4)	103
$N(B3)-H(B2)\cdots S(B2)$	x  y = 1	. <i>z</i>	0.86	3.10	3.560 (3)	115
$C(B2) - H(B4) \cdots S(A2)$	$x  \frac{3}{2} - y$	$z - \frac{1}{2}$	1.01	3.05	3.562 (3)	113



Fig. 3. A projection of the unit cell on the (010) plane. The hydrogen bonds are shown as dotted lines.

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## The Structure of Manganese Dichloride Tetrahydrate: A Neutron-Diffraction Study\*

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The hydrogen atoms in the room-temperature form of  $MnCl_2.4H_2O$  have been located by neutrondiffraction analysis. The data provide independent confirmation and refinement of the hydrogen positions and hydrogen-bonding scheme deduced by Baur by consideration of the electrostatic energy of the crystal, utilizing the results of the X-ray analysis of Zalkin and co-workers. The H–O–H angles in the 4 different water molecules are 104.3, 106.1, 111.4, and 112.4° (standard deviation about 0.3° for each). One hydrogen bond is clearly bifurcated, as deduced by Baur; in addition, there is another atomic configuration which may be regarded as a very unevenly bifurcated hydrogen bond. Among the remaining hydrogen bonds there are significantly different from those from the work of Zalkin *et al.*; however, some of the thermal parameters are significantly different. In the least-squares refinement scattering factors (relative to the factor for H) for Mn, O, and Cl were obtained which are slightly different from those previously tabulated.

#### Introduction

Neutron-diffraction analysis of the room-temperature ( $\alpha$ ) form of manganese dichloride tetrahydrate (MnCl<sub>2</sub>.4H<sub>2</sub>O) was undertaken to locate the hydrogen atoms as accurately as possible. Reliable hydrogen coordinates were required both for establishing the pattern of hydrogen bonding and for possible use in connection with nuclear magnetic resonance (n.m.r.) studies of the substance in its antiferromagnetic state.

The heavy-atom structure of the  $\alpha$  form of manganous chloride tetrahydrate was determined precisely in an X-ray analysis by Zalkin, Forrester & Templeton (1964), and a set of approximate coordinates for the hydrogen atoms was obtained in the final stages of the analysis. A previous attempt at neutron-diffraction analysis of  $MnCl_2.4H_2O$  was reported briefly (Gardner, 1960), but final results have not been published. An n.m.r. study of the compound at room temperature (El Saffar, 1965) did not furnish proton-proton vectors; the spectrum is unusual, there being only a single bell-shaped peak with a width of about 12 gauss and no dipole-dipole splitting.

Because of an error in the use of a computer program, Zalkin *et al.* did not give a complete description of the hydrogen bonding. Baur (1965*a*) showed, however, that all of their eight experimental positions for the hydrogen atoms except the position for H(32) fit into a reasonable hydrogen bonding scheme. Baur also calculated the hydrogen positions of least electrostatic energy consistent with the known heavy-atom positions and with assumed values for the H–O–H angle and the O–H bond length, using a procedure with which he had previously been successful in predicting hydrogen positions in close agreement with those from neutron diffraction (Baur, 1965*b*). For atom H(32) a new position 0.73 Å from the X-ray position was

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