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The Crystal Structures of the Isostructural Compounds Hydrazinium Fluoroborate and Hydrazinium Perchlorate*

By J. W. Conant† and R. B. Roof, Jr

University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87544, *USA*

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Crystals of hydrazinium perchlorate (HPC) and hydrazinium fluoroborate (HFB) are isostrucutral. They are monoclinic, space group $C2/c$, with 8 formula units per cell. The unit-cell dimensions for HPC are: $a=14{\cdot}412\pm7$, $b=5{\cdot}389\pm5$, $c=12{\cdot}797\pm3$ Å, $\beta=113{\cdot}09\pm0{\cdot}05°$; and for HFB are: $a=14{\cdot}006\pm8$, $b=5{\cdot}316\pm4$, $c=12{\cdot}387\pm5$ Å, $\beta=112{\cdot}87\pm0{\cdot}05°$. Three-dimensional intensity measurements were made with a single-crystal orienter and Mo $K\alpha$ radiation by the stationary-crystal, stationary-counter technique with balanced Zr–Y filters. The HFB structure was solved by the symbolic addition method followed by a full-matrix least-squares refinement. The final HFB positions were used as input parameters for the HPC structure and were refined by least-squares. The R index for HPC is 0·057 for 649 observed reflections, and for HFB is 0·091 for 233 observed reflections. In the perchlorate tetrahedra the Cl–O distances range from 1·414 to 1·435 Å and the O–Cl–O angles vary from 106·0 to 111·9°. In the fluoroborate tetrahedra the B–F distances range from 1·339 to 1·379 Å and the F–B–F angles vary from 106·5 to 111·9°. The hydrogen atoms were not clearly resolved in difference Fourier syntheses of either structure, but reasonable positions were obtained by a least-squares procedure which constrained the geometry of the hydrazinium ion.

Introduction

The structure determination of hydrazinium perchlorate (HPC) was begun some years ago at the Aerojet-General Corporation as part of a study of compounds of interest in the missile propellant industry. The purpose of determining the structures of HPC and hydrazinium perchlorate hemihydrate (HPCHH) (Conant, Corrigan & Hoogsteen, 1963; Liminga, 1967), was to provide insight into the dehydration of HPCHH and its transformation to HPC, and to investigate the hydrogen bonding system. Other investigations (Carelton & Lewis, 1966) have suggested that the dehydration reaction occurs in two steps: dissolution followed by recrystallization. But when a single crystal of HPCHH was viewed microscopically on a hot-stage, the crystal was observed to crumble into tiny HPC single crystals as the water molecules diffused out of their columns in the crystal of HPCHH.

Experimental

HFB crystals were produced by neutralizing a solution of fluoroboric acid with aqueous hydrazine. The compound was recrystallized from 2-propanol, and needles elongated along **b** and having cleavage normal to **b** were obtained. All HFB data were taken on a crystal cut to a cube about 0·1 mm on an edge.

HPC crystals were produced by neutralization of aqueous solutions of hydrazine and perchloric acid and recrystallization from ethanol. The crystals convert to hydrazine perchlorate hemihydrate (HPCHH) in relative humidities above 20 per cent at room temperature so they must be handled in a dry atmosphere. All HPC data were taken on a crystal $0{\cdot}2\times0{\cdot}2\times0{\cdot}3$ mm in size sealed in a thin-walled glass capillary.

The lattice constants were obtained by least-squares analysis of 21 reflections for HFB and 25 reflections for HPC measured with Mo $K\alpha_1$ ($\lambda=0{\cdot}70926$ Å) radiation. A single-crystal orienter was used on a General Electric Co. XRD-5 spectrogoniometer. The values found are, for HFB: $a=14{\cdot}006\pm8$, $b=5{\cdot}316\pm4$, $c=12{\cdot}387\pm5$ Å, $\beta=112{\cdot}87\pm0{\cdot}05°$; and for HPC: $a=14{\cdot}412\pm7$, $b=5{\cdot}389\pm5$, $c=12{\cdot}797\pm3$ Å, $\beta=113{\cdot}09\pm0{\cdot}05°$. The calculated densities with $Z=8$ are 1·859 for HFB and 1·910 g.cm^{-3} for HPC. Systematic extinctions hkl with $h+k=2n+1$ and $h0l$ with $l=2n+1$ indicate space group ($C2/c$ or Cc). As shown below, the structure can be described satisfactorily in space group $C2/c$. Intensity measurements were made with the single-crystal orienter and Mo $K\alpha$ radiation by the stationary-crystal, stationary-counter technique with balanced Zr–Y filters. Absorption corrections were made by comparing intensities of the reflections from planes normal to the rotation axis at $\chi=90°$ as functions of 2θ and φ. A 2θ-dependent background was estimated by an off-spot balanced filter count. The HFB crystal was mounted on the [100] reciprocal axis and the hemisphere of reflections with $2\theta\leq40°$ was measured, yielding 392 independent reflections. The HPC crystal was mounted on the [010] reciprocal axis and the hemisphere of reflections with $2\theta\leq50°$ was measured, yielding 802 independent reflections. In general, $F(hkl)$ was measured twice on each structure. According to the criterion ($I-$background) $\geq3{\cdot}0$

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† J. W. Conant is an Industrial Staff Member at LASL from the Aerojet Nuclear Systems Company, P. O. Box 13070 Sacramento, California 95813.

$(I+\text{background})^{1/2}$, 233 reflections for HFB and 649 reflections for HPC were observed to be greater than zero. The quantity $R_F=\sum 2(\|F_1|-|F_2\|)/\sum(F_1+F_2)$, an estimate of the average agreement between equivalent reflections F_1 and F_2 is 0·038 for HFB and 0·023 for HPC.

Determination and refinement of the structure

Attempts to solve the HFB structure, based on the two-dimensional model of Conant, Corrigan & Sparks (1964), did not succeed. It was later discovered that the two-dimensional projection must be shifted by $0,0,-\frac{1}{4}$ to conform with the three-dimensional solution.

Normalized HFB structure factors, E, were calculated and sorted into classes through use of codes furnished by Stewart (1964). The statistical averages and the distributions of the reflections indicated that the structure contains a center of symmetry, hence space group $C2/c$ was selected. A code originally written by Bednowitz (1965) and modified by Cady (1967) was used to determine the signs of 48 reflections in terms of the symbols $+$, $-$, A, B, C. Since A, B, C may have $+$ or $-$ values, eight E maps are possible. Only one of these ($A=+$, $B=-$, $C=-$) made any sense with regard to the expected tetrahedral arrangement of F atoms surrounding a B atom. (Later structure factor calculations revealed that the signs of the 48 E values determined by the symbolic addition procedure were all correct.) Atomic positions from this map were subjected to full-matrix least-squares refinement using anisotropic temperature parameters. The quantity minimized was $\sum(|F_o|-|F_c^*|)^2$ where

$$F_c^*=K|F_c|\left\{1+g\left[\frac{2(1+\cos^4 2\theta)}{(1+\cos^2 2\theta)^2}\right]\text{Lp}\,.\,F_c^2\right\}^{-1/2},$$

K is a scale factor, F_c is the usual calculated structure factor, g is an extinction parameter (Zachariasen, 1963; Larson, 1967), and Lp is the Lorentz and polarization factor. Scattering factors for H atoms were taken from Stewart, Davidson & Simpson (1965) and for all other atoms from Cromer & Mann (1968). Unit weights were used on the refinement as they resulted in the lowest R values and the narrowest spread of chemically equivalent interatomic distances. The refined parameters for HFB were used as starting parameters for full-matrix least-squares refinement of the HPC structure. After several cycles of refinement, with unobserved reflections omitted, $R=\sum|\Delta F|/\sum|F_o|$, was 0·106 for HFB and 0·076 for HPC.

While the structure must be extensively hydrogen-bonded, the current data are not sufficiently precise for the hydrogen atoms to be clearly resolved in the difference electron-density maps of either structure. The Los Alamos least-squares program has recently been modified to include constraints on interatomic distances (Larson, 1969), using the procedure suggested by Waser (1963). The hydrogen atoms were located by utilizing additional observational equations of the type

$$D_{ij}-d_{ij}=\frac{\partial d_{ij}}{\partial x_i}\Delta x_i+\frac{\partial d_{ij}}{\partial x_j}\Delta x_j$$

Table 1. *Final least-squares parameters*

(*a*) Hydrazinium perchlorate

	x	y	z	$\beta_{11}\times 10^4$	$\beta_{22}\times 10^4$	$\beta_{33}\times 10^4$	$\beta_{12}\times 10^4$	$\beta_{13}\times 10^4$	$\beta_{23}\times 10^4$
Cl	0·1067 ± 1	0·0772 ± 4	0·4231 ± 2	33 ± 1	210 ± 7	39 ± 2	−17 ± 5	18 ± 2	−5 ± 6
O(1)	0·1515 ± 6	0·0678 ± 14	0·3415 ± 6	100 ± 6	408 ± 31	102 ± 7	−64 ± 25	155 ± 11	−106 ± 26
O(2)	0·1783 ± 6	0·0348 ± 17	0·5347 ± 6	86 ± 6	660 ± 46	69 ± 6	−103 ± 28	−54 ± 10	230 ± 28
O(3)	0·0663 ± 7	0·3211 ± 15	0·4218 ± 8	97 ± 6	357 ± 32	151 ± 10	175 ± 25	149 ± 13	68 ± 28
O(4)	0·0293 ± 6	−0·1031 ± 18	0·3987 ± 7	81 ± 3	702 ± 47	107 ± 8	−337 ± 30	90 ± 11	−209 ± 33
N(1)	0·1556 ± 5	0·3982 ± 13	0·1522 ± 6	37 ± 4	247 ± 27	52 ± 5	−2 ± 18	28 ± 8	−5 ± 21
N(2)	0·1599 ± 5	0·5904 ± 13	0·2344 ± 5	49 ± 4	199 ± 25	48 ± 5	28 ± 20	22 ± 7	8 ± 21
H(1)	0·0909 ± 26	0·3042 ± 110	0·1313 ± 46	$B=4\cdot0$ Å^2					
H(2)	0·1574 ± 44	0·4772 ± 32	0·0820 ± 20						
H(3)	0·2137 ± 32	0·2807 ± 100	0·1844 ± 47						
H(4)	0·0995 ± 29	0·7012 ± 77	0·2020 ± 24						
H(5)	0·1607 ± 52	0·5119 ± 31	0·3058 ± 22						

$g=3\cdot02\pm21\times10^{-6}$

(*b*) Hydrazinium fluoroborate

	x	y	z	$\beta_{11}\times 10^4$	$\beta_{22}\times 10^4$	$\beta_{33}\times 10^4$	$\beta_{12}\times 10^4$	$\beta_{13}\times 10^4$	$\beta_{23}\times 10^4$
B	0·1072 ± 24	0·0721 ± 58	0·4240 ± 23	62 ± 21	392 ± 159	46 ± 29	−6 ± 109	80 ± 48	10 ± 111
F(1)	0·1465 ± 11	0·0763 ± 24	0·337 ± 12	139 ± 17	406 ± 66	127 ± 17	−83 ± 55	204 ± 28	−67 ± 60
F(2)	0·1864 ± 12	0·0246 ± 32	0·5237 ± 12	111 ± 13	840 ± 104	102 ± 15	−101 ± 58	−36 ± 25	306 ± 68
F(3)	0·0654 ± 13	0·3029 ± 27	0·4246 ± 13	167 ± 18	397 ± 71	130 ± 18	224 ± 60	169 ± 27	5 ± 57
F(4)	0·0346 ± 12	−0·1075 ± 31	0·3997 ± 11	132 ± 16	814 ± 96	92 ± 15	−466 ± 70	139 ± 26	−195 ± 64
N(1)	0·1554 ± 13	0·3915 ± 30	0·1518 ± 13	69 ± 15	239 ± 73	31 ± 15	35 ± 58	45 ± 24	12 ± 65
N(2)	0·1581 ± 12	0·5901 ± 34	0·2302 ± 12	89 ± 17	277 ± 82	17 ± 15	95 ± 62	78 ± 25	62 ± 64
H(1)	0·0861 ± 47	0·3063 ± 231	0·1256 ± 94	$B=4\cdot0$ Å^2					
H(2)	0·1676 ± 91	0·4517 ± 53	0·0814 ± 45						
H(3)	0·2115 ± 68	0·2703 ± 202	0·1975 ± 86						
H(4)	0·1056 ± 72	0·7242 ± 121	0·1919 ± 35						
H(5)	0·1495 ± 101	0·5289 ± 52	0·3022 ± 54						

$$+\frac{\partial d_{ij}}{\partial y_i}\Delta y_i+\frac{\partial d_{ij}}{\partial y_j}\Delta y_j$$
$$+\frac{\partial d_{ij}}{\partial z_i}\Delta z_i+\frac{\partial d_{ij}}{\partial z_j}\Delta z_j\,,$$

where d_{ij} is the observed distance and D_{ij} is the 'correct' distance. These additional observation equations were included in the formation of the normal equations. By heavily weighting these equations, the difference between the observed distance and the 'correct' distance may be made arbitrarily small. The D_{ij} were set at the following values: bonded N–H = 1·0, non-bonded N–H within the same hydrazine group = 2·033, and H–H = 1·633 Å. These D_{ij} were chosen so as to constrain the hydrogens atoms to lie in a torus 1·886 Å in diameter in a plane perpendicular to the N–N bond and 0·333 Å above the nitrogen atom. An isotropic thermal factor of 4·00 Å^2 was applied to the hydrogen atoms and was held constant.

Table 2. *Observed and calculated structure factors*

The column headings are l, $10F_o/K$, $10F_c^*/K$

(*a*) Hydrazinium perchlorate

H= 0	K= 0	
2	-36	684
4	778	761
6	758	744
8	342	363
10	112	147
12	360	353
H= 0	K= 2	
0	994	1027
1	239	245
2	213	227
3	313	298
4	70	61
5	374	373
6	123	107
7	132	126
8	84	86
9	253	262
10	70	91
11	228	234
12	121	120
13	-51	30
H= 0	K= 4	
0	424	419
1	404	389
2	64	48
3	372	359
4	154	140
5	308	306
6	211	200
7	136	146
8	85	75
9	281	284
10	-51	40
H= 0	K= 6	
0	335	356
1	-54	44
2	-50	19
3	88	68
4	70	80
H= 1	K= 1	
-14	-52	30
-13	62	71
-12	363	390
-11	172	154
-10	379	374
-9	217	208
-8	54	54
-7	259	277
-6	109	137
-5	91	103
-4	219	248
-3	757	745
-2	245	240
-1	725	699
0	852	843
1	114	115
2	1443	1263
3	445	439
4	635	594
5	118	128
6	536	554
7	385	383
8	473	490
9	128	120
10	158	168
11	178	176
12	-51	58
13	80	84
H= 1	K= 3	
-12	-52	54
-11	218	215
-10	-47	37
-9	326	317
-8	-46	67
-7	295	277
-6	-44	41
-5	131	116
-4	136	140
-3	426	424
-2	105	99
-1	598	603
0	377	377
1	241	270
2	125	138
3	339	328
4	-40	20
5	126	133
6	83	97
7	442	448
8	109	109
9	176	164
10	116	122
11	262	258
H= 1	K= 5	
-9	166	170
-8	111	110
-7	122	115
-6	256	259
-5	-48	21
-4	210	216
-3	148	132
-2	76	63
-1	255	241
0	232	236
1	90	104
2	450	440
H= 1	K= 5	
3	191	169
4	65	70
5	118	118
6	152	160
7	70	67
8	190	200
H= 2	K= 0	
-14	-49	18
-12	166	154
-10	898	893
-8	381	372
-6	541	546
-4	878	1289
-2	566	550
0	180	188
2	1122	1135
4	322	339
6	614	602
8	595	558
10	381	381
12	-46	20
H= 2	K= 2	
-13	160	171
-12	90	101
-11	88	78
-10	346	352
-9	382	392
-8	128	131
-7	198	163
-6	-40	42
-5	267	280
-4	190	127
-3	372	361
-2	416	414
-1	453	467
0	356	352
1	752	866
2	169	185
3	173	180
4	72	76
5	209	240
6	156	166
7	259	270
8	190	182
9	308	304
10	202	203
11	170	179
12	-50	40
H= 2	K= 4	
-11	76	79
-10	202	172
-9	323	328
-8	66	56
-7	233	217
-6	133	131
-5	220	207
-4	308	301
-3	171	171
-2	52	37
-1	638	618
0	82	79
1	587	587
2	261	243
3	247	228
4	241	229
5	415	412
6	-47	13
7	268	276
8	137	112
9	134	140
10	55	47
H= 2	K= 6	
-5	-52	8
-4	207	227
-3	-51	16
-2	83	86
-1	61	48
0	-50	4
1	-52	64
2	198	202
3	-51	39
H= 3	K= 1	
-14	179	185
-13	119	123
-12	64	61
-11	214	210
-10	351	345
-9	-42	35
-8	577	573
-7	482	487
-6	256	233
-5	215	217
-4	553	551
-3	404	386
-2	1487	1282
-1	332	319
0	186	164
1	695	736
2	-28	45
3	398	417
4	354	403
5	485	473
6	-39	45
7	274	263
8	55	71
9	184	166
10	258	251
11	-48	17
H= 3	K= 1*	
12	106	115
H= 3	K= 3	
-13	202	208
-12	-49	6
-11	322	304
-10	115	117
-9	50	34
-8	-45	8
-7	411	399
-6	160	164
-5	101	97
-4	218	223
-3	558	523
-2	212	209
-1	94	96
0	296	267
1	644	661
2	44	50
3	572	575
4	119	118
5	503	509
6	-45	8
7	340	343
8	-45	23
9	262	262
10	-48	16
11	-50	17
H= 3	K= 5	
-9	-53	24
-8	273	282
-7	117	114
-6	-52	4
-5	87	76
-4	168	175
-3	103	124
-2	378	391
-1	115	92
0	87	101
1	214	207
2	155	156
3	97	109
4	245	252
5	128	137
6	67	73
7	129	152
H= 4	K= 0	
-14	391	384
-12	262	256
-10	369	366
-8	754	731
-6	91	79
-4	824	941
-2	1042	1070
0	1319	1285
2	897	893
4	797	848
6	550	561
8	183	176
10	-45	64
12	321	313
H= 4	K= 2	
-14	155	161
-13	-51	36
-12	149	167
-11	222	229
-10	49	29
-9	484	471
-8	215	207
-7	-40	6
-6	-39	3
-5	273	272
-4	105	87
-3	191	172
-2	130	131
-1	870	843
0	619	623
1	122	136
2	63	37
3	523	534
4	237	242
5	361	353
6	330	334
7	384	389
8	162	184
9	194	194
10	-50	66
11	82	93
H= 4	K= 4	
-11	272	277
-10	121	105
-9	276	264
-8	160	161
-7	184	185
-6	97	112
-5	403	387
-4	-52	10
-3	250	241
-2	199	200
-1	143	145
0	271	266
1	433	422
2	190	194
3	381	374
4	86	76
5	86	78
6	-50	42
7	304	328
8	-50	28
H= 4	K= 4	
9	146	159
H= 4	K= 6	
-5	-52	5
-4	-50	19
-3	66	87
-2	131	136
-1	-50	55
0	283	276
1	56	50
2	-49	35
H= 5	K= 1	
-14	82	90
-13	-50	23
-12	540	536
-11	168	156
-10	163	156
-9	152	163
-8	461	455
-7	234	239
-6	436	418
-5	521	479
-4	280	244
-3	566	559
-2	602	547
-1	346	332
0	249	298
1	252	239
2	377	396
3	430	452
4	395	399
5	277	259
6	462	462
7	-46	26
8	272	283
9	204	195
10	53	50
11	102	101
H= 5	K= 3	
-13	74	81
-12	-50	51
-11	227	210
-10	-47	35
-9	324	318
-8	70	73
-7	375	366
-6	69	65
-5	360	356
-4	57	40
-3	569	549
-2	67	79
-1	676	650
0	-39	25
1	75	96
2	-41	21
3	514	509
4	76	74
5	424	418
6	161	150
7	76	84
8	114	121
9	290	288
H= 5	K= 5	
-9	161	158
-8	162	175
-7	67	58
-6	213	221
-5	122	109
-4	71	81
-3	151	149
-2	-49	41
-1	185	194
0	287	285
1	-45	8
2	194	176
3	192	197
4	123	127
5	114	120
H= 6	K= 0	
-14	120	89
-12	295	250
-10	662	637
-8	545	529
-6	1042	1001
-4	190	374
-2	499	486
0	463	440
2	620	600
4	156	144
6	219	198
8	359	343
10	-51	49
H= 6	K= 2	
-14	-44	8
-13	194	173
-12	136	131
-11	122	110
-10	304	314
-9	315	334
-8	77	58
-7	193	223
-6	310	317
-5	463	475
-4	332	348
-3	326	335
-2	330	288
-1	464	667
H= 6	K= 2	
0	428	424
1	563	551
2	370	360
3	517	545
4	234	239
5	351	348
6	67	51
7	235	245
8	167	179
9	54	62
10	56	57
H= 6	K= 4	
-11	-51	18
-10	171	168
-9	321	315
-8	-50	41
-7	180	168
-6	155	152
-5	-46	22
-4	97	97
-3	407	412
-2	199	204
-1	337	332
0	-44	20
1	162	142
2	181	191
3	411	419
4	-47	41
5	260	271
6	56	42
7	127	133
H= 7	K= 1	
-15	-54	45
-14	-50	19
-13	129	119
-12	-50	34
-11	215	186
-10	339	319
-9	186	174
-8	273	301
-7	391	371
-6	418	430
-5	59	70
-4	471	459
-3	56	69
-2	387	398
-1	363	366
0	-38	31
1	258	266
2	91	106
3	74	73
4	675	649
5	389	379
6	225	240
7	82	68
8	56	47
9	-49	25
10	236	249
H= 7	K= 3	
-13	220	215
-12	-49	2
-11	355	336
-10	53	60
-9	147	147
-8	67	78
-7	549	533
-6	159	181
-5	217	206
-4	53	65
-3	132	103
-2	-40	11
-1	428	441
0	-42	18
1	521	500
2	149	150
3	55	44
4	144	134
5	515	526
6	-48	34
7	136	144
8	-49	9
H= 7	K= 5	
-9	-52	22
-8	124	132
-7	172	183
-6	91	101
-5	95	110
-4	219	209
-3	-51	22
-2	111	111
-1	95	104
0	103	115
1	112	111
2	-48	36
3	65	51
4	167	172
H= 8	K= 0	
-14	280	249
-12	74	95
-10	195	175
-8	423	388
-6	218	226
-4	231	267
-2	261	263
0	60	60
2	349	330
4	519	507
6	379	370
H= 8	K= 0	
8	-50	28
H= 8	K= 2	
-14	136	138
-13	129	109
-12	58	70
-11	299	306
-10	52	62
-9	461	455
-8	330	335
-7	507	518
-6	136	146
-5	559	575
-4	-40	17
-3	270	257
-2	253	275
-1	-39	34
0	247	245
1	391	377
2	119	121
3	417	420
4	339	347
5	57	74
6	246	265
7	297	310
8	-50	10
H= 8	K= 4	
-11	188	192
-10	-45	50
-9	141	147
-8	88	73
-7	363	387
-6	-46	39
-5	291	293
-4	-46	34
-3	-46	4
-2	208	216
-1	151	152
0	52	61
1	214	214
2	61	73
3	201	184
4	-47	26
5	-49	45
H= 9	K= 1	
-14	143	134
-13	-51	28
-12	297	274
-11	111	102
-10	-44	15
-9	124	137
-8	364	350
-7	-40	12
-6	536	503
-5	543	502
-4	-41	72
-3	77	65
-2	185	196
-1	116	118
0	543	549
1	264	256
2	228	223
3	132	116
4	191	201
5	97	118
6	311	330
7	95	99
8	-51	49
H= 9	K= 3	
-13	-53	16
-12	-49	6
-11	223	214
-10	-48	12
-9	303	328
-8	61	83
-7	80	40
-6	63	72
-5	753	725
-4	-44	26
-3	127	310
-2	60	65
-1	-43	5
0	-56	30
1	355	355
2	-45	25
3	262	257
4	-49	43
5	202	224
6	-50	55
H= 9	K= 5	
-7	-48	17
-6	49	92
-5	164	162
-4	53	72
-3	98	111
-2	-50	12
-1	71	77
0	228	236
1	-53	58
H= 10	K= 0	
-14	94	64
-12	149	114
-10	242	254
-8	109	194
-6	429	492
-4	195	164
-2	124	130
H= 10	K= 0	
0	94	65
2	641	615
4	108	121
6	186	197
H= 10	K= 2	
-13	116	87
-12	115	111
-11	110	109
-10	192	199
-9	322	328
-8	65	82
-7	278	318
-6	415	416
-5	88	104
-4	298	286
-3	560	559
-2	76	79
-1	212	208
0	179	182
1	74	92
2	372	368
3	331	350
4	59	68
5	111	109
6	58	99
H= 10	K= 4	
-10	-53	61
-9	173	187
-8	57	71
-7	106	107
-6	127	111
-5	98	105
-4	-46	10
-3	265	261
-2	-47	42
-1	64	47
0	-48	14
1	-46	26
2	130	150
3	185	202
H= 11	K= 1	
-14	96	97
-13	69	67
-12	-50	1
-11	-47	22
-10	288	291
-9	182	176
-8	218	294
-7	115	100
-6	260	248
-5	-42	32
-4	601	563
-3	134	131
-2	54	66
-1	103	91
0	219	205
1	64	65
2	347	348
3	93	106
4	307	341
5	120	126
6	-49	24
H= 11	K= 3	
-12	-50	1
-11	77	76
-10	-49	8
-9	308	332
-8	-46	9
-7	286	300
-6	-47	40
-5	90	59
-4	-46	32
-3	227	221
-2	58	49
-1	277	269
0	86	90
1	176	164
2	-48	55
3	103	119
4	-48	5
H= 12	K= 0	
-14	109	76
-12	112	112
-10	-45	25
-8	161	383
-6	41	119
-4	256	250
-2	474	462
0	123	112
2	210	218
4	267	272
H= 12	K= 2	
-13	178	179
-12	-50	51
-11	130	160
-10	94	119
-9	-47	19
-8	303	282
-7	516	498
-6	-44	23
-5	221	192
-4	244	243
-3	-44	43
-2	264	263
-1	250	216
0	63	61
H= 12	K= 2	
1	197	185
2	130	149
3	190	186
4	125	148
H= 12	K= 4	
-8	-51	37
-7	251	239
-6	-48	13
-5	115	103
-4	-53	56
-3	-48	14
-2	166	166
-1	130	111
0	-50	58
H= 13	K= 1	
-13	69	67
-12	73	72
-11	-47	23
-10	93	109
-9	-48	63
-8	294	321
-7	-46	37
-6	299	319
-5	179	183
-4	131	121
-3	-43	26
-2	330	319
-1	64	67
0	361	365
1	90	78
2	68	75
3	-50	53
4	210	166
H= 13	K= 3	
-10	-48	20
-9	98	124
-8	-48	16
-7	94	98
-6	-48	20
-5	380	381
-4	61	48
-3	52	41
-2	-45	9
-1	97	94
0	-48	39
1	209	196
H= 14	K= 0	
-12	142	144
-10	-46	84
-8	186	159
-6	451	388
-4	-44	23
-2	204	165
0	302	282
2	250	238
H= 14	K= 2	
-11	164	179
-10	-47	11
-9	-46	92
-8	138	141
-7	151	128
-6	243	215
-5	184	182
-4	-50	3
-3	247	274
-2	165	170
-1	64	54
0	150	156
1	136	136
H= 15	K= 1	
-11	-50	37
-10	177	187
-9	74	70
-8	-47	3
-7	-50	15
-6	272	279
-5	68	61
-4	317	242
-3	71	71
-2	149	142
-1	100	94
0	149	160
1	-50	50
H= 15	K= 3	
-6	-50	40
-5	55	56
-4	-48	27
H= 16	K= 0	
-10	85	117
-8	170	165
-6	53	53
-4	305	291
-2	247	212
H= 16	K= 2	
-7	190	203
-6	60	74
-5	58	41
-4	130	131

Table 2 (*cont.*)

(*b*) Hydrazinium fluoroborate

H= 0	K= 0	
2	319	317
4	506	490
6	146	165
8	-85	1
10	106	88
H= 0	K= 2	
0	646	664
1	-52	14
2	-57	5
3	858	858
4	133	154
5	-74	46
6	245	289
7	-83	17
8	103	151
9	-87	10
10	-91	14
H= 0	K= 4	
0	248	224
1	244	256
2	168	184
3	-74	47
4	150	136
5	101	91
6	88	39
H= 1	K= 1	
-11	103	164
-10	213	196
-9	-85	38
-8	-82	72
-7	-81	59
-6	339	252
-5	-69	16
-4	327	278
-3	518	499
-2	317	271
-1	535	464
0	618	539
1	70	6
2	1119	1134
3	227	257
4	737	789
5	150	138
6	234	195
7	339	343
8	105	116
9	-87	32
10	-89	47
H= 1	K= 3	
-9	-87	47
-8	-87	96
-7	-82	34
-6	-80	34
H= 1	K= 3	
-5	171	146
-4	82	93
-3	141	152
-2	157	156
-1	88	88
0	267	318
1	144	139
2	-67	78
3	-70	41
4	-75	32
5	398	368
6	-81	14
7	289	314
8	-87	70
H= 1	K= 5	
-2	87	76
-1	128	83
0	92	90
1	-79	67
H= 2	K= 0	
-10	593	664
-8	-84	44
-6	504	514
-4	1544	1275
-2	207	224
0	-55	12
2	709	790
4	242	240
6	652	680
8	284	277
10	143	158
H= 2	K= 2	
-10	-92	154
-9	194	248
-8	-82	17
-7	682	650
-6	177	159
-5	-74	43
-4	236	197
-3	647	635
-2	211	280
-1	64	89
0	493	533
1	468	509
2	277	276
3	119	163
4	412	395
5	160	147
6	179	197
7	-84	53
8	-92	10
9	281	311
H= 2	K= 4	
-7	-90	62
-6	-87	20
-5	-82	13
-4	106	71
-3	-75	51
-2	113	117
-1	243	240
0	-68	5
1	317	308
2	119	79
3	220	177
4	105	97
5	173	164
H= 3	K= 1	
-11	-92	79
-10	-90	25
-9	104	107
-8	264	147
-7	349	341
-6	589	500
-5	674	604
-4	222	241
-3	261	265
-2	1076	1156
-1	74	65
0	-89	60
1	459	466
2	146	176
3	249	248
4	166	199
5	320	338
6	251	270
7	-86	85
8	119	90
9	-90	60
H= 3	K= 3	
-9	-98	46
-8	-98	77
-7	101	68
-6	208	231
-5	594	554
-4	210	219
-3	497	489
-2	163	139
-1	335	347
0	278	265
1	163	199
2	-87	35
3	291	324
4	78	48
5	286	268
6	-84	14
7	-86	8
H= 4	K= 0	
-10	225	254
H= 4	K= 0	
-8	540	486
-6	764	627
-4	839	844
-2	521	562
0	917	989
2	1085	1190
4	505	503
6	-86	75
8	-93	23
H= 4	K= 2	
-10	-92	100
-9	354	301
-8	-86	13
-7	-82	16
-6	161	146
-5	222	226
-4	-72	54
-3	245	247
-2	270	309
-1	854	930
0	277	254
1	215	222
2	-64	18
3	136	142
4	-75	28
5	273	269
6	100	79
7	131	160
8	96	110
H= 4	K= 4	
-7	164	176
-6	-86	16
-5	122	109
-4	-83	95
-3	-75	18
-2	-72	49
-1	128	153
0	163	178
1	195	213
2	163	156
3	-82	104
4	-84	19
H= 5	K= 1	
-11	-96	61
-10	-95	55
-9	-89	122
-8	343	350
-7	-85	89
-6	-78	131
-5	376	349
-4	436	487
-3	134	147
-2	751	830
-1	120	140
0	279	307
H= 5	K= 1	
1	136	135
2	-67	58
3	258	223
4	427	406
5	-83	81
6	101	105
7	-85	55
8	-88	56
H= 5	K= 3	
-9	-93	13
-8	-89	58
-7	256	257
-6	94	75
-5	133	108
-4	101	95
-3	-73	57
-2	-67	44
-1	411	439
0	-68	73
1	105	76
2	-68	58
3	151	149
4	92	70
5	106	116
6	124	96
H= 6	K= 0	
-10	395	329
-8	743	751
-6	734	770
-4	236	227
-2	577	615
0	664	686
2	-77	62
4	120	117
6	-90	48
H= 6	K= 2	
-10	169	166
-9	-91	51
-8	-88	87
-7	-82	110
-6	99	115
-5	410	425
-4	115	113
-3	-71	90
-2	309	304
-1	235	244
0	612	563
1	464	392
2	92	80
3	320	307
4	102	114
5	-84	29
6	-84	21
H= 6	K= 4	
-6	-90	82
-5	98	92
-4	-85	21
-3	192	185
-2	135	168
-1	-75	42
0	93	88
1	-76	7
2	-79	64
H= 7	K= 1	
-11	122	149
-10	-95	75
-9	107	126
-8	-88	37
-7	115	157
-6	560	323
-5	252	247
-4	-76	116
-3	-70	74
-2	-72	128
-1	77	88
0	-60	42
1	108	109
2	145	141
3	-81	56
4	263	260
5	215	193
6	118	145
H= 7	K= 3	
-9	-92	71
-8	-92	62
-7	259	275
-6	107	106
-5	-79	21
-4	-75	25
-3	235	203
-2	-69	6
-1	-65	89
0	-68	11
1	226	221
2	160	121
3	-79	27
4	127	122
H= 8	K= 0	
-10	-95	55
-8	-99	95
-6	421	443
-4	-77	98
-2	387	403
0	265	224
2	233	218
4	100	95
6	-99	75
H= 8	K= 2	
-10	-93	50
-9	393	457
-8	209	234
-7	350	379
-6	104	126
-5	218	211
-4	153	157
-3	99	87
-2	-70	41
-1	171	141
0	121	104
1	119	90
2	91	59
3	214	185
4	115	123
H= 8	K= 4	
-4	-84	28
-3	122	137
-2	-93	94
-1	-78	31
H= 9	K= 1	
-10	-94	56
-9	-92	36
-8	-91	78
-7	-86	58
-6	152	163
-5	286	298
-4	-80	23
-3	114	100
-2	408	408
-1	116	86
0	164	146
1	118	94
2	122	109
3	-81	14
4	-84	24
H= 9	K= 3	
-8	-92	30
-7	-92	76
-6	-85	91
-5	464	449
-4	-81	13
-3	-80	3
-2	-79	87
-1	-74	52
0	-76	9
1	123	115
H= 10	K= 0	
-10	108	95
-8	-90	36
-6	-85	62
-4	181	183
-2	-83	58
H= 10	K= 0	
0	264	179
2	304	268
H= 10	K= 2	
-9	-95	140
-8	-90	13
-7	180	185
-6	205	189
-5	-85	35
-4	123	116
-3	239	211
-2	-75	53
-1	-71	10
0	-76	48
1	-74	50
2	250	195
H= 11	K= 1	
-9	-95	118
-8	198	203
-7	-89	17
-6	-89	6
-5	-68	42
-4	144	124
-3	-82	34
-2	-85	69
-1	-76	19
0	-75	45
1	-79	13
2	-85	46
H= 12	K= 0	
-8	-95	201
-6	-94	87
-4	-88	10
-2	-90	105
0	-79	48
H= 12	K= 2	
-6	-90	8
-5	-88	21
-4	100	103
-3	-86	72
-2	101	87
H= 13	K= 1	
-6	146	126
-5	-88	73
-4	-89	54
-3	-93	64

The nitrogen atoms may have associated with them either two or three hydrogen atoms depending on the orientation of the hydrazinium ions. Least-squares calculations with the hydrazinium ion in each of the two orientations allowed a selection to be made on the basis of slightly smaller sum of residuals squared. The inclusion of the hydrogen atoms in the structure-factor calculation with the constraints outlined above reduced the R index for HPC from 0·076 to 0·057 and for HFB from 0·106 to 0·091. The final least-squares parameters for the two structures are listed in Table 1. An extinction parameter was used in the HPC structure calculation but in the calculation of the HFB structure its value tended to be negative and it was removed prior to the final least-squares cycles. The calculated and observed structure factors are given in Table 2.

The rather large standard errors on the position and thermal parameters indicated that an analysis of these thermal ellipsoids would probably not yield meaningful results. An analysis was attempted and this prediction proved valid.

Discussion

The discussion that follows is applicable to either structure but is slanted toward the better known HPC. Also there is no known hemihydrate of HFC. Two types of ionic fragments make up the structure. The anion is composed of a central chlorine atom surrounded by four oxygen atoms arranged at the corners of a slightly distorted tetrahedron. The cation may be thought of as a bi-tetrahedron with the two nitrogen atoms acting as centers of regular tetrahedra which are joined together at a corner. The six remaining corners are occupied by five hydrogen atoms and a lone pair of electrons. Interatomic distances and bond angles for the two structures are listed in Table 3. The N(1)–N(2) distances in the structures are in good agreement with the value of 1·447 ± 0·009 Å found in hydrazinium monohydrate (Liminga & Olovsson, 1964) and with 1·436 ± 0·009 Å found in hydrazinium hydrazinedithiocarboxylate (Braibanti, Lanfredi & Tiripicchio, 1964). Reasonable H bond distances between H atoms and atoms in the anions were found.

Table 3. *Interatomic distances and bond angles in hydrazinium perchlorate and hydrazinium fluoroborate*

Bonds	HPC *X* = Cl, *Y* = O	HFB *X* = B, *Y* = F
N(1)–N(2)	1·461 ± 0·009 Å	1·425 ± 0·019
X —*Y*(1)	1·428 ± 0·006	1·379 ± 0·026
—*Y*(2)	1·415 ± 0·007	1·325 ± 0·029
—*Y*(3)	1·435 ± 0·007	1·360 ± 0·031
—*Y*(4)	1·418 ± 0·007	1·339 ± 0·030
Y(1)–*Y*(2)	2·355 ± 0·011	2·166 ± 0·020
–*Y*(3)	2·328 ± 0·010	2·201 ± 0·019
–*Y*(4)	2·345 ± 0·010	2·221 ± 0·018
Y(2)–*Y*(3)	2·289 ± 0·012	2·225 ± 0·021
–*Y*(4)	2·294 ± 0·011	2·199 ± 0·019
Y(3)–*Y*(4)	2·339 ± 0·012	2·221 ± 0·020
H(1)–*Y*(3)	2·096 ± 0·038	1·965 ± 0·060
H(2)–*Y*(3)	2·235 ± 0·035	2·316 ± 0·075
H(3)–N(2)	1·991 ± 0·015	1·945 ± 0·035
H(4)–*Y*(4)	2·084 ± 0·013	2·052 ± 0·048
H(5)–	Not involved in hydrogen bonding	
Angles		
Y(1)–*X* —*Y*(2)	111·87 ± 0·01	106·46 ± 0·09
—*Y*(3)	108·79 ± 0·01	106·94 ± 0·08
—*Y*(4)	110·96 ± 0·01	109·50 ± 0·08
Y(2)–*X* —*Y*(3)	106·90 ± 0·01	111·87 ± 0·09
—*Y*(4)	108·10 ± 0·01	111·16 ± 0·08
Y(3)–*X* —*Y*(4)	110·14 ± 0·01	110·70 ± 0·09
N(1)–H(1)–*Y*(3)	147·13 ± 0·28	153·63 ± 1·02
N(1)–H(2)–*Y*(3)	144·61 ± 0·20	130·48 ± 0·86
N(1)–H(3)–N(2)	170·87 ± 0·10	164·81 ± 0·46
N(2)–H(4)–*Y*(4)	167·57 ± 0·01	160·22 ± 0·51
N(2)–H(5)–	Not involved in hydrogen bonding	

The structure may be described as a spiral column of hydrazinium ions surrounded by six columns of anion tetrahedra. The axes of the columns are parallel to the *b* axis. Of the five hydrogen atoms associated with the hydrazinium ion, one [H(3)] is utilized to bond the hydrazinium ions together in a spiral chain, three [H(1), H(2), H(4)] are engaged in bonding the anion tetrahedra to the hydrazinium spiral chain, and one [H(5)] does not appear to be involved in bonding. Fig. 1 shows the structure of the hydrazinium perchlorate in stereo.

While the HPC structure may be derived from HPCHH, the mechanism of the transformation is not clear at this time. Although both structures have the same space group, *C*2/*c*, the lattice constants *a* and *b* of the two structures are radically different and a simple transformation involving small translations or rotations is not readily visualized.

Final calculations were performed on a CDC-6600 computer with programs written by Larson, Roof & Cromer (1963, 1964, 1965). The authors are indebted to A. C. Larson for suggesting the constraint approach for determining hydrogen atom position and for modifying computer codes to accomplish this type of least-squares refinement.

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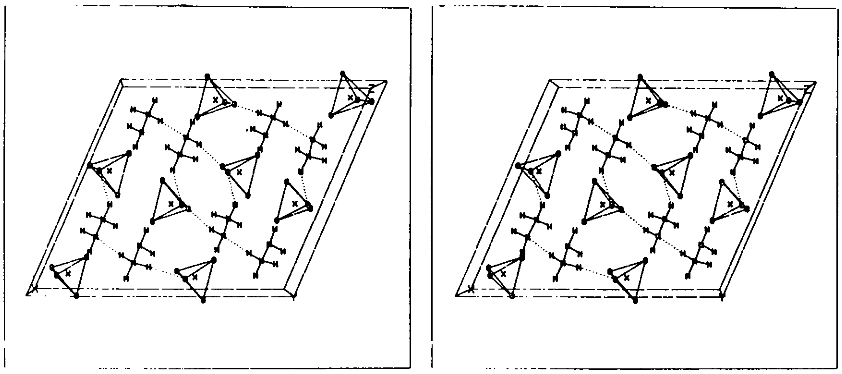

Fig. 1. A stereo view of the structure of HPC. The origin of the cell is at the lower rear right and the view is parallel to the *b* axis. The dotted lines represent the proposed hydrogen bond contacts. The symbol × represents the chlorine atom; other atoms are represented by their chemical symbols.

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The Crystal Structure of 4*H*-Cyclopenta[2,1-*b*: 3,4-*b*′]dithiophene at −160°C

By P. B. Koster, F. van Bolhuis and G. J. Visser

Laboratorium voor Structuurchemie, Rijksuniversiteit, Groningen, Bloemsingel 10, Groningen, Netherlands

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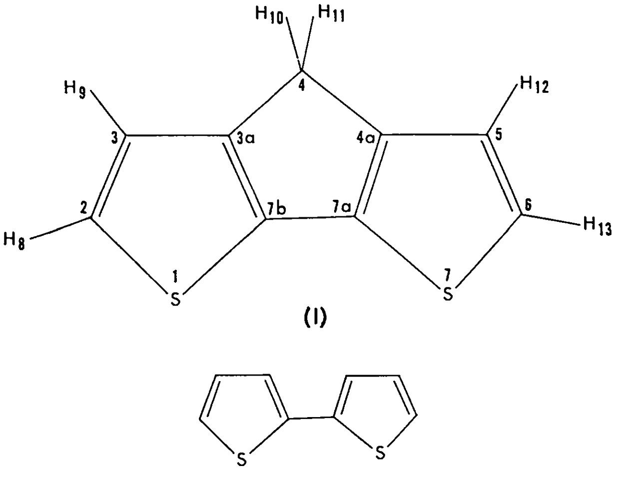
The crystal structure of 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene, $C_9H_6S_2$, has been determined from three-dimensional diffractometer data taken at −160°C to detect possible hyperconjugation effects. The crystals are monoclinic, space group $P2_1/c$, $a=12{\cdot}500$, $b=11{\cdot}154$, $c=11{\cdot}284$ Å, $\beta=98{\cdot}00°$, $Z=8$. The positional and anisotropic thermal parameters were refined by the method of least squares, $R=0{\cdot}032$ for 8146 reflexions. The observed bond lengths do not indicate the presence of hyperconjugation effects. The molecule is approximately planar, the largest deviation from the least-squares plane being 0·035 Å for C and S. There is much strain in the molecule; the angles S–C–C and C–C–C range from 102 to 139°. As to the values of the bond lengths and angles the molecule has the symmetry *mm*. Estimated standard deviations are 0·002 Å for C–C and C–S, 0·02 Å for C–H and 0·1° for C–S–C, C–C–C and C–C–S.

Introduction

The synthesis of the six isomeric cyclopentadithiophenes, $C_9H_6S_2$ (Wynberg & Kraak, 1964) has encouraged studies of the properties of these thiophene analogues of fluorene. Charge transfer properties (Kraak & Wynberg, 1968), spectra of ions (Janssen & de Jong, 1967) and aromatic character (Kraak, Wiersema, Jordens & Wynberg, 1968) have been or are being studied in the Laboratory of Organic Chemistry of this University. Preliminary results of these studies indicate interesting differences between the properties of the isomeric cyclopentadithiophenes and the corresponding dithienyls. For instance, the ultraviolet absorption bands of the cyclopentadithiophenes in solution generally lie at longer wavelengths than those of the corresponding dithienyls. A suitable explanation for the observed shifts could not be given by qualitative discussion of the following effects: (*a*) The increase in coplanarity of the thiophene rings because of the presence of the CH_2 bridge (see Fig. 1), (*b*) possible hyperconjugation *via* the CH_2 group, or (*c*) the strain in the molecule. We thought it, therefore, worth while to do an accurate determination of the bond lengths and angles for one of the isomers $C_9H_6S_2$ by means of X-ray diffraction at low temperature (−160°C). The isomer chosen is 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (I). For this compound the U.V. shifts are +0 and +10 for the 2,2′-di-



(I)

(II)

Fig. 1. 4*H*-Cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (I) and the corresponding 2,2′-dithienyl (II).