The noncondensable gas was determined to be 1.036 mmol of carbon monoxide. Condensable materials which were not stopped at −112° were passed through Ascarite and then a trap filled with magnesium perchlorate cooled to 0°. The remaining material was germane (0.618 mmol). Nitric acid (1 ml, 8 *M*) was distilled into the hydrolysis vessel containing the solid substance. The tube was partially immersed in an oil bath at 75° for 0.75 hr in order to oxidize all Ge-containing species to Ge(IV) for determination as the mannitol complex; 0.323 mmol of Ge was found. The total Ge recovered was 0.941 mmol or 89% of theory. In another experiment, 0.986 mmol of $KGeH_3CO_2$ was hydrolyzed overnight with *ca.* 3 ml of 4 *M* HCl. A whitish solid was deposited in the reaction tube. A quantitative yield of carbon monoxide (0.986 mmol) was obtained in addition to 0.236 mmol of germane.

In general, quantitative yields of carbon monoxide were produced. However, the GeH_4:CO ratio varied widely from *ca.* 0.1 to 0.6, with the usual ratio in the neighborhood of 0.55. Unfortunately no more than 90% of the total germanium was ever accounted for in any of the runs.

Kolbe Electrolysis[40-42] of $KGeH_3CO_2$.—Attempts were made to couple electrolytically generated GeH_3 radicals to form digermane. An electrolysis cell with 1-cm^2 platinum foil electrodes *ca.* 3 mm apart was constructed to permit electrolysis on the vacuum line. Electrolyses of *ca.* 0.3 *M* $KGeH_3CO_2$ solutions (10-ml quantities were used) were carried out at 0° at current densities around 1 A/cm^2. The pressure was maintained between 100 and 300 mm by periodically opening a stopcock leading through a train of −196° cold traps to the vacuum pump. The electrolyte was magnetically stirred. One electrolysis was performed in water; the voltage was varied randomly between 10 and 30 V during a 1-hr period. After 3 min of electrolysis, an orange-yellow solid had formed, indicating decomposition of the $KGeH_3CO_2$. Fractionation of the condensable gases showed only trace amounts of digermane; germane and carbon dioxide also were identified. A second 1-hr electrolysis at 25 V in *ca.* 80% methanol yielded a white precipitate; no digermane was produced. A third 1-hr electrolysis was carried out at 10 V in aqueous 1 *M* $KHSO_4$. A greenish white solid slowly formed on the walls of the cell. The solid eventually developed a yellow cast. Fractionation of the volatiles indicated *ca.* 5% yield of digermane based on the $KGeH_3CO_2$ used.

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A Neutron Diffraction Study of the Reaction Product of Acetonitrile and Hydrogen Chloride: Chloroacetiminium Chloride, $[CH_3C(Cl){=}NH_2{}^+]Cl^-$[1]

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The crystal structure of $CH_3CN \cdot 2HCl$ has been determined by three-dimensional neutron diffraction analysis at −5° and refined to a final weighted *R* factor of 8.5% for all 511 reflections observed. Crystals of the compound are orthorhombic, of space group Pnma, with $a = 8.72 \pm 0.01$, $b = 6.93 \pm 0.01$, and $c = 8.63 \pm 0.01$ Å and with four formula units per unit cell ($d_{obsd} = 1.43$, $d_{calcd} = 1.45$ g/cm^3). The compound does not contain the bichloride ion as was previously postulated; the chemical structure is that of an imine hydrohalide, $[CH_3C(Cl){=}NH_2]^+Cl^-$, not that of a nitrilium salt, $[CH_3CNH]^+[HCl_2]^-$. All atoms except two methyl hydrogens lie in mirror planes. The Cl^- ion is involved as an acceptor in two hydrogen bonds, 3.07 and 3.08 Å in length, which lie in the molecular plane and which serve to link the planar chloroacetiminium ions into infinite chains. The values 1.265 ± 0.007, 1.471 ± 0.010, and 1.694 ± 0.010 Å were found for the C–N, C–C, and C–Cl bond lengths, respectively.

Introduction

The hydrogen halides form numerous addition compounds with various aliphatic and aromatic nitriles. The freezing point diagram of the system CH_3CN–HCl indicates the existence of four intermediate compounds, $CH_3CN \cdot HCl$, $2CH_3CN \cdot 3HCl$, $CH_3CN \cdot 5HCl$, and $CH_3CN \cdot 7HCl$, all with melting points well below room temperature.[4] Another addition compound, $CH_3CN \cdot 2HCl$, first postulated by Gautier[5] in 1869, was not found in the above-mentioned cryoscopic study.

Hantzsch[6] prepared $CH_3CN \cdot 2HCl$, as well as $CH_3CN \cdot 2HBr$ and $CH_3CN \cdot 2HI$, in solid form and found that, although the latter two compounds can be made at room temperature, the dihydrochloride forms only below about −16°. Several studies have been carried out on crystalline dihydrohalides in the attempt to determine their molecular structures.[7,8] The three main structural proposals may be given as **1**—**3**.

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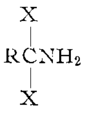
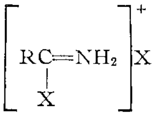


$\mathrm{RC(X)_2NH_2}$

1[9]

$[RC{\equiv}NH]^+HX_2^-$

2[8,9]



$[\mathrm{RC(X){=}NH_2}]^+X^-$

3[8,10]

Structure **2**, which involves a bihalide ion, is particularly intriguing in view of recent structural and mechanistic interest in such species. Since no conclusive structural evidence was available, we have undertaken combined neutron and X-ray single-crystal investigations of $CH_3CN \cdot 2HCl$ and, less completely, an X-ray study of $CH_3CN \cdot 2HBr$.[11] A brief communication of the major findings of the neutron study has appeared.[12]

Experimental Section

Single crystals suitable for diffraction study were prepared by bubbling HCl directly into Spectroquality acetonitrile[13] at −16° under anhydrous conditions. The HCl gas, of 99.3% minimum purity, was predried by bubbling through H_2SO_4. During the preparation HCl was absorbed slowly at first and then rapidly after a 5–10-min induction period. After 30–40 min white crystals of suitable size for X-ray study appeared on the sides of the flask. After many trials it was found possible, by adding HCl slowly, to grow crystals several millimeters on an edge for neutron investigation. Analysis of the crystals by titration established the formula to be $CH_3CN \cdot 1.96HCl$. Several measurements on crystals in sealed capillary tubes gave a melting point of 22–23.3°.

Unit Cell and Space Group.—Crystals sealed in glass capillaries were examined by Weissenberg and precession techniques. The unit cell was determined to be orthorhombic, and the lattice constants $a = 8.72 \pm 0.01$, $b = 6.93 \pm 0.01$, and $c = 8.63 \pm 0.01$ Å were obtained by least-squares refinement of peak locations measured by neutron diffractometry. The calculated crystal density for four molecules per unit cell is 1.45 g/cm^3; the observed density, established by flotation in a $CHCl_3$–C_6H_6 mixture, is 1.43 g/cm^3 at 18°.

From systematic absences of reflections $hk0$ for $h = 2n + 1$, $0kl$ for $k + l = 2n + 1$, $h00$ for $h = 2n + 1$, $0k0$ for $k = 2n + 1$, and $00l$ for $l = 2n + 1$, the diffraction symbol is mmmPn·a. Of the two possible space groups Pnma and Pn2$_1$a, the former was subsequently established by the zero-moment test,[14] which indicated a center of symmetry, and by the successful structure determination and refinement.

Data Collection.—A well-formed crystal weighing 4.4 mg with dimensions about 1.1 × 1.9 × 2.3 mm was sealed in a glass capillary with the b axis along the tube axis. The crystal was oriented and checked for suitability by X-ray means and then transferred to the Oak Ridge automatic three-circle neutron diffractometer[15] for data collection. The crystal was maintained at a temperature of about −5° by use of a thermoelectric cooling device.[16] The method of data collection was essentially that described previously;[17] a θ–2θ step scan was used, and background was obtained by averaging readings taken on both sides of a peak. Essentially complete three-dimensional data (511 independent reflections) were collected to a $(\sin \theta)/\lambda$ value of 0.603 at λ 1.08 Å. The observed integrated intensity of each reflection was corrected for absorption[18] ($\mu = 2.251$ cm^{-1}), and all intensities were put on an absolute scale by calibration with a standard NaCl crystal.

Solution of the Structure

The structure was solved from the three-dimensional neutron Patterson function with some assistance from an X-ray Patterson projection of $CH_3CN \cdot 2HBr$. The most obvious feature of the neutron Patterson of $CH_3CN \cdot 2HCl$ was a concentration of all peaks at values of $y = 0$ and $^1/_2$, consistent with the location of the crystallographic "molecules" on the mirror planes at $y = {}^1/_4$ and $^3/_4$, as is required by symmetry if the space group is Pnma. It was also noted that the stronger interactions, *i.e.*, Cl–Cl, Cl–N, and N–N, appeared to be concentrated near $z = 0$ and $^1/_2$, thus indicating atomic z parameters close to 0 and $^1/_2$. The remaining x parameters were then assigned from the Patterson peak locations. A three-dimensional Fourier including 136 strong reflections gave a good indication of the final structure, but contained one strong peak which was inconsistent with the final model. Since X-ray diffraction data of $CH_3CN \cdot 2HBr$, essentially isomorphous with $CH_3CN \cdot 2HCl$, were available, the [010] Patterson projection of this compound was examined. The location of the Br–Br peaks suggested that an error had been made in the assignment of the Cl–Cl vectors. Revised parameters taken from the neutron Patterson quickly led to a Fourier map in which the hydrogen atoms were all clearly defined, and the correct model was obviously that of the imine hydrohalide as given by **3**.

Refinement

At the next stage a full-matrix least-squares refinement[19] was carried out utilizing properly weighted observed structure factors F_o. In the final stage of refinement each parameter change was less than one-tenth the magnitude of the associated standard error. Of 511 reflections included, 136 were below the level of observation. The number of parameters varied was 58. The final weighted residual

$$R = \frac{[\Sigma w(F_o - F_c)^2]^{1/2}}{[\Sigma w F_o^2]^{1/2}}$$

was 0.085 for all reflections and 0.078 omitting unobserved reflections for which $|F_c|$ was less than $|F_o|$. Input data were weighted according to the equation[20]

$$w_{hkl}^{-1} = \frac{1}{4}\frac{F_o^2}{E^2}\left[\frac{1}{n}(E + 2B) + (0.02E)^2\right],$$

where w is the reflection weight, E is the integrated intensity, n is the number of repetitions of the measurement, and B is the background count. This weighting

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TABLE I

FINAL ATOMIC PARAMETERS WITH STANDARD ERRORS[a]

Atom	x	y	z	β_{11}[b]	β_{22}	β_{33}	β_{12}[c]	β_{13}	β_{23}[c]
Cl(1)	951 (5)	2500	−84 (6)	63 (5)	347 (18)	146 (8)	0	15 (5)	0
Cl(2)	2171 (4)	2500	5624 (5)	50 (5)	309 (14)	85 (5)	0	1 (4)	0
C(1)	2887 (6)	2500	70 (7)	58 (8)	259 (18)	94 (8)	0	−1 (7)	0
C(2)	3528 (9)	2500	1647 (8)	116 (12)	264 (25)	72 (9)	0	4 (8)	0
N(1)	3678 (4)	2500	−1159 (5)	38 (6)	305 (16)	74 (6)	0	1 (4)	0
H(1)	3156 (18)	1348 (26)	2278 (14)	334 (29)	703 (62)	191 (20)	−122 (38)	−65 (20)	215 (30)
H(2)	4743 (20)	2500	1539 (18)	110 (26)	868 (106)	159 (26)	0	−34 (19)	0
H(3)	3151 (13)	2500	−2266 (14)	75 (14)	306 (37)	87 (16)	0	−4 (13)	0
H(4)	4873 (13)	2500	−1036 (15)	25 (14)	327 (41)	165 (20)	0	25 (12)	0

[a] All parameters × 10^4 with least-squares standard errors given in parentheses. [b] The temperature factor is of the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [c] Values of 0 are required by symmetry considerations.

scheme is not purely statistical but allows empirically for possible variations in beam intensity and absorption correction errors and the like.

The final position and temperature parameters, with standard deviations, are given in Table I. All atoms, except two methyl hydrogens related by the mirror planes, lie in the mirror plane at $y = {}^1/_4$ and are restricted by symmetry to four variable-temperature parameters.[21] The neutron scattering factors used in the refinement were $b_C = 0.66$, $b_{Cl} = 0.99$, $b_N = 0.94$, and $b_H = -0.378$, all in units of cm × 10^{-12}.

Observed and calculated values of the structure factors on an absolute scale are listed in Table II. Two reflections, 002 and 020, appear to be affected by extinction but were retained in the refinement. These reflections are tagged with an asterisk in the table. All F_o values preceded by a minus sign in the table were unobserved and were assigned a value of F_{min}; such reflections were included in the refinement when $|F_c|$ was greater than $|F_o|$. During data collection 15 $hk0$ reflections were accidentally omitted. When the omission was discovered, the original crystal had partially decomposed, and it did not seem feasible or necessary to make a new set of measurements. The calculated values of these reflections were used in a final Fourier synthesis. The section at $y = {}^1/_4$ from this synthesis (see Figure 1) clearly delineates the structure.

As a check on the final least-squares refinement, a difference synthesis ($F_o - F_c$), in which F_c included all atoms, was calculated. The resulting map was virtually featureless, giving further verification of the accuracy of the least-squares parameters. Another difference synthesis, for which F_c included all atoms but hydrogen, was calculated, and the section at $y = {}^1/_4$ is shown in Figure 2. The two out-of-plane methyl hydrogen atoms are projected onto the section for clarity. This difference plot clearly delineates the hydrogen atoms and thereby provides evidence against methyl group disorder.

Bond distances and angles calculated[22] from the final least-squares parameters are listed, uncorrected for thermal effects, in Tables III and IV and most of them are also shown in Figure 3.

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS (×100) FOR $CH_3CN \cdot 2HCl$

	F(OBS)	F(CALC)
H= 0 K= 0		
2	985	1237*
4	75	-33
6	476	461
8	125	86
10	112	88
H= 0 K= 1		
1	270	263
3	498	482
5	339	309
7	147	-192
9	-57	24
H= 0 K= 2		
0	1023	-1102*
2	888	-879
4	77	-69
6	376	-390
8	-57	-62
10	131	-99
H= 0 K= 3		
1	96	80
3	569	-560
5	178	-160
7	110	130
9	-57	-13
H= 0 K= 4		
0	900	922
2	482	479
4	105	122
6	237	216
8	103	92
H= 0 K= 5		
1	-57	-70
3	339	350
5	98	78
7	-57	-45
H= 0 K= 6		
0	475	-480
2	273	-287
4	-57	-36
6	123	-126
H= 0 K= 7		
1	-57	19
3	126	-141
5	-57	-63
H= 0 K= 8		
0	190	206
2	189	128
H= 1 K= 0		
1	143	145
2	154	-140
3	238	234
4	195	-182
5	368	318
6	363	-376
7	-57	3
8	218	-197
9	129	111
10	253	266
H= 1 K= 1		
1	381	-358
2	104	-112
3	91	-74
4	-57	-42
5	212	-203
6	177	112
7	[illegible]	[illegible]
8	156	110
9	205	-277
10	-57	-64
H= 1 K= 2		
1	-57	-81
2	229	212
3	219	-235
4	[illegible]	39
5	210	-212
6	664	[illegible]
7	-57	-5
8	84	106
9	102	-80
10	171	-200
H= 1 K= 3		
1	335	328
2	-57	14
3	72	-53
4	158	117
5	277	285
6	188	-189
7	493	486
8	-57	-67
9	284	278
H= 1 K= 4		
1	-57	19
2	178	-171
3	259	230
4	-57	11
5	109	128
6	367	-350
7	-74	22
8	80	-38
9	80	41
H= 1 K= 5		
1	189	-197
2	76	-0
3	-57	8
4	97	-70
5	162	-149
6	220	94
7	316	-321
8	108	57
H= 1 K= 6		
1	-57	5
2	-57	78
3	135	-117
4	-57	27
5	-57	-77
6	148	153
7	-57	18
H= 1 K= 7		
1	-57	98
2	-57	-4
3	-57	4
4	-57	35
5	86	59
H= 1 K= 8		
1	-57	-12
2	-57	-38
H= 2 K= 0		
0	576	-550
1	76	-60
2	541	-549
3	-57	-11
4	356	350
5	165	148
6	-57	-67
7	469	471
8	155	158
9	-57	5
10	-57	51
H= 2 K= 1		
1	96	-95
2	160	-158
3	365	-324
4	731	-718
5	346	-321
6	124	135
7	180	148
8	135	110
9	100	158
10	-57	57
H= 2 K= 2		
0	615	596
1	142	-116
2	393	387
3	113	120
4	193	-219
5	189	-184
6	-57	24
7	433	-426
8	134	-136
9	-57	17
H= 2 K= 3		
1	-57	-62
2	301	270
3	390	371
4	473	464
5	187	158
6	115	-85
7	75	-80
8	56	-89
9	-57	-122
H= 2 K= 4		
0	461	-467
1	150	164
2	219	-214
3	189	-149
4	-57	58
5	150	171
6	78	37
7	259	262
8	-57	62
H= 2 K= 5		
1	81	19
2	126	-151
3	214	-245
4	265	-267
5	-57	-58
6	-57	41
7	85	17
8	90	91
H= 2 K= 6		
0	259	232
1	-57	-66
2	156	146
3	-57	59
4	-57	-21
5	-57	-77
6	-57	-20
H= 2 K= 7		
1	-57	8
2	-57	49
3	92	103
4	133	140
5	87	34
H= 2 K= 8		
0	106	-98
1	-57	29
2	-57	-75
H= 3 K= 0		
1	724	743
2	444	435
3	254	-221
4	447	408
5	402	-379
6	143	135
7	287	283
8	-57	5
9	103	-127
H= 3 K= 1		
1	619	-593
2	259	238
3	94	-96
4	526	499
5	-57	80
6	172	-153
7	99	103
8	271	-290
9	-57	20
H= 3 K= 2		
1	704	-688
2	387	-379
3	292	272
4	399	-357
5	219	225
6	-57	-136
7	202	-164
8	106	17
9	-57	64
H= 3 K= 3		
1	485	453
2	112	-142
3	90	59
4	454	-479
5	-57	-86
6	228	229
7	76	-62
8	171	146
9	108	-42
H= 3 K= 4		
1	408	476
2	240	254
3	162	-179
4	257	247
5	121	-114
6	118	106
7	-57	73
8	-57	-29
H= 3 K= 5		
1	259	-268
2	81	119
3	-57	-9
4	253	295
5	-57	63
6	109	-123
7	-57	42
H= 3 K= 6		
1	257	-251
2	143	-127
3	-57	60
4	128	-144
5	87	89
6	-57	-91
H= 3 K= 7		
1	126	120
2	101	-60
3	-57	-16
4	107	-111
H= 4 K= 0		
0	643	-630
1	127	-145
2	120	80
3	176	-172
4	483	455
5	132	-73
6	220	-220
7	206	-203
8	369	-363
9	82	48
H= 4 K= 1		
1	-57	12
2	420	-396
3	205	-188
4	175	16
5	68	78
6	607	-615
7	376	381
8	277	-293
9	-57	-89
H= 4 K= 2		
0	595	572
1	271	251
2	92	-99
3	-57	34
4	409	-391
5	115	121
6	179	197
7	176	170
8	289	298
9	-57	-94
H= 4 K= 3		
1	69	-18
2	187	182
3	169	166
4	140	88
5	-57	-73
6	405	428
7	288	-309
8	241	240
H= 4 K= 4		
0	345	-357
1	234	-235
2	90	72
3	-57	28
4	242	248
5	149	-150
6	-57	-121
7	91	-79
8	192	-196
H= 4 K= 5		
1	-57	-16
2	138	-112
3	89	-92
4	120	-77
5	-57	50
6	204	-233
7	213	185
H= 4 K= 6		
0	174	165
1	98	101
2	-70	-38
3	-57	2
4	174	-158
5	83	81
6	-57	62
H= 4 K= 7		
1	-57	8
2	-57	71
3	-57	41
4	-57	25
H= 5 K= 0		
1	523	-495
2	228	-221
3	863	-886
4	414	-395
5	432	-413
6	90	122
7	74	-128
8	214	241
9	-57	139
H= 5 K= 1		
1	418	404
2	-57	11
3	456	-431
4	179	-169
5	339	-350
6	269	-279
7	-57	70
8	160	-177
9	155	-123
H= 5 K= 2		
1	475	459
2	164	173
3	738	705
4	379	393
5	404	408
6	175	-158
7	-57	79
8	180	-185
H= 5 K= 3		
1	300	-321
2	168	-54
3	347	363
4	171	183
5	221	232
6	167	177
7	-57	-12
8	173	165
H= 5 K= 4		
1	327	-333
2	109	-128
3	491	-479
4	279	-272
5	281	-298
6	101	117
7	-57	-44
H= 5 K= 5		
1	178	183
2	-57	58
3	196	-202
4	94	-106
5	129	-159
6	-57	-116
H= 5 K= 6		
1	178	180
2	-57	79
3	264	268
4	94	134
5	191	145
H= 5 K= 7		
1	-57	-87
2	-57	-17
H= 6 K= 0		
0	525	-540
1	214	222
2	295	-289
3	552	553
4	362	-364
5	266	266
6	-57	50
7	176	-213
8	92	-81
H= 6 K= 1		
1	193	-175
2	275	266
3	113	-113
4	585	599
5	142	-136
6	408	404
7	99	-125
8	146	149
H= 6 K= 2		
0	377	302
1	286	-236
2	301	313
3	453	-465
4	261	297
5	272	-248
6	-57	-47
7	147	197
8	111	78
H= 6 K= 3		
1	184	218
2	152	-166
3	102	41
4	481	-492
5	-91	117
6	201	-306
7	94	96
H= 6 K= 4		
0	204	-219
1	160	208
2	247	-239
3	294	298
4	164	-191
5	197	182
6	-57	27
H= 6 K= 5		
1	152	-133
2	-57	91
3	82	-28
4	287	310
5	-57	-66
H= 6 K= 6		
0	116	118
1	-57	-114
2	-57	112
3	196	-163
4	139	113
H= 7 K= 0		
1	125	166
2	170	-163
3	386	399
4	83	-95
5	-57	13
6	106	78
7	203	-243
H= 7 K= 1		
1	377	377
2	-57	80
3	-57	-18
4	102	109
5	106	87
6	192	227
7	128	108
H= 7 K= 2		
1	131	-142
2	189	176
3	370	-373
4	-57	10
5	-57	-10
6	88	-44
7	210	214
H= 7 K= 3		
1	276	-266
2	86	-78
3	-57	-24
4	-57	-76
5	-57	-29
6	208	-173
H= 7 K= 4		
1	-57	101
2	144	-162
3	238	277
4	-57	16
5	-57	21
H= 7 K= 5		
1	133	150
2	-57	53
3	-57	13
4	84	44
H= 7 K= 6		
1	104	-59
2	81	77
H= 8 K= 0		
0	260	263
1	90	-106
2	236	-208
3	344	-342
4	121	-126
5	275	-292
6	-57	-60
H= 8 K= 1		
1	102	136
2	251	292
3	-57	96
4	-57	3
5	-57	-70
6	92	-66
H= 8 K= 2		
0	236	-211
1	-57	48
2	183	182
3	288	307
4	147	134
5	246	269
6	-57	45
H= 8 K= 3		
1	117	-134
2	186	-170
3	-57	-17
4	-57	17
5	-57	33
H= 8 K= 4		
0	99	134
1	-57	-32
2	-57	-99
3	202	-209
4	149	-115
H= 8 K= 5		
1	79	82
2	98	92
H= 9 K= 0		
1	182	-199
2	185	198
3	-57	-74
4	-57	71
5	-57	61
H= 9 K= 1		
1	-57	53
2	203	-222
3	369	379
4	127	-121
5	286	272
H= 9 K= 2		
1	211	178
2	162	-168
3	-57	78
4	-57	-68
H= 9 K= 3		
1	-57	-30
2	209	179
3	314	-308
H= 9 K= 4		
1	143	-134
2	124	103
H=10 K= 0		
0	133	106
1	-57	-100
2	413	412
3	109	86
H=10 K= 1		
1	-57	-41
2	-57	-31
H=10 K= 2		
0	149	-92
1	-57	90
2	349	-363

Description of Structure

The molecular structure indicated in Figure 1 is clearly that of a chloro-substituted imine hydrochloride. The reaction of anhydrous HCl and CH_3CN at low temperature results in the addition of HCl across the C≡N bond, with concomitant loss of triple-bond character by this bond and protonation of the nitrogen atom. The chloroacetiminium cations and chloride anions are linked by N–H···Cl hydrogen bonds into infinite chains extending parallel to the axis a. Each entire chain of ions $CH_3(Cl)C{=}NH_2^+$ and Cl^- is precisely planar except for the two hydrogen atoms of each methyl group that are mirror equivalent. Adjacent asymmetric units within a chain are related by

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(21) H. A. Levy, *Acta Cryst.*, **9**, 679 (1956).

(22) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, A Fortran Crystallographic Function and Error Program," Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

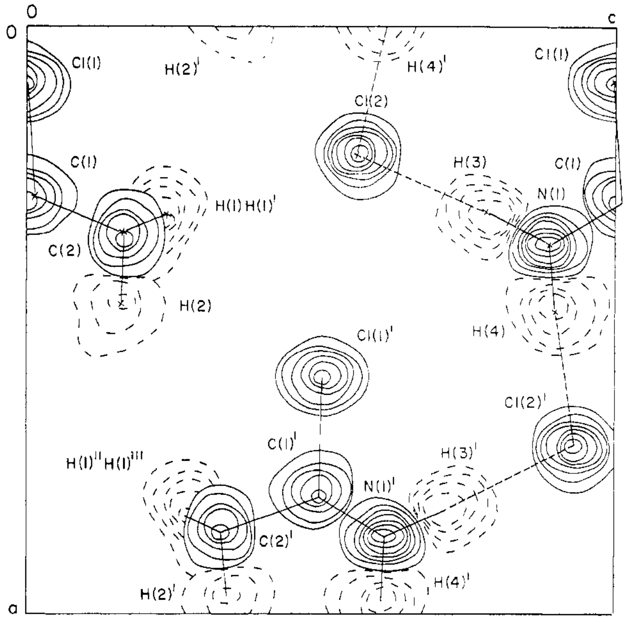

Figure 1.—Fourier section at $y = {}^1/_4$ in the unit cell. Positive contours are at intervals of 500, and negative contours (dashed circles) are at intervals of 300, both on the same arbitrary scale. The atoms in the asymmetric unit are Cl(1), C(1), C(2), H(1), H(2), N(1), H(3), H(4), and Cl(2). The out-of-plane methyl hydrogen atoms [H(1), H(1)', H(1)'', and H(1)'''] have been projected onto the plane, and final positional parameters, obtained from a full-matrix anisotropic least-squares refinement, are indicated on the section with crosses (×). Bonded atoms in the chloroacetiminium ion are connected by light solid lines. Dashed lines indicate hydrogen-bonding interactions.

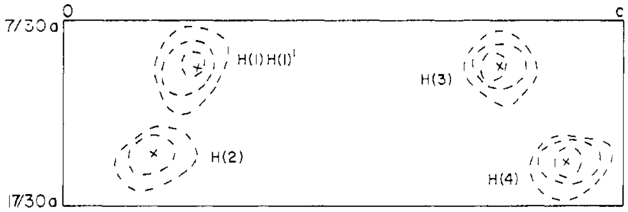

Figure 2.—Difference Fourier section at $y = {}^1/_4$ in the unit cell showing hydrogen atoms only. Dashed circles (negative contours) are at intervals of 300, on the same scale as in Figure 1. The out-of-plane methyl hydrogen atoms [H(1) and H(1)'] have been projected onto the plane. Final positional parameters from the anisotropic least-squares refinement are indicated on the section with crosses (×).

Table III

Bond Distances in $CH_3CN \cdot 2HCl^a$

Bond	Distance, Å	Bond	Distance, Å
Cl(1)–C(1)	1.694 (7)	N(1)–H(4)	1.048 (12)
C(1)–C(2)	1.471 (10)	N(1)–Cl(2)	3.071 (7)
C(1)–N(1)	1.265 (7)	N(1)–Cl(2)'	3.081 (7)
C(2)–H(1)	1.019 (18)	H(4)–Cl(2)'	2.035 (13)
C(2)–H(2)	1.064 (20)	H(3)–Cl(2)	2.011 (13)
N(1)–H(3)	1.060 (14)		

[a] Least-squares standard errors are given in parentheses.

the *a* glide, as are adjacent chains within a given layer at $y = {}^1/_4$ or $y = {}^3/_4$. Only secondary valence forces act between chains.

Table IV

Bond Angles in $CH_3CN \cdot 2HCl^a$

Atoms	Angle, deg	Atoms	Angle, deg
Cl(1)–C(1)–C(2)	116.8 (6)	N(1)–H(3)–Cl(2)	179.4 (10)
Cl(1)–C(1)–N(1)	118.6 (5)	C(1)–C(2)–H(2)	107.3 (11)
N(1)–C(1)–C(2)	124.6 (5)	C(1)–C(2)–H(1)	111.9 (9)
C(1)–N(1)–H(3)	121.2 (7)	H(2)–C(2)–H(1)	111.4 (11)
C(1)–N(1)–H(4)	117.3 (8)	H(1)–C(2)–H(1)'	103.1 (20)
N(1)–H(4)–Cl(2)'	175.7 (11)	H(3)–N(1)–H(4)	121.5 (7)

[a] Least-squares standard errors are given in parentheses.

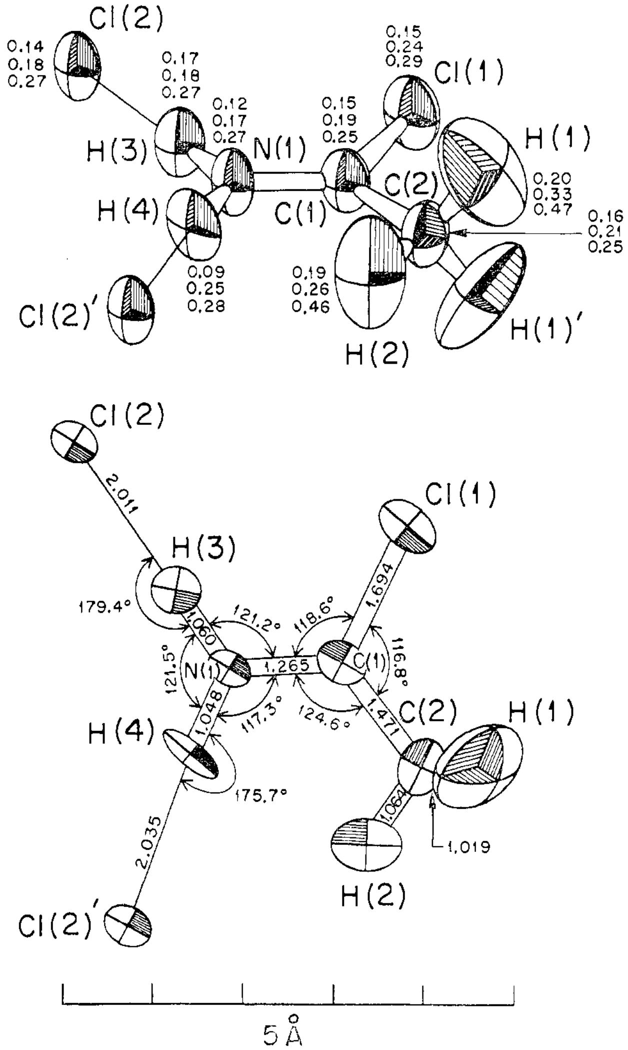

Figure 3.—Two views of the 50% probability thermal ellipsoids: bottom, view in the *b*-axis direction, showing bond distances and most of the bond angles; top, view in direction 60° from that of the bottom drawing, showing root-mean-square atomic displacements in principal-axis directions.

Among previously determined structures there appear to be no close analogs of the chloroacetiminium ion with which the structure of the ion can be compared. However, the bond lengths and angles found seem reasonable for the pattern of chemical linkages in the ion. The planarity of the ion and the nearly 120° bond angles about atoms C(1) and N(1) are consistent with approximate sp^2 hybridization of these atoms. The C–Cl bond length of 1.694 ± 0.010 Å is somewhat shorter than the corresponding bond in vinyl chloride (1.740 ± 0.008, 1.72 ± 0.01, and 1.736 ± 0.010 Å,[23]

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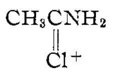
[23] L. E. Sutton, Ed., "Interatomic Distances," Special Publication No 11, The Chemical Society, London, 1958.

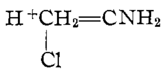
from two electron diffraction[24,25] studies and a microwave study[26]), acetyl chloride[27] (1.77 ± 0.02 Å), and acryloyl chloride[28] (1.74 ± 0.02 Å), in each of which the chlorine atom is also attached to a carbon atom in sp^2 hybridization. The C—C bond length of 1.471 ± 0.010 Å is also short compared with the value of about 1.51 Å[29] to be expected for an sp^2–sp^3 bond. The C=N bond length of 1.265 ± 0.007 Å may be compared with C=N distances of 1.284 ± 0.0049 Å in glyoxime,[30] 1.253 ± 0.011 Å in dimethylglyoxime,[31] 1.303 ± 0.006 and 1.277 ± 0.007 Å in bis(glyoximato)nickel(II),[32] 1.29 ± 0.028 and 1.30 ± 0.028 Å in bis(dimethylglyoximato)nickel(II),[33] 1.288 ± 0.010 Å in formamidoxime,[34] and 1.276 Å (error not given) in formaldoxime.[35] For comparison, a reliable average value[29] for the C—N single bond length is 1.472 ± 0.005 Å, and the C≡N triple bond length in acetonitrile has been reported from microwave studies to be 1.157 Å.[36]

The shortening of the C–Cl bond in the chloroacetiminium ion relative to the C–Cl bond in vinyl chloride may be qualitatively explained by invoking the resonance structure **4** (which, unlike the corresponding structure for vinyl chloride, does not involve a charge separation) as an important contributing structure. Similarly, the shortening of the C–C bond might be explained in part as due to the contribution of the hyperconjugated structure **5**. However, structure **5** is an excited structure relative to **4** or **6** and would not be expected to be of much significance. An alternative explanation of the observed shortening of the C–Cl and C–C bonds in terms of high s character of the bonds appears attractive. Making use of the correlation between bond length and s character of carbon for various types of bonds to C presented by Dewar and Schmeising,[37] we find that the per cent s character predicted for the unsaturated carbon atom by the observed C–Cl and C–C bond lengths to be 41 and 47%, respectively. The latter value would be revised downward if thermal corrections to the observed bond length were applied. The rather consistent picture that emerges then is that a redistribution of the s character in the bonds about the central carbon atom presumably induced by the attached electronegative Cl and NH_2^+ [38,39] has resulted in a reduced carbon atom bond radius and shortened bonds. An alternative explanation in terms of nonbonded interactions[40] seems less attractive but cannot be ruled out.



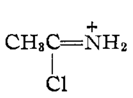
$CH_3C(=Cl^+)NH_2$

4



$H^+CH_2(Cl)=CNH_2$

5



$CH_3C(Cl)=\overset{+}{N}H_2$

6

The uncorrected C–H distances were found to be 1.019 and 1.064 Å for C(2)–H(1) and C(2)–H(2), respectively. Upon application of a "riding-model"[22] correction, these became 1.12 and 1.15 Å. Although these are almost certainly overcorrected, the agreement with the C–H distance in acetonitrile (1.10–1.11 Å, depending on the detailed interpretation of the microwave data[36]) is quite reasonable considering the large magnitude of the thermal motion. The N(1)–H(3) and N(1)–H(4) distances of 1.06 and 1.05 Å, respectively have not been corrected because the thermal parameters of atoms H(3) and H(4) are not appreciably greater than those of N(1). These distances reflect the presence of the positive charge on the NH_2 group, and the low thermal motion is consistent with the hydrogen bonding which results in two N–H···Cl bonds 3.07 and 3.08 Å in length. These hydrogen bonds are nearly linear (N–H···Cl angles of 176 and 179°) and appear to be somewhat shorter than normal.

The shapes and orientations of the ellipsoids[41] in Figure 3 seem reasonably consistent with the structure. The largest displacements are generally parallel to *b*, except for atom H(1). Attempts were made during the refinement to account for the large thermal motion of the methyl hydrogen atoms, using a disordered model. However, the three-dimensional Fourier and, particularly, the difference Fourier maps did not show evidence of disorder. Because of the possibility that the adduct might have been $CH_3CN \cdot xHCl$, with x less than 2, attempts at further refinement were made by varying the "atom multipliers" of the H and Cl atoms from HCl, to allow for fractional occupancy of the sites of these atoms in the structure. However, the atom multipliers showed very little change, and the R factors were unchanged.

Conclusion

Neutron diffraction analysis has established that the bichloride ion $[Cl\text{–}H\text{–}Cl]^-$ does not exist in the compound $CH_3CN \cdot 2HCl$ in the solid state, contrary to previous suggestions. The compound is found to be a chloro-substituted imine hydrochloride, in which chloroacetiminium cations are linked into infinite chains with

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[24] L. H. Kaplan, Ph.D. Thesis, Purdue University, Lafayette, Ind., 1958; *Dissertation Abstr.*, **19**, 3130 (1959).

[25] P. A. Akishin, L. V. Vilkov, and U. I. Vesnin, *Dokl. Akad. Nauk SSSR*, **126**, 310 (1959).

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[27] Y. Morino, K. Kuchitsu, M. Iwasaki, K. Arakawa, and A. Takahashi, *Nippon Kagaku Zasshi*, **75**, 647 (1954). Cited in ref 23.

[28] T. Ukaji, *Bull. Chem. Soc. Japan*, **30**, 737 (1957).

[29] L. E. Sutton, Ed., "Interatomic Distances Supplement," Special Publication No. 18, The Chemical Society, London, 1965.

[30] M. Calleri, G. Ferraris, and D. Viterbo, *Acta Cryst.*, **20**, 73 (1966).

[31] W. H. Hamilton, *ibid.*, **14**, 95 (1961). See also L. L. Merritt and E. Lanterman, *ibid.*, **5**, 811 (1952).

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[33] D. E. Williams, G. Wohlaur, and R. E. Rundle, *J. Am. Chem. Soc.*, **81**, 755 (1959). See also L. E. Godycki and R. E. Rundle, *Acta Cryst.*, **6**, 487 (1953).

[34] D. Hall, *ibid.*, **18**, 955 (1965).

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[36] C. C. Costain, *ibid.*, **29**, 864 (1958). See also: L. F. Thomas, E. I. Sherrard, and J. Sheridan, *Trans. Faraday Soc.*, **51**, 619 (1955); M. Kessler, H. Ring, R. Trambarulo, and W. Gordy, *Phys. Rev.*, **79**, 54 (1950).

[37] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **11**, 96 (1960).

[38] M. G. Brown, *Trans. Faraday Soc.*, **55**, 694 (1959).

[39] H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).

[40] B. L. Carroll and L. S. Bartell, *Inorg. Chem.*, **7**, 219 (1968).

[41] C. K. Johnson, "ORTEP, A Fortran Thermal Ellipsoid Plot Program for Crystal-Structure Illustrations," Report ORNL-3794, revised, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

the chloride ions by N–H···Cl hydrogen bonds. Except for two hydrogen atoms of each methyl group, the atoms of each chain are exactly coplanar.

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The Microwave Spectrum, Structure, and Dipole Moment of Difluorophosphine Oxide[1]

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The microwave spectra of HF_2PO, DF_2PO, and $HF_2P^{18}O$ have been analyzed. The structural parameters are $d(PH) = 1.387 \pm 0.01$ Å, $d(PF) = 1.539 \pm 0.003$ Å, $d(PO) = 1.437 \pm 0.006$ Å, $\angle HPO = 117.9 \pm 2°$, $\angle FPO = 116.3 \pm 1°$, $\angle HPF = 101.9 \pm 1.5°$, and $\angle FPF = 99.8 \pm 0.5°$. The dipole moment was evaluated as 2.65 ± 0.03 D.

Introduction

Difluorophosphine oxide (HF_2PO) was first reported by Treichel, Goodrich, and Pierce[2] as a by-product in the decomposition of HPF_4. This compound and the sulfide analog have now been synthesized and characterized.[3,4] These compounds were the first phosphoryl or thiophosphoryl halides synthesized in which a hydrogen replaced one of the halogens. Their structures are expected to be analogous to the X_3PO series and their chemical and physical properties support this.[3,4] This study was undertaken to determine the detailed structural parameters of HF_2PO and its dipole moment.

Experimental Section

Apparatus.—The spectra were obtained with a conventional Stark modulated spectrometer described previously.[5] The transitions were measured with a precision of about 0.2 Mc. The absorption cell was maintained at about −78° during runs.

Materials.—HF_2PO was prepared by the reaction of F_2POPF_2 with HBr.[4] The DF_2PO was synthesized by substituting DBr enriched to about 75%. $HF_2P^{18}O$ was synthesized by treating PF_2Br with 70% enriched $H_2^{18}O$.

Spectrum.—The transitions which were assigned for the three isotopic species are listed in Table I. The rotational constants obtained from the 1_{11}–2_{12}, 1_{01}–2_{11}, and 1_{11}–2_{21} transitions are collected in Table II. The assignment was based on the Stark effect, frequency fit, and expected isotope shifts. Also the near identity of $I_A + I_C - I_B$ (Table II) indicates a plane of symmetry containing hydrogen and oxygen. This is expected for HF_2PO and further supports the assignment.

Stark Effect.—The Stark shift measurements were made with a precision dc power supply[6] (Fluke, Model 413B). The effective guide spacing was determined using the $0 \rightarrow 1$ of OCS ($\mu = 0.7152$).[7] The second-order Stark coefficients measured for HF_2PO are listed in Table III. Several of the assigned low J transitions exhibited Stark effects nonlinear in E^2. This was due to near degeneracies connected by the μ_c component of the dipole moment. One of these was measured and the experimental data are plotted (circles) in Figure 1.

Analysis

Structure.—HF_2PO has six independent structural parameters and the data from three isotopic species should provide seven independent pieces of information. Using conventional methods, described next, we have obtained the structural parameters listed in Table IV. For the convenience of the reader, four bond angles are listed in Table IV although only three are independent. The derived structure is illustrated in Figure 2.

The structural parameters were derived from the coordinates of the atoms. The fluorine "b" coordinate was determined from $I_A + I_C - I_B = 4M_F b_F^2$. The "$a$" and "$c$" coordinates of the oxygen and the "c" coordinate of the hydrogen were determined from Kraitchman's equations.[8] The "a" coordinate of the hydrogen was too small to be determined this way and was evaluated along with the remaining coordinates from I_A, I_C, and $\Sigma m_i a_i = \Sigma m_i c_i = \Sigma m_i a_i c_i = 0$.

The uncertainties in Table IV were estimated by making additional calculations in which the initial moments of inertia were altered to include their range of experimental uncertainty. The structure can, therefore, be considered a mixed r_s, r_0[9] structure with associated experimental error. The larger uncertainty associated with the hydrogen parameters reflects the difficulty in locating the hydrogen owing to its small "a" coordinate. There is another uncertainty in the parameters arising from vibrational effects which is more difficult to estimate. By analogy with simpler systems it seems reasonable to expect the structural parameters with attached uncertainties to encompass the well-defined average structure.[10]

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[1] This research was supported by a grant (GP 6814) from the National Science Foundation, Washington, D. C.

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