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The Crystal Structure of Tetracarbonyl (Acrylonitrile) Iron

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The crystal structure of tetracarbonyl(acrylonitrile)iron, $(CO)_4(CH_2=CH-CN)Fe$, at low temperature, has been determined by three-dimensional methods. In a monoclinic unit cell,

$$a=12{\cdot}09,\ b=11{\cdot}45,\ c=6{\cdot}585\ \text{Å};\ \beta=110{\cdot}4^\circ,$$

space group $P2_1/a$, there are four monomeric molecules. After anisotropic refinement, $R=0{\cdot}094$. The co-ordination round the iron atom is essentially a trigonal bipyramid; the apices are occupied by two carbonyl groups with Fe–C $=1{\cdot}99\pm0{\cdot}01$ Å and the equatorial plane contains two more Fe–C bonds of length $1{\cdot}76\pm0{\cdot}01$ Å and one bond from iron to the C:C double bond of acrylonitrile with Fe–C $=2{\cdot}09$ and $2{\cdot}10\pm0{\cdot}01$ Å. The equatorial plane consists of the iron atom, the two carbon atoms and two oxygen atoms of the carbonyl groups and the two carbon atoms of the double bond. The mean C–O bond length is $1{\cdot}13\pm0{\cdot}02$ Å and Fe–C–O is always linear. The dimensions in the co-ordinated acrylonitrile are $CH_2=CH$ = 1·40, CH – C = 1·45, C – N = 1·20 Å, all ±0·02 Å; C – CN is linear and the C – C – C angle is 116° ± 1°.

Introduction

Acrylonitrile (or vinyl cyanide), $CH_2=CH-CN$ forms complexes with metals, e.g. *bis* acrylonitrile nickel (Schrauzer, 1959) and tetracarbonyl (acrylonitrile) iron (Kettle & Orgel, 1960). Several modes of coordination are possible, but the spectroscopic evidence has been interpreted as indicating a strong interaction between the metal and the carbon–carbon double bond and none between the metal and the cyanide group.

The X-ray crystal-structure analysis of tetracarbonyl(acrylonitrile) iron was undertaken to establish the stereochemistry of the complex and to determine the bond lengths with sufficient accuracy to indicate the nature of the bonding; accordingly three-dimensional methods were used and observations made at low temperature.

Experimental

A sample of the compound was provided by Dr S. F. A. Kettle. It melts at 40 °C. and readily sublimes at room temperature forming pale yellow crystals on cold surfaces. It is decomposed by light and in air and so it had to be stored in sealed tubes. Samples which were left undisturbed in the dark for some time were found to have changed; sometimes single crystals grew whiskers and sometimes several small crystals had formed one large one. Crystals were most conveniently examined in a petri dish which was surrounded by solid carbon dioxide and into which a stream of carbon dioxide was blown gently to maintain an inert atmosphere. When the dish was mounted on the stage of a binocular microscope a further stream of carbon dioxide was blown from below to prevent condensation of moisture from obscuring the view.

Single crystals, suitable for X-ray work, were sealed into glass capillary tubes. After prolonged exposure to X-rays they became polycrystalline and then decomposed. Eventually all the crystals decomposed before we could obtain photographs of a crystal set about [*b*]. However, for each of the [*a*] and [*c*] axes we obtained all the intensity photographs from one crystal which was not visibly different at the end of the exposures.

For observations with Co $K\alpha$ radiation, the crystals were cooled in a stream of cold nitrogen with an apparatus adapted from that described by Robertson (1960). Unit-cell dimensions were measured from rotation and Weissenberg photographs, a, c and $\sin\beta$ being determined by a least-squares method of successive approximation; the results were

$$a=12{\cdot}09\pm0{\cdot}03,\quad b=11{\cdot}45\pm0{\cdot}02,\quad c=6{\cdot}58_5\pm0{\cdot}01\ \text{Å}\,,$$
$$\beta=110{\cdot}4\pm0{\cdot}7^\circ\ \text{at}\ 120\pm10\ ^\circ\text{K}.$$

The space group was uniquely determined as $P2_1/a$ and, with four formula units (M.W. = 220·96) per unit cell ($U=854{\cdot}3$ Å^3), the calculated density was 1·72 g.cm.$^{-3}$; this seemed a reasonable value compared with that of other iron carbonyl complexes (direct observation was rendered impossible by the reactivity of the compound). A crystal 0·15 mm. in diameter was set about the [*a*] axis and a set of equi-inclination Weissenberg photographs was taken for the layer lines $0kl\ldots4kl$, the temperature of the crystal being 120 ± 10 °K. Some photographs of several crystals at this temperature set about the [*c*] axis were obtained. Another crystal 0·15 mm. in diameter was set about the [*c*] axis and a set of equi-inclination Weissenberg photographs taken for $hk0\ldots hk3$; at the end of this time it was found that a gradual 'softening' of a

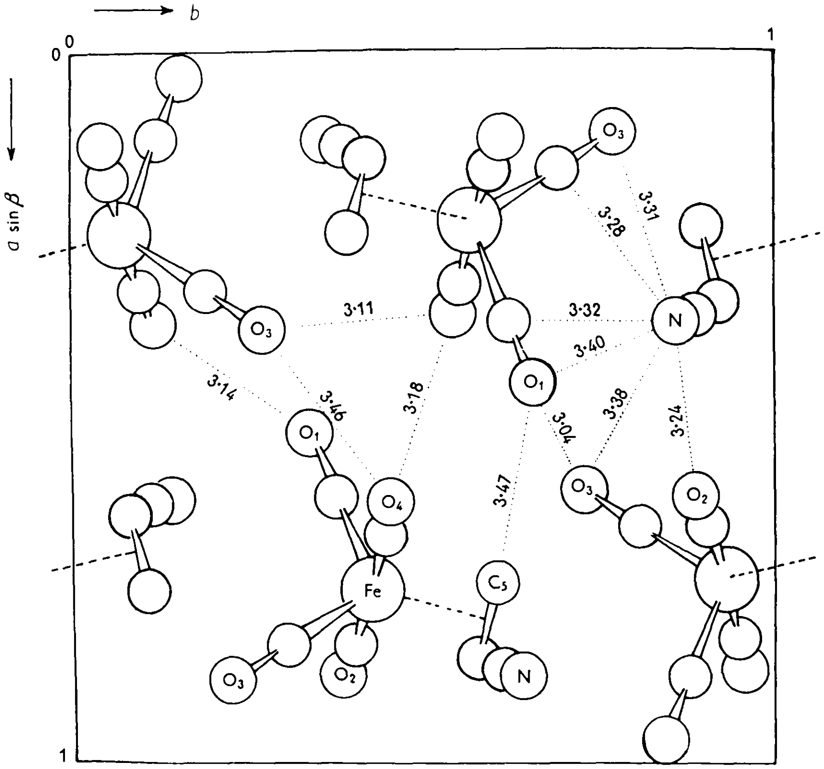

Fig. 1. Projection of the structure down [001] showing the designations of all the atoms in one molecule. The numbers are distances in Å between the pairs of atoms indicated by dotted lines.

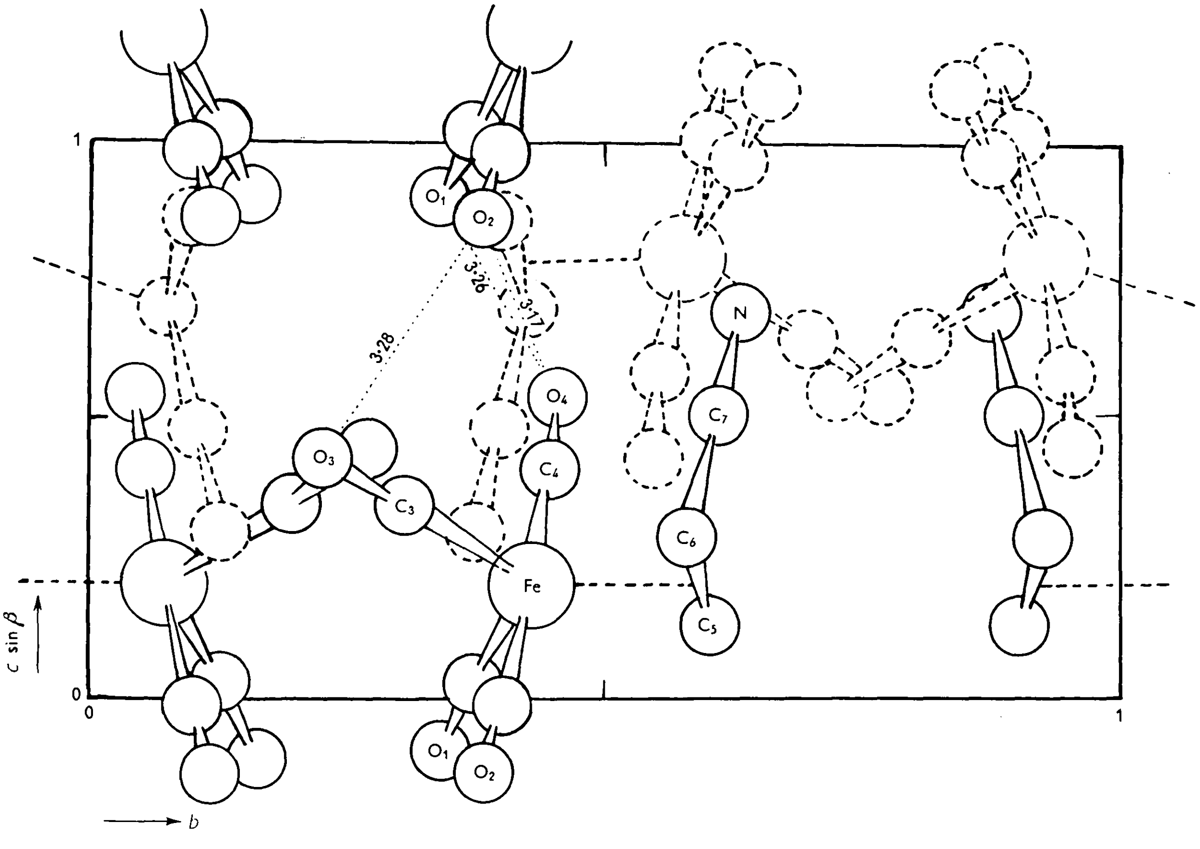

Fig. 2. Projection of the structure down [100]. The numbers are distances in Å between the pairs of atoms indicated by dotted lines and show the closest approach of a molecule to its neighbour in the next unit cell along [c].

Dewar tube had led to a rise in the temperature to about 220 °K. For both sets of multiple-film photographs, intensities were estimated visually with the aid of a calibration strip; then Lorentz and polarization corrections were applied on the Leeds University Ferranti Pegasus computer (which will now be called 'the computer') with a programme written by Dr F. M. Lovell, and Phillips (1954) corrections were applied with a programme written by one of us (A. R. L.). To correlate the layer lines and allow for the difference in temperature a set of simultaneous equations was set up to solve for $-\Delta B_l$ (i.e. the temperature factor required to reduce the lth layer line about [c] to the same effective temperature, 120 °K., as used for photographs about [a]) and the scale factor; the calculation was carried out on the computer with a programme written by one of us (A. R. L.). The average value of $-\Delta B$ was $1{\cdot}8 \pm 0{\cdot}1$ Å^2 for all layer lines. No absorption correction was applied; the absorption coefficient is 43 cm.$^{-1}$.

Structure determination

Patterson projections down [001] and [100] served to locate the iron atoms and showed that they occupied general positions in the space group $P2_1/a$. With the co-ordinates $x/a = 0{\cdot}240$, $y/b = 0{\cdot}073$ and $z/c = 0{\cdot}212$ the agreement indices for the iron atom only were $R_{hk0} = 0{\cdot}44$, $R_{0kl} = 0{\cdot}53$. Attempts to solve the structure in projection were unsuccessful.

The signs of the structure factors were calculated for all (hkl) reflections for the iron atom only. A three-

Table 1. *Observed and calculated structure factors*

Values are 10 times absolute scale. Reflections too weak to be observed have been omitted

l	F_o	F_c
0 0 l		
1	79	25
2	86	50
3	544	−515
4	217	195
5	229	189
6	153	123
0 1 l		
1	373	−369
2	620	506
3	216	223
4	277	270
5	155	−135
6	202	−198
0 2 l		
0	570	620
1	102	60
2	342	−249
3	330	−311
4	217	207
5	236	231
0 3 l		
1	270	−290
2	189	−191
3	532	562
4	477	286
5	146	−106
6	461	−435
0 4 l		
0	1027	−1038
1	777	−787
2	211	197
6	161	−148
0 5 l		
1	438	−426
2	478	−457
3	109	−70
4	375	375
6	225	−167
0 6 l		
0	830	−848
2	269	281
3	436	415
4	266	−270
5	330	−317
6	94	−100
0 7 l		
2	109	−78
4	60	−50
5	60	200
0 8 l		
0	221	−198
1	193	144
2	380	343
3	135	129
5	303	−239
0 9 l		
1	294	271
2	203	202
3	97	−79
4	292	−283
0 10 l		
1	137	119
0 11 l		
1	218	222
2	220	245
3	146	−146
0 12 l		
1	131	169
2	229	−265
1 1 l		
6	407	−415
4	347	300
3	349	307
2	128	80
1	748	−854
0	108	−140
−1	666	783
−2	639	673
−3	494	−458
−4	341	−353
1 2 l		
5	443	−443
3	277	233
1	379	−410
0	652	−901
−1	545	−642
−2	208	195
−3	240	232
−4	216	−207
−5	523	−538
1 3 l		
6	148	139
2	222	−227
1	528	−570
0	149	145
−1	228	−159
−2	79	−52
−3	64	−60
−4	64	−53
1 4 l		
5	298	−342
4	496	−451
3	450	398
2	106	129
1	212	−183
0	698	−747
−1	262	207
−2	277	274
−3	522	508
−5	461	−519
1 5 l		
6	133	137
4	219	−231
3	385	−346
2	360	350
1	357	368
0	471	472
−1	469	−482
−2	245	−207
−4	365	367
−5	241	−234
1 6 l		
5	113	−85
3	163	159
2	310	328
1	325	323
0	366	−330
−1	304	346
−3	122	106
1 7 l		
4	156	−189
3	178	−176
2	156	161
1	801	897
−1	428	−429
−2	253	−229
−3	442	407
−4	227	212
−5	83	69
1 8 l		
5	283	312
4	111	109
3	140	140
2	264	−252
1	385	395
0	64	37
−1	127	132
−2	374	−334
−3	116	−85
−5	186	160
1 9 l		
4	96	−103
2	133	−116
1	167	148
0	198	−194
−1	295	−259
−3	155	124
−4	219	204
1 10 l		
4	168	147
3	338	−343
2	309	−349
0	385	353
−2	139	−126
−3	126	−129
1 11 l		
3	110	105
2	189	−203
1	191	−166
0	208	−187
−1	312	351
−2	112	−100
−3	48	−55
1 12 l		
2	162	−205
0	143	125
2 0 l		
6	123	−121
5	288	−351
4	311	−315
3	395	397
2	234	285
−1	247	−188
−2	1133	1018
−3	339	372
−5	563	−667
2 1 l		
6	230	195
5	175	155
4	220	−218
3	229	−192
2	231	232
1	373	342
0	74	11
−1	423	−447
−2	181	−183
−3	190	−129
−4	115	−59
−5	112	113
2 2 l		
5	165	−172
2	304	315
1	185	−187
0	636	−760
−1	145	−93
−2	90	101
−3	604	585
−4	158	−154
−5	214	−212
2 3 l		
6	267	300
5	251	251
4	468	−512
3	334	−336
2	69	−41
1	1144	1378
0	633	−708
−1	385	326
−2	491	−565
−3	269	256
−4	244	290
−6	213	−266
2 4 l		
5	189	171
3	59	43
2	211	−201
1	386	365
0	262	230
−1	256	−241
−2	112	−96
−3	426	−403
−4	171	152
−6	193	206
2 5 l		
4	197	−100
3	181	−186
2	72	48
1	462	500
0	73	62
−1	213	−177
−3	450	416
−4	410	453
2 6 l		
5	171	138
4	125	141
3	150	−158
2	206	−224
1	202	215
0	714	759
−1	450	437
−2	443	−475
−3	471	−497
−5	255	319
2 7 l		
5	138	−33
4	80	103
3	268	297
2	145	−144
0	228	−222
−1	135	−123
−2	213	−185
2 8 l		
3	149	−146
2	295	−293
1	297	−297
0	300	404
−1	272	273
−2	252	−235
−3	197	−172
−4	180	215
2 9 l		
4	176	181
3	66	86
2	150	−123
1	299	−309
0	214	−198
−1	286	290
−3	325	−340
−4	222	−267
2 10 l		
2	139	−128
1	65	−75
0	161	−147
−1	202	−181
−2	140	112
2 11 l		
3	156	161
2	230	−240
1	198	−213
0	128	100
−1	302	352
−2	162	179
2 12 l		
0	135	−165
−1	191	−210
2 10 l		
−3	189	80
3 1 l		
6	175	179
4	391	−344
2	150	149
1	1069	1267
0	380	403
−1	593	−645
−2	811	−846
−3	186	150
−4	603	527
−5	144	−121
3 2 l		
5	274	287
4	461	413
3	110	72
2	337	−327
1	443	−380
0	282	285
−1	610	−568
−2	974	−976
−3	418	−412
−4	282	271
−5	258	235
−6	80	83
3 3 l		
6	180	159
5	144	129
3	146	−135
2	233	−184
1	117	−83
0	524	−576
−1	327	337
−3	207	193
−4	302	270
−6	156	−162
3 4 l		
5	138	147
4	259	244
3	251	−210
2	683	−720
1	347	341
0	503	508
−1	226	250
−2	282	−281
−3	198	−187
−5	426	414
3 5 l		
5	122	122
3	325	316
2	357	−369
1	473	−498
0	366	−361
−1	556	547
−2	386	362
−4	440	−449
−5	121	−116

Table 1 (*cont.*)

l	F_o	F_c
3 6 l		
5	200	100
4	122	−105
3	234	−204
2	189	−182
1	232	207
0	349	320
−1	441	390
−2	151	139
−3	135	−101
−5	117	117
3 7 l		
5	201	−195
4	246	290
1	382	−396
−1	224	215
−2	357	321
−3	310	−295
−4	534	−568
3 8 l		
4	140	−161
3	214	223
2	103	90
1	97	104
0	377	−373
−1	106	79
−2	103	−60
−3	224	185
−4	220	−186
3 9 l		
2	71	62
1	151	−148
0	157	123
−1	62	−52
−2	158	169
−3	166	−174
3 10 l		
3	181	190
2	309	358
1	207	−203
0	336	−294
−1	269	−267
−2	208	193
−3	170	171
3 11 l		
2	261	310
0	267	261
−1	153	−150
3 12 l		
0	288	−263
4 0 l		
5	340	400
3	130	−109
2	612	−683
1	485	459
0	572	−556
−1	627	995
−2	849	−1028
−3	804	−873
−4	140	−134
−5	378	348
4 1 l		
4	219	215
3	230	198
2	262	−223
1	346	−320
0	275	−268
−1	231	−188
−2	433	431
−3	534	−486
−4	224	−208
4 2 l		
5	125	139
3	173	−131
2	546	−450
0	351	334
−1	155	160
−2	160	−162
−3	312	−269
−5	459	346
4 3 l		
5	120	−150
4	238	256
3	284	273
2	120	−114
1	810	−861
0	145	−107
−1	525	513
−2	201	203
−3	184	−169
−4	793	−721
−6	100	96
4 4 l		
5	94	−79
3	217	193
1	244	233
−1	90	92
−2	191	155
−3	460	405
−4	136	179
−5	168	−154
−6	155	183
4 5 l		
[illegible]	134	−154
3	241	255
1	562	−563
0	203	250
−1	445	407
−2	330	289
−3	201	−169
−4	226	−149
4 6 l		
5	200	−231
3	207	174
2	654	657
0	436	−223
−1	414	−376
−2	340	343
−3	362	321
−5	347	−350
4 7 l		
4	123	98
2	135	147
−1	120	−83
−3	107	156
−5	251	250
4 8 l		
4	168	−161
2	145	154
1	130	−114
0	485	−445
−1	306	−284
−2	160	168
−3	354	308
−4	181	−163
−5	151	−180
4 9 l		
3	235	−240
2	105	102
1	302	309
0	152	130
−1	389	−359
−2	148	−131
−3	250	239
−4	102	98
4 10 l		
3	145	−161
1	128	−115
4 11 l		
1	355	349
−1	207	−188
4 12 l		
0	405	386
5 1 l		
3	327	273
2	302	−302
1	560	−541
−1	414	445
−2	326	352
−3	232	−202
5 2 l		
3	382	296
2	772	754
1	231	217
0	284	−308
−1	144	−147
−2	161	183
−3	353	296
5 3 l		
1	150	−158
0	163	−141
−1	112	74
−2	204	209
−3	297	217
5 4 l		
2	725	748
1	116	82
0	269	−281
−1	138	−156
−2	445	473
−3	426	469
5 5 l		
2	155	166
1	603	643
0	196	−167
−1	244	−255
−2	409	−421
−3	188	170
5 6 l		
1	340	−314
0	87	−78
−1	477	−436
−2	298	290
−3	244	209
5 7 l		
3	228	−225
2	245	223
1	261	223
0	355	322
−1	347	−392
−2	463	−461
5 8 l		
3	229	−234
2	372	−325
0	171	160
−1	75	−65
−2	231	−220
−3	205	−211
5 9 l		
3	159	−264
−2	145	−95
5 10 l		
2	181	−193
1	117	110
0	445	377
−1	317	306
−2	435	−255
−3	285	−347
5 11 l		
1	126	−113
−2	282	295
6 0 l		
3	402	443
2	780	915
1	90	111
0	414	−427
−1	612	−540
−3	782	755
6 1 l		
1	97	56
−1	296	−275
−2	261	−254
−3	384	355
6 2 l		
2	363	341
1	155	−140
0	163	−157
−1	287	−275
−2	339	−366
−3	364	273
6 3 l		
3	504	−414
1	143	164
0	585	538
−1	757	−796
−2	102	−150
−3	381	364
6 4 l		
3	375	−317
2	322	−304
1	299	−254
0	200	184
−1	420	417
−2	170	−163
6 5 l		
3	353	−310
1	431	424
0	185	188
−1	155	−155
−2	305	−301
6 6 l		
2	398	−354
0	422	371
−1	119	100
−2	234	−250
−3	612	−557
6 7 l		
1	135	−102
0	70	−61
−1	84	40
6 8 l		
2	226	−223
1	286	254
−1	120	129
−3	341	−311
6 9 l		
1	221	−220
0	121	−106
−1	198	142
−2	205	309
6 11 l		
−2	324	316
7 1 l		
3	380	−353
2	335	307
1	279	−277
0	108	92
−1	234	−305
−2	521	−511
7 2 l		
3	128	−182
2	500	−494
−1	474	471
−3	512	−492
7 3 l		
0	253	220
−1	275	−217
−2	135	148
7 4 l		
2	341	−361
1	190	−184
0	544	500
−1	337	355
−2	361	−281
−3	347	−351
7 5 l		
1	312	−242
−1	207	235
−2	344	274
7 6 l		
−2	254	−134
7 7 l		
3	457	501
1	317	−233
−1	349	307
−2	402	334
7 8 l		
2	248	247
−1	242	−274
−2	282	270
7 9 l		
1	88	−94
0	138	−148
−1	225	139
7 10 l		
1	213	222
0	276	−325
−1	77	−73
−2	153	202
−3	272	152
7 11 l		
−1	175	−156
8 0 l		
3	256	−324
2	236	−260
0	820	805
−3	739	−662
8 1 l		
3	284	268
1	178	−135
0	211	−208
−1	145	138
−3	213	135
8 2 l		
2	288	−255
0	297	265
−1	282	284
−3	342	−263
8 3 l		
2	403	414
1	224	−210
0	204	−276
−1	215	193
−2	467	496
−3	449	−219
8 4 l		
1	177	−136
0	373	−357
−1	123	−107
−2	165	157
8 5 l		
3	229	190
0	249	−231
−1	335	312
−2	379	394
8 6 l		
3	294	268
2	277	264
1	142	138
0	546	−481
−1	312	−209
−3	360	331
8 7 l		
2	257	−270
−1	124	−95
8 8 l		
2	287	315
−1	99	−115
−3	232	210
8 9 l		
1	125	140
−1	127	−148
−2	312	−354
9 1 l		
1	286	−300
0	232	−296
−1	321	317
−2	445	524
9 2 l		
0	235	−316
−1	412	−409
−2	242	224
−3	470	431
9 3 l		
−1	143	221
9 4 l		
3	234	225
1	233	218
0	146	−161
−1	400	−383
−2	171	194
−3	251	242
9 5 l		
0	335	292
−1	497	−438
−2	162	−350
9 6 l		
2	136	249
1	207	108
0	64	−84
−1	143	73
9 7 l		
1	322	393
−1	274	−245
−2	345	−315
9 8 l		
−1	123	−93
9 9 l		
0	151	156
10 0 l		
0	473	−474
−1	457	−450
−2	203	222
−3	220	224
10 1 l		
−1	117	−62
−2	220	−201
−3	132	−83
10 2 l		
1	170	172
0	256	−239
−1	213	−171
−3	261	251
10 3 l		
1	233	227
−1	105	−72
−2	555	−543
−3	128	−73
10 4 l		
1	91	108
0	213	219
−3	236	−237
10 5 l		
1	189	192
0	289	270
−1	130	−154
−2	231	−261
−3	117	148
10 6 l		
1	97	−108
0	236	257
−1	314	325
−2	215	−263
−3	106	−259
10 7 l		
−2	126	164
10 8 l		
−1	221	194
−2	123	−138
11 1 l		
1	256	283
0	244	219
−1	412	−456
−2	407	−417
11 2 l		
1	241	−262
0	217	229
11 3 l		
0	105	114
−1	251	220
11 4 l		
0	100	128
−1	344	339
−2	137	−126
11 5 l		
1	157	−167
0	261	−214
−1	256	256
−2	322	375
11 6 l		
0	178	175
−1	204	150
11 7 l		
−1	153	140
−2	176	174
12 0 l		
−1	470	440
−2	248	−230
12 1 l		
0	104	−78
−1	82	83
−2	196	237
12 2 l		
0	243	155
−1	306	274
−2	112	−81
12 3 l		
−1	164	188
−2	159	209
12 4 l		
−1	178	−134
13 1 l		
−1	124	100
−2	138	165
13 2 l		
−1	[illegible]	−95

Table 2. *Final fractional co-ordinates and standard deviations*

	x/a	y/b	z/c	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
Fe	0·2396	0·4247	0·2053	0·002 Å	0·002 Å	0·003 Å
C_1	−0·373	0·373	0·025	0·014	0·013	0·014
C_2	−0·160	0·399	−0·007	0·013	0·011	0·014
C_3	−0·160	0·304	0·355	0·014	0·012	0·015
C_4	−0·322	0·448	0·418	0·013	0·011	0·016
C_5	−0·251	0·604	0·136	0·015	0·012	0·016
C_6	−0·141	0·579	0·292	0·015	0·013	0·016
C_7	−0·128	0·608	0·513	0·015	0·012	0·016
O_1	−0·459	0·342	−0·090	0·010	0·009	0·010
O_2	−0·117	0·381	−0·136	0·010	0·009	0·010
O_3	−0·110	0·227	0·450	0·009	0·008	0·010
O_4	−0·369	0·456	0·541	0·012	0·010	0·012
N	−0·114	0·634	0·697	0·012	0·011	0·013

dimensional Fourier synthesis was calculated with a programme written by Pilling, Lovell & Bujosa (Cruickshank *et al.*, 1961). The four carbonyl groups were easily identified and there were five other peaks of 4–5 e.Å^{-3}. As there are only four atoms in acrylonitrile one of these peaks was spurious; to determine which, and also to find which peak represented a nitrogen atom, a cycle of least-squares refinement was carried out. The co-ordinates of all five positions were taken as those of carbon atoms, which, with the iron atom and the four carbonyl groups, were included in the structure-factor calculation. The scattering factor of Watson & Freeman (1961) was used for Fe and of Berghuis *et al.* (1955) for carbon and oxygen with isotropic temperature factors corresponding to mean square amplitudes of vibration of 0·02 Å^2 for iron and 0·03 Å^2 for the other atoms. R was 0·36 and large shifts in the temperature factors of two of the five 'carbon' atoms identified the spurious and the nitrogen atoms. The structure is depicted in Figs. 1 and 2 in projection along [001] and [100] respectively.

Refinement

Refinement was carried out by the method of least squares with a programme written by Cruickshank & Pilling (1961). After 3 cycles of isotropic refinement the isotropic vibration parameter for iron (0·018 Å^2) was greater than that of some of the light atoms, an effect which seemed attributable to neglect of the effect of anomalous dispersion. The real contribution of the anomalous dispersion, 3·8*e*, was subtracted from the scattering factor for iron and another cycle of refinement carried out; this gave a vibration parameter of 0·0023 Å^2 for iron compared with 0·012 Å^2, the smallest value for a carbon atom. A three-dimensional difference synthesis also indicated that the scattering factor of iron was now too low, and so an anomalous dispersion correction of 2 electrons was used; this proved satisfactory for 2 cycles of isotropic and 5 cycles of anisotropic refinement. Refinement was complete when the largest shift in a parameter was 0·3 times the corresponding standard deviation. To check the scattering factor of iron a final difference section was calculated and showed a small trough of $-\frac{1}{4}$ e.Å^{-3} at this position and zero at the positions of the carbonyl carbon atoms. The final observed and calculated structure factors are shown in Table 1; for these $R_{hkl} = 0{\cdot}094$.

In the least-squares refinement the function minimized was $R' = \Sigma w(|F_o| - |F_c|)^2$ where the weighting factor w was

$$1/\{6{\cdot}66 + |F_o| + 0{\cdot}00625|F_o|^2\};$$

this made the average value of R' for a set of planes within a range of $|F_o|$ approximately constant for all ranges of $|F_o|$. An approximate scale factor had been obtained from a Wilson plot for the *hk*0 projection and the scale factor was one of the parameters in the refinement.

In Table 2 the atomic co-ordinates and their standard deviations are given. Table 3 shows the final values, referred to the monoclinic crystal axes, for the tensor components describing the anisotropic vibration of the atoms; the standard deviations calculated in the least squares refinement are also shown. The tensor components U_{ij} are those occurring in the temperature factor

$$\exp\left(-2\pi^2(h^2a^{*2}U_{11} + 2hka^*b^*U_{12} + \ldots)\right),$$

so that, for instance, U_{11} is the mean-square amplitude of vibration of the atom parallel to the a^* axis.

Although the vibration parameters are small, an analysis of the thermal motion was carried out with a programme written by Bujosa & Cruickshank

Table 3. *Thermal parameters*

(× 10^3 Å^2)

	U_{11}	σ	U_{22}	σ	U_{33}	σ	U_{12}	σ	U_{23}	σ	U_{13}	σ
Fe	4	1	13	1	15	1	−1	1	1	1	4	1
C_1	2	7	25	7	8	7	8	6	7	6	11	7
C_2	0	6	9	6	9	7	−4	5	−1	5	−6	7
C_3	7	7	12	6	21	8	−4	5	−12	5	−9	7
C_4	0	6	9	6	18	8	10	5	0	5	−3	7
C_5	15	7	4	6	30	9	2	5	−2	5	−3	8
C_6	19	7	15	7	23	9	1	6	−17	6	14	8
C_7	20	7	3	6	32	9	5	5	8	6	23	8
O_1	10	5	31	5	15	5	−7	4	3	4	−7	5
O_2	17	5	21	5	12	5	5	4	−1	4	14	5
O_3	14	5	9	4	25	6	6	4	3	4	3	5
O_4	34	6	24	5	40	7	1	5	−2	5	25	7
N	12	6	18	6	20	7	5	5	5	5	7	6

(Cruickshank, 1956; Cruickshank *et al.*, 1961). The results showed that the assumption that the molecule moved as a rigid body was justified within experimental error, a particularly satisfactory result in view of the uncertainty in the correction for the anomalous dispersion of the iron atom. As shown in Table 4, most of the motion was translational, so that very small corrections in the co-ordinates would be required to allow for the systematic error due to rotational oscillation; these corrections were calculated by Cruickshank's improved procedure (1961) and the largest change in a co-ordinate was 0·003 Å (in x for O_4). In Table 5 the corrected co-ordinates are shown in Å, X', Y and Z' being measured with respect to orthogonal axes parallel to a, b and c^*.

Table 4. *Principal axes of the translational and rotational tensors with respect to orthogonal axes parallel to the crystallographic a, b and c* axes*

Mean square amplitude of translation	Direction cosines		
0·004 Å²	−0·935	0·253	−0·249
0·018	−0·228	0·108	0·968
0·013	0·271	0·962	−0·044
Root mean square angular oscillation			
0°	−0·979	0·168	−0·120
2·6	−0·023	0·489	0·872
2·1	0·205	0·856	−0·474

Table 5. *Corrected atomic co-ordinates with respect to orthogonal axes*

	X'	Y	Z'
Fe	−3·367 Å	4·862 Å	1·267 Å
C_1	−4·570	4·269	0·151
C_2	−1·915	4·566	−0·045
C_3	−2·745	3·480	2·193
C_4	−4·856	5·127	2·577
C_5	−3·345	6·914	0·835
C_6	−2·376	6·628	1·803
C_7	−2·723	6·960	3·166
O_1	−5·342	3·912	−0·555
O_2	−1·098	4·368	−0·839
O_3	−2·364	2·592	2·780
O_4	−5·707	5·222	3·339
N	−2·974	7·261	4·302

Dimensions of the molecule

The molecule is monomeric and consists of five ligands arranged about the iron in the form of a trigonal bipyramid as depicted in Fig. 3. The bond lengths and angles were calculated from the corrected co-ordinates as given by the computer to four decimal places, not from the rounded-off values in Table 5. The bond lengths are shown in Fig. 3. Their standard deviations are 0·012–0·014 Å for Fe–C, 0·016–0·019 Å for C–O, 0·020 Å for C–N and 0·022 Å for C–C. The bond angles and their standard deviations are shown in Table 6. The equatorial plane of the trigonal bipyramid contains the iron atom, C_1, O_1, C_3 and O_3 and the two carbon atoms, C_5 and C_6 which constitute one ligand; the equation of the plane is

$$0·704X' - 0·157Y' - 0·693Z' + 3·999 = 0$$

and the maximum deviation from it is +0·038 Å for C_6.

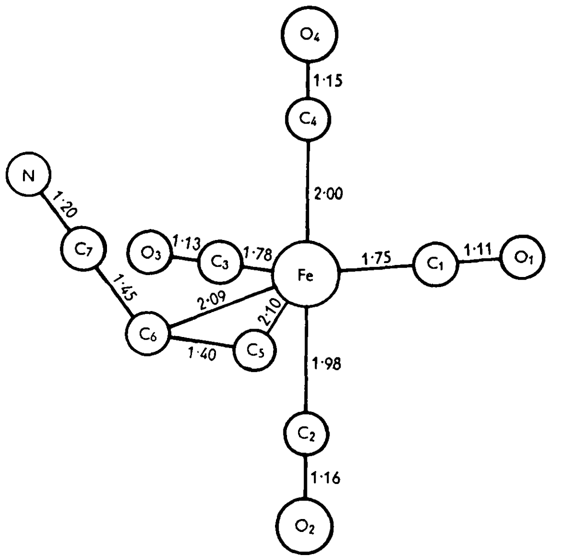

Fig. 3. The bond lengths, Å in tetracarbonyl(acrylonitrile) iron.

The acrylonitrile group is also planar, the equation is

$$0·405X' + 0·905Y' - 0·132Z' - 4·790 = 0\,.$$

It is not parallel to the O_4–O_2 axis of the trigonal bipyramid, the angle between this axis and the normal to the plane being 76·4°. Probably this represents an equilibrium between the repulsion between N and O_4 which are separated by 3·54 Å and the attraction between the π bond system and the iron.

Discussion

The structure consists of monomeric molecules held only by van der Waals forces and so accounts for the high volatility of the solid. All the intermolecular separations of less than 3·5 Å were calculated; there were no abnormally short values, and the more important ones are shown in Figs. 1 and 2.

As predicted by Kettle & Orgel (1960) from a study of the infra-red spectrum, only the olefine group of the acrylonitrile molecule is co-ordinated to the iron. The dimensions of the uncomplexed molecule, determined spectroscopically (Costain & Stoicheff, 1959), are C : C = 1·339, C–C = 1·426, C : N = 1·164 Å, $C\text{–}\hat{C}\text{–}C = 122° 37'$, and C–C–N was assumed to be linear. Formation of the complex has resulted in two significant changes; the bond length of the olefinic bond has increased by 3 times the standard deviation to 1·40 Å, and the C–C–C angle has been reduced by 6 times the standard deviation to 116°. A similar increase in bond length has been found in other olefine complexes (e.g. Alderman, Owston & Rowe, 1960). The observed increase in the olefine bond length is in agreement with the theory that the olefine–metal bonding consists of a σ-bond formed between electrons in the filled π bonding orbital on the olefine and an empty orbital on the metal, and of a π-bond formed between electrons in a filled orbital on the metal and an empty anti-bonding orbital on the ligand. The geometry of the molecule indicates that both these orbitals on the iron atom lie in the equatorial plane. Bond angles can be affected by environmental factors as well as by the hybridization ratio on the central atoms. In this structure there does not seem to be an environmental factor favouring a decrease in the $C\text{–}\hat{C}\text{–}C$ angle, so that it may be attributed to a change in the hybridization ratio which now includes a larger proportion of p character in the carbon–carbon bonds.

The four independent C–O bond lengths do not differ significantly from their mean value 1·13 Å which is the same as that in carbon monoxide. The Fe–C–O groups are all linear.

Table 6. *Bond angles and their standard deviations*

$C_5\text{–}Fe\text{–}C_1$	102·0°	±0·6°	$Fe\text{–}C_1\text{–}O_1$	179°	±1°
$C_1\text{–}Fe\text{–}C_3$	108·1		$Fe\text{–}C_2\text{–}O_2$	178	
$C_3\text{–}Fe\text{–}C_6$	110·9		$Fe\text{–}C_3\text{–}O_3$	179	
$C_6\text{–}Fe\text{–}C_5$	39·0		$Fe\text{–}C_4\text{–}O_4$	177	
$C_2\text{–}Fe\text{–}C_1$	91·8	±0·6°	$Fe\text{–}C_5\text{–}C_6$	70·4	±0·7°
$C_2\text{–}Fe\text{–}C_3$	88·4		$Fe\text{–}C_6\text{–}C_5$	70·6	
$C_2\text{–}Fe\text{–}C_5$	90·1				
$C_2\text{–}Fe\text{–}C_6$	87·0		$C_5\text{–}C_6\text{–}C_7$	116	±1°
$C_4\text{–}Fe\text{–}C_1$	87·2				
$C_4\text{–}Fe\text{–}C_3$	91·3		$C_6\text{–}C_7\text{–}N$	178	±1°
$C_4\text{–}Fe\text{–}C_5$	90·7				
$C_4\text{–}Fe\text{–}C_6$	94·2				

If the centre of the olefine bond is considered as one ligand position, the iron atom is surrounded by five ligands at the corners of an approximately trigonal bipyramid. In the equatorial plane, the observed bond angles (Table 6) differ from the 'ideal' values, $C_1\text{–}Fe\text{–}C_3 = 120°$ and $C_5\text{–}Fe\text{–}C_1 = C_6\text{–}Fe\text{–}C_3 = 100{\cdot}5°$, in a direction which suggests that the $Fe\text{–}C_3\text{–}O_3$ bond is repelled by the cyanide group. If the five bonding orbitals on the iron are formed by hybridization of the $3d_{z^2}$, the $4s$ and the three $4p$ orbitals, the configuration predicted (Kimball, 1940) is a trigonal bipyramid, as we have found; further, this hybridization should lead to longer apical than equatorial bonds in agreement with our observation for the Fe–carbonyl carbon bonds: apical = 1·99 ± 0·01 Å, equatorial = 1·76 ± 0·01 Å. (As the 'trigonal' axis lies almost along the [10$\bar{1}$] axis of the crystal, see Fig. 4, the bond lengths are sensitive to errors in β. For example if β is reduced by 1° the apical bond length decreases by 0·02 Å, but the observed difference in the two kinds of bond length is 0·23 Å which is highly significant.)

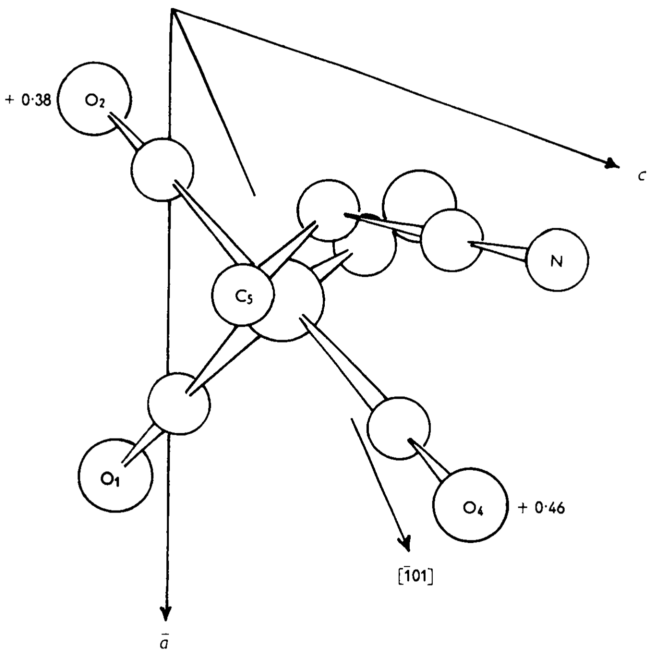

Fig. 4. One molecule viewed down the [010] axis showing the relation between the $O_2\text{–}Fe\text{–}O_4$ direction and [$\bar{1}$01]. The fractional y co-ordinates of O_2 and O_4 are marked.

This is the second compound of iron in which a trigonal bipyramidal configuration has been found; the first was iron pentacarbonyl which was investigated by electron diffraction by Ewens & Lister (1939). In that determination the bond lengths were assumed to be equal, the mean value being 1·84 ± 0·03 Å, which is in agreement with our mean value of 1·85 Å (two lengths of 1·99 Å and three of 1·76 Å). Although the observed dipole moment and some interpretations of the infra-red spectrum have since favoured a tetragonal-pyramidal configuration for iron pentacarbonyl, Cotton & Parish (1960) in the most recent survey of the evidence consider a trigonal bipyramid to be more probable. They also, on the basis of the infra-red spectra of a number of complexes $L\text{Fe(CO)}_4$ (where L is Ph_3P, $CH_3.NC$, C_2H_5NC, C_6H_5NC) deduce that these five-co-ordinated complexes are based on a trigonal bipyramid with L in the apical position. Our results support the view that five-co-ordinate Fe(O) compounds are trigonal bipyramids but in our compound (with $L = CH_2 : CH.C \vdots N$) the substitution is equatorial. It should be possible to distinguish between apical and equatorial substitution from the infra-red spectra, the former giving rise to 3 and the latter to 4 carbonyl stretching frequencies. Kettle & Orgel reported a weak peak at 2226 cm.$^{-1}$ (the normal $C \vdots N$ region) and a medium one at 2110 cm.$^{-1}$ and two strong peaks one with an almost resolved shoulder in the 2050–1950 cm.$^{-1}$ region; it thus appears that, as predicted, there are four peaks in the carbonyl region 2110–1950 cm.$^{-1}$, the one at 2110 cm.$^{-1}$ corresponding to a particularly strong C–O bond.

Two factors other than the hybridization of the

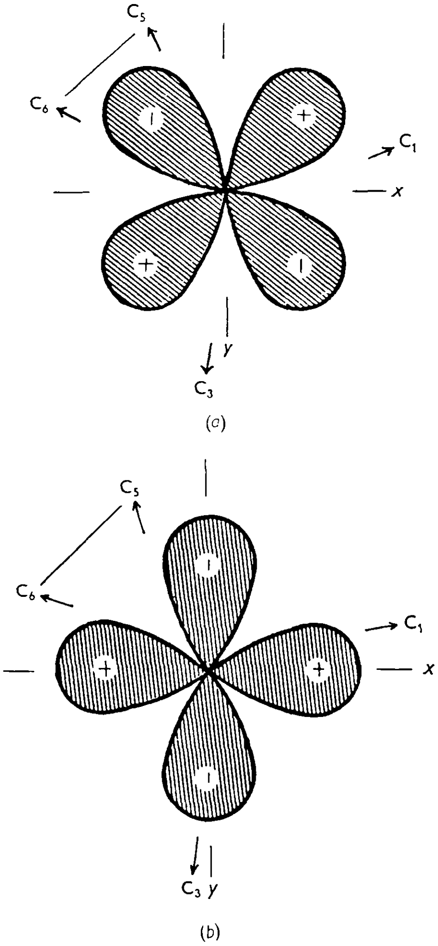

Fig. 5. The equatorial plane showing the suggested orientation of (*a*) the d_{xy} and (*b*) the $d_{x^2-y^2}$ orbitals with respect to the ligands.

iron should affect the Fe–C bond lengths, ligand field repulsion and π-bonding; both arise from the filled orbitals on the iron, d_{xz}, d_{yz}, d_{xy} and $d_{x^2-y^2}$. The z direction is that of the O_2–C_2–Fe–C_4–O_4 so that there is no filled orbital directed towards these two carbonyl groups and both the d_{xz} and d_{yz} orbitals have the correct symmetry for the formation of π-bonds. Comparison with the equatorial plane shows that both factors should tend to favour longer equatorial than apical bonds. In the equatorial plane it is not possible to choose directions for x and y such that there is no filled d_{xy} or $d_{x^2-y^2}$ orbital pointing towards a ligand. The arrangement which would give the best opportunity for π-bonding is shown in Fig. 5; this allows the d_{xz} and d_{yz} orbitals to form π bonds with C_1 and C_3 respectively while the d_{xy} orbital can form π bonds with both. Thus there would be two π bonds to each carbonyl as for C_2 and C_4 but the geometry is somewhat less favourable for overlap and so a longer Fe–C bond would be predicted. The electrons in the filled $d_{x^2-y^2}$ orbital should tend to repel C_1 and C_3, again giving a longer equatorial bond. Nevertheless, the observed equatorial bond lengths are significantly shorter than the axial ones indicating that the hybridization effect is of over-riding importance.

So far it has not been possible to discover whether the radius of iron in compounds containing iron–carbon bonds varies with the oxidation state of the iron. The results of Hock & Mills (1961) for $Fe_2(CO)_6MeC:CMe$ suggest that the difference must be small; their mean Fe(O)–CO bond length is 1·766 Å while the mean Fe(II)–CO bond length is 1·784 Å. These are comparable with the corresponding equatorial bond lengths. The iron–olefine carbon bond lengths are not significantly different from the Fe(O)-π-bond carbon, 2·13 ± 0·01 Å, found by Hock & Mills (1961) or even the Fe(II)-π-bond carbon in ferrocene 2·05 ± 0·02 Å (Dunitz, Orgel & Rich, 1956). The arrangement in Fig. 5 shows the $d_{x^2-y^2}$ orbital with the correct symmetry to form a π bond to an empty orbital on the olefine.

The system of orbital directions in Fig. 5, chosen to give optimum π-bonding in the observed configuration, also gives more π-bonding than could be attained if the acrylonitrile were attached in an apical position; this may account for the preferred equatorial substitution.

We are grateful to Dr Kettle for giving us the compound, to our colleagues (Cruickshank *et al.*, 1961) for the use of their programmes and to the Director of the Leeds University Computing Laboratory for the use of the computer. One of us (A. R. L.) thanks the D.S.I.R. for a Studentship. Some of the apparatus was provided by the Royal Society and Imperial Chemical Industries Ltd.

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