TABLE VIII
INTERMOLECULAR DISTANCES[a]

Atom A	Equiv position	Translation	Atom B	Distance A–B, Å
H9	2	0, 0, 1	H11	2.54
H9	2	0, 0, 1	H12	2.44
H9	2	0, 0, 1	H13	2.54
H9	1	1, 0, 0	H7	2.71
H10	1	1, 0, 0	H7	2.50
H11	2	0, 0, 1	H11	2.65
H12	2	1, 0, 1	H8	2.66
H2	1	−1, 0, 0	H4	2.48
H3	2	1, 0, 0	H21	2.78
H4	2	0, 0, 0	H21	2.76
H4	1	1, 0, 0	H7	2.79
C*M*1	2	0, 0, 1	H9	2.75
O*A*1	1	−1, 0, 0	H5	2.58
O*A*1	1	−1, 0, 0	H11	2.88
O*A*1	2	1, 0, 0	H8	2.67
O*A*1	3	1, 1, 1	H22	2.91
C*R*9	1	1, 0, 0	H7	2.99
O*A*2	1	−1, 0, 0	H4	2.96
O*A*2	1	−1, 0, 0	H10	2.72
O*A*2	2	1, 0, 0	H3	2.67
O*A*2	3	1, 0, 1	H13	2.67
C*R*4	1	1, 0, 0	H2	2.99
O*A*1	3	1, 1, 1	C*A*2	3.168
O*A*1	3	1, 1, 1	C*M*2	3.39

[a] The interatomic distance is from A in the equivalent position specified to B in position 1. The code is 1 is x, y, z; 2 is $-x$, $-y$, $-z$; 3 is $-x$, $-1/2 + y$, $-1/2 - z$, with the unit translations given with respect to x, y, and z.

square displacement is approximately normal to the plane of the ring, with the largest displacement usually in the plane of the ring. Hence the displacements are in agreement with an oscillation of the rings about the ring centers. In the acetyl groups the largest mean-square displacement is normal to the plane of the acetyl group, in agreement with a wagging motion about the corresponding C–C bond. The fact that the mean-square displacements are in excellent agreement with the expected molecular vibrations suggests that absorption errors are minimal and that the integrated intensity was indeed measured in the data collection process.

All the interatomic distances less than 3.5 Å were calculated and surveyed for any unusual interactions. The H–H contacts less than 2.8 Å together with the H–heavy atom contacts less than 3.0 Å and heavy atom–heavy atom contacts less than 3.4 Å are tabulated in Table VIII. Assuming the usual van der Waals radii,[12] the shortest contacts are simply van der Waals contacts between the appropriate atoms.

Acknowledgments.—The author wishes to thank the National Research Council of Canada and the U. S. Naval Weapons Center for financial support of this research.

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Crystallographic Studies on Sulfur Dioxide Insertion Compounds. I. The Butadieneiron Tricarbonyl–Sulfur Dioxide–Boron Trifluoride Adduct

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The reaction of BF_3 gas with a solution of butadieneiron tricarbonyl in SO_2 has been shown to give rise to a compound of stoichiometry $C_4H_6Fe(CO)_3 \cdot SO_2 \cdot BF_3$. The structure of this species has been elucidated by single-crystal X-ray diffraction studies. The compound crystallizes in the noncentrosymmetric monoclinic space group $P2_1$ (C_2^2; no. 4) with $a = 6.583 \pm 0.011$ Å, $b = 11.782 \pm 0.023$ Å, $c = 7.401 \pm 0.009$ Å, $\beta = 92.41 \pm 0.06°$, $Z = 2$, $\rho_{\text{calcd}} = 1.886$ g cm^{-3}, and $\rho_{\text{obsd}} = 1.79 \pm 0.05$ g cm^{-3}. Intensity data complete to $\sin \theta = 0.40$ (Mo Kα radiation) were collected on a 0.01°-incrementing Supper-Pace Buerger automated diffractometer, and the structure was solved using Patterson, Fourier, and least-squares refinement techniques; all nonhydrogen atoms were located accurately, the final discrepancy index being $R_F = 6.60\%$ for the 813 independent, nonzero reflections. The inserted sulfur dioxide molecule is S bonded to a terminal methylene group of the modified butadiene ligand (which, now, is involved in a π-allyl$\rightarrow$Fe(CO)$_3$ linkage) and is O bonded to the central iron atom. The remaining oxygen of the SO_2 moiety is linked to the boron atom of a BF_3 molecule.

Introduction

Transition metal complexes containing sulfur dioxide as a ligand are well known;[2] infrared and X-ray diffraction studies[3] have shown that the SO_2 molecule bonds to the metal through its sulfur atom.

Wojcicki and coworkers have systematically investigated SO_2 as an insertion ligand and have shown that it inserts into a metal–alkyl or metal–aryl bond (M–R) to produce an *S*-sulfinate[4–10]

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(1) Fellow of the Alfred P. Sloan Foundation, 1968–1970.

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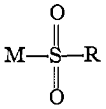
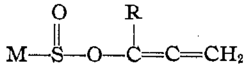


$M{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}R$

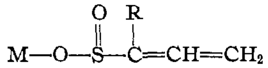
This structural type has been confirmed by an X-ray crystallographic study on *cis*-$(CH_3SO_2)Mn(CO)_3$bipy.[11]

Sulfur dioxide also inserts into σ-allyl complexes of the transition metals, but insertion is often accompanied by allylic rearrangement (*viz.*, $MCH_2CH{=}CR_2 + SO_2 \rightarrow MSO_2CR_2CH{=}CH_2$);[12,13] crystallographic studies on products of this type of reaction are currently in progress.[14] The insertion of SO$_2$ into 2-alkynylmetal complexes ($MCH_2C{\equiv}CR$) has variously been interpreted as yielding allenyl(oxy)sulfinyl[15]



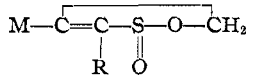
$M{-}\overset{\overset{O}{\|}}{S}{-}O{-}\overset{\overset{R}{|}}{C}{=}C{=}CH_2$

or allenyl-*O*-sulfinate[16]



$M{-}O{-}\overset{\overset{O}{\|}}{S}{-}\overset{\overset{R}{|}}{C}{=}CH{=}CH_2$

derivatives; recent crystallographic studies, however' show this product to be a sultine, *i.e.*,[17]



$M{-}\underset{\underset{R}{|}}{C}{=}C{-}\underset{\underset{O}{\|}}{S}{-}O{-}CH_2$

The title compound, $C_4H_6Fe(CO)_3\cdot SO_2\cdot BF_3$, represents a novel type of SO$_2$ insertion product. It was prepared by the reaction of an SO$_2$ solution of butadieneiron tricarbonyl with BF$_3$ gas at −30° under nitrogen.[18] The ^{1}H nmr spectrum indicated that the π-bonded butadiene system had been attacked by SO$_2$, and a single-crystal X-ray diffraction study was undertaken to elucidate the precise nature of the product. A preliminary account of this work has appeared elsewhere.[18]

Unit Cell and Space Group

Crystals suitable for X-ray diffraction studies were supplied to us by Professor H. D. Kaesz of the University of California at Los Angeles. They had been grown under nitrogen from a 1:2 nitromethane–dichloromethane solution at an *n*-hexane interface.[18] They form yellow needlelike parallelepipeds, crystallizing in the monoclinic system.

Examination of $h0l$ and $h1l$ Weissenberg and $0kl$, $1kl$, $hk0$, and $hk1$ precession photographs revealed the systematic absence $0k0$ for $k = 2n + 1$ (only), consistent with space groups $P2_1$ (C_2^2; no. 4) or $P2_1/m$ (C_{2h}^2; no. 11).[19] [The successful solution of the crystal structure, *vide infra*, shows the noncentrosymmetric $P2_1$ to be the correct space group.]

Unit cell parameters, determined by a least-squares analysis of high-angle reflections on zero-layer precession photographs taken at ambient temperature (~24°) and calibrated with $Pb(NO_3)_2$ ($a_{24°} = 7.8566$ Å), are $a = 6.583 \pm 0.011$ Å, $b = 11.782 \pm 0.023$ Å, $c = 7.401 \pm 0.009$ Å, and $\beta = 92.41 \pm 0.06°$. The unit cell volume is 573.4 Å^3. The observed density ($\rho_{obsd} = 1.79 \pm 0.05$ g cm^{-3}, by flotation in bromoform–hexane[20]) is consistent with that calculated for mol wt 325.84 and $Z = 2$ ($\rho_{calcd} = 1.886$ g cm^{-3}).

Data Collection and Reduction

Intensity data were collected on a 0.01°-incrementing Supper-Pace Buerger automated diffractometer, using a stationary-background, ω-scan, stationary-background counting technique.

Details specific to the present analysis include the following. (i) Mo Kα radiation ($\bar{\lambda}$ 0.7107 Å) was used. (ii) Scan angle (ω) is $[2.0 + (1.0/L)]°$, where $1/L$ is the Lorentz factor. (iii) Scan speed ($d\omega/dt$) is 2°/min. (iv) Initial and final backgrounds, $B_1(hkl)$ and $B_2(hkl)$, were each counted for one-fourth the time required for the appropriate ω scan. (v) $I(hkl)$, the net intensity of the reflection hkl, was calculated as $I(hkl) = \{C(hkl) - 2[B_1(hkl) + B_2(hkl)]\}$, where $C(hkl)$ is the count associated with the ω scan. All remaining details and experimental precautions were as described in a previous publication.[21]

Data were collected from a single crystal of dimensions 0.34 × 0.64 × 0.10 mm (referred to $10\bar{1}$, 010, and 101). Using equiinclination Weissenberg geometry, data complete to $\sin\theta = 0.40$[22] (*i.e.*, quadrants hkl and $hk\bar{l}$ of levels $h0$–$13l$) were collected with the crystal mounted on its b axis, and data for quadrants hkl and $hk\bar{l}$ of levels $0kl$–$4kl$ were collected with the crystal now remounted along its a direction.

Data were assigned deviations according to the following scheme, where $\delta(hkl) = 3[C(hkl) + 4B_1(hkl) + 4B_2(hkl)]^{1/2}$: $I(hkl) > 4900$, $\sigma\{I(hkl)\} = 0.1[I(hkl)]$; $4900 \geqslant I(hkl) > \delta(hkl)$, $\sigma\{I(hkl)\} = 7.0[I(hkl)]^{1/2}$; $\delta(hkl) \geqslant I(hkl)$, reflection rejected as being not significantly above background.

Of 1034 reflections collected from the b mounting, 118 were rejected; of the 937 reflections from the a mounting, 182 were rejected. All data were corrected for Lorentz and polarization effects, and absorption corrections were made ($\mu = 15.76$ cm^{-1}) using the Gaussian quadrature numerical integration technique for a crystal of essentially arbitrary shape.[23] Transmission factors ranged from 0.6161 to 0.8490 for the b mounting and from 0.4226 to 0.8041 for the a mounting (the crystal volume was 0.0223 mm^3).

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(20) Density measurement was performed by D. A. T. Young at the University of California at Los Angeles.

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(22) This is the limit of observable reflections on long-exposure Weissenberg photographs. Data in the range $0 < \theta \leq 4°$ were not collected due to interference with low-angle diffracted beams by the lead backstop on the diffractometer.

(23) Using a local version of the IBM 7094 program GNABS: C. W. Burnham, *Amer. Mineral.*, **51**, 159 (1966).

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTOR AMPLITUDES (IN ELECTRONS × 10.00) FOR $C_4H_6Fe(CO)_3 \cdot SO_2 \cdot BF_3$[a]

K	L	FO	FC
****************			
H = -7			
0	1	153	161
0	2	105	107
0	3	79	82
1	1	104	93
1	2	85	77
2	1	137	143
2	2	83	72
3	2	175	35
****************			
H = -6			
0	1	80	91
0	2	75	92
0	4	114	108
0	5	116	97
1	1	102	123
1	2	98	93
1	3	65	59
1	4	95	102
1	5	79	58
2	1	119	134
2	2	115	85
2	3	144	127
2	4	97	79
2	5	72	66
3	1	74	59
3	2	123	167
3	4	113	133
4	1	154	157
4	2	140	26
4	3	153	143
5	1	54	63
5	2	58	62
5	4	116	120
6	1	121	123
6	2	53	49
7	2	139	140
****************			
H = -5			
0	1	96	120
0	2	135	143
0	3	217	235
0	4	169	191
0	5	176	171
0	6	75	59
1	1	203	211
1	2	164	173
1	3	136	131
1	4	112	121
1	5	141	135
1	6	91	78
2	1	199	203
2	2	203	188
2	3	101	114
2	5	150	161
3	1	226	195
3	2	94	100
3	3	184	194
3	6	98	115
4	1	61	78
4	2	217	216
4	3	67	56
4	4	119	108
4	5	95	103
5	2	103	103
5	3	137	155
5	4	89	87
5	5	152	146
6	1	53	67
6	2	114	124
6	3	57	73
6	4	145	141
7	1	162	169
7	2	115	112
7	3	117	116
7	4	95	91
8	2	132	143
8	3	91	65
9	1	184	188
9	2	59	43
****************			
H = -4			
0	1	565	535
0	2	139	122
0	3	275	241
0	4	100	104
0	5	96	86
0	6	199	191
0	7	98	45
1	1	233	234
1	2	133	127
1	3	196	190
1	4	188	187
1	5	140	132
1	6	78	72
1	7	103	102
2	1	323	318
2	2	67	69
2	3	164	152
2	4	309	306
2	5	56	60
2	6	192	184
3	1	107	101
3	2	203	211
3	3	233	226
3	5	187	195
3	6	96	71
4	1	271	273
4	2	109	101
4	3	101	137
4	4	243	240
4	5	122	101
4	6	117	126
5	1	121	124
5	2	209	224
5	3	118	119
5	4	65	62
5	5	103	80
6	1	223	232
6	3	130	134
6	4	47	32
6	6	92	56
7	1	94	64
7	2	99	100
7	4	131	128
7	5	65	50
8	1	86	54
8	3	99	87
8	4	102	100
9	2	61	52
9	3	125	99
9	4	89	80
10	1	126	108
10	2	77	46
10	3	86	93
11	1	101	51
****************			
H = -3			
0	1	161	176
0	2	376	361
0	3	59	47
0	4	57	64
0	5	315	319
0	7	95	101
1	1	367	362
1	2	271	262
1	3	174	170
1	4	153	161
1	5	170	174
1	6	204	197
1	7	97	74
2	1	164	171
2	2	120	123
2	3	323	303
2	4	95	100
2	5	265	253
2	6	62	61
2	7	88	80
3	1	97	93
3	2	416	430
3	3	176	182
3	4	302	286
3	5	104	97
3	6	52	7
4	1	353	345
4	2	231	233
4	3	239	234
4	4	138	143
4	5	104	99
4	6	87	95
4	7	89	87
5	1	149	149
5	2	317	334
5	3	101	109
5	4	183	184
5	5	111	108
5	6	145	147
6	1	63	37
6	2	249	250
6	3	95	35
6	4	153	159
6	5	147	150
6	6	105	109
7	1	113	113
7	2	187	193
7	3	113	121
7	4	134	147
7	5	122	118
7	6	149	152
8	1	222	221
8	2	83	79
8	3	209	206
8	4	121	122
8	5	156	152
9	1	91	60
9	2	223	215
9	3	186	179
9	4	152	152
10	1	126	128
10	2	71	72
10	3	155	155
11	1	125	127
11	2	98	98
11	3	48	28
12	1	76	51
****************			
H = -2			
0	1	89	108
0	2	98	70
0	3	88	36
0	4	222	213
0	6	98	92
0	8	60	45
1	1	58	54
1	2	107	96
1	3	329	319
1	4	159	149
1	5	290	278
1	6	86	99
1	8	109	103
2	1	234	235
2	2	53	42
2	3	78	64
2	4	194	190
2	5	120	99
2	6	166	143
2	7	101	77
2	9	76	37
3	1	620	602
3	2	271	273
3	3	312	312
3	4	188	194
3	6	206	197
4	1	448	437
4	2	312	298
4	4	217	223
4	5	73	76
4	6	114	147
4	7	106	94
5	1	236	234
5	2	76	116
5	3	456	458
5	4	86	106
5	5	219	230
5	6	109	119
5	7	109	113
6	1	200	207
6	2	273	268
6	3	165	164
6	4	301	316
6	5	103	87
6	6	156	151
6	7	67	76
7	1	277	284
7	2	261	258
7	3	295	279
7	4	64	60
7	5	170	177
7	6	85	89
8	1	85	82
8	2	287	287
8	3	103	92
8	4	173	175
8	5	96	104
8	6	97	82
9	1	298	307
9	2	105	103
9	3	137	137
9	4	75	80
9	5	79	55
10	1	112	98
10	2	140	153
10	3	73	78
10	4	106	100
10	5	74	55
11	1	61	51
11	2	80	64
11	3	145	130
12	1	74	60
12	2	87	80
****************			
H = -1			
0	2	228	203
0	3	482	441
0	6	65	62
0	7	94	93
0	8	176	181
1	2	440	454
1	3	147	137
1	4	455	446
1	5	202	194
1	6	163	171
1	7	176	199
2	1	702	839
2	2	314	306
2	3	78	97
2	4	400	402
2	5	323	318
2	6	181	179
2	7	107	108
2	8	95	83
3	1	355	345
3	2	464	434
3	3	220	222
3	4	169	160
3	5	265	254
3	6	216	211
3	7	146	157
3	8	81	54
4	1	403	377
4	2	179	186
4	3	206	206
4	4	432	432
4	5	202	205
4	6	135	145
4	7	80	70
5	1	217	216
5	2	520	529
5	3	71	89
5	4	178	177
5	5	106	111
5	7	120	122
6	1	379	374
6	2	173	176
6	3	297	311
6	4	100	110
6	5	63	69
7	1	83	90
7	2	361	380
7	3	92	85
7	4	167	176
7	5	103	78
7	6	76	24
7	7	96	97
8	1	229	239
8	2	53	51
8	3	108	103
8	4	112	116
8	5	126	129
8	6	124	135
9	1	96	85
9	2	80	94
9	3	91	93
9	4	107	99
9	5	122	122
9	6	96	94
10	1	140	139
10	2	45	48
10	3	116	114
10	4	107	120
10	5	91	85
11	1	75	77
11	2	151	145
11	3	45	45
11	4	78	36
12	1	154	154
12	2	77	49
12	3	184	174
****************			
H = 0			
0	2	481	449
0	3	158	122
0	4	86	79
0	5	411	405
0	6	122	49
0	7	167	155
0	8	83	87
1	2	532	519
1	3	503	465
1	4	164	168
1	5	108	110
1	6	254	251
1	7	109	89
1	8	158	164
2	1	49	303
2	2	383	385
2	3	676	680
2	4	250	241
2	5	341	335
2	6	142	135
2	7	102	120
2	8	107	103
3	1	271	247
3	2	205	208
3	3	390	375
3	4	231	219
3	5	240	240
3	6	137	98
3	7	141	119
4	0	275	269
4	1	409	382
4	2	391	371
4	3	303	285
4	4	303	296
4	5	199	197
4	6	49	34
4	7	143	108
5	1	265	276
5	2	98	95
5	3	153	156
5	4	129	145
5	5	137	109
5	6	173	163
5	7	91	49
6	0	416	416
6	2	282	286
6	3	91	46
6	4	73	74
6	5	150	141
6	6	74	45
6	7	134	125
7	1	313	314
7	2	118	117
7	3	158	157
7	4	107	110
7	5	88	95
7	6	153	144
8	0	267	238
8	1	150	140
8	2	82	83
8	3	211	211
8	4	135	137
8	5	85	88
9	1	82	83
9	2	277	277
9	3	192	178
9	4	134	131
9	5	78	79
9	6	78	84
10	0	187	161
10	1	104	76
10	2	121	160
10	3	103	111
10	4	86	96
10	5	103	109
11	1	165	174
11	2	96	95
11	3	109	113
11	4	109	99
12	0	209	227
12	1	82	65
12	2	151	152
12	3	53	33
13	1	156	147
****************			
H = 1			
0	2	86	110
0	4	214	223
0	5	99	90
0	6	140	135
0	8	104	81
1	2	186	176
1	3	158	175
1	4	84	28
1	5	249	222
1	6	162	158
1	8	76	49
2	1	364	395
2	2	368	333
2	3	279	283
2	4	402	414
2	5	53	40
2	6	145	143
2	7	100	107
2	8	125	103
3	0	358	327
3	1	324	320
3	2	653	627
3	3	317	291
3	4	159	150
3	5	75	37
3	6	193	185
3	7	173	131
4	0	305	302
4	1	718	705
4	2	134	90
4	3	156	172
4	4	335	350
4	6	167	179
4	7	133	133
5	0	132	145
5	1	252	252
5	2	229	237
5	3	380	402
5	4	96	103
5	5	302	310
5	6	143	158
5	7	121	130
6	0	72	60
6	1	302	292
6	2	236	252
6	3	45	48
6	4	330	329
6	5	99	107
6	6	149	169
7	0	228	232
7	1	288	287
7	2	215	215
7	3	217	219
7	4	88	72
7	5	185	188
7	6	67	81
8	0	179	178
8	1	79	83
8	2	198	196
8	3	98	99
8	4	125	125
8	5	60	66
8	6	93	99
9	0	196	192
9	1	228	228
9	2	221	230
9	3	114	106
9	4	53	51
9	5	80	52
10	0	117	119
10	1	163	144
10	2	120	144
10	3	94	95
10	4	80	73
10	5	81	59
11	0	112	116
11	1	121	115
11	2	64	52
11	3	169	159
11	4	81	41
12	0	31	27
12	1	97	107
12	2	93	84
12	3	54	20
13	0	78	90
13	1	55	40
****************			
H = 2			
0	0	358	319
0	1	56	67
0	2	234	230
0	3	241	237
0	4	91	69
0	5	169	177
1	0	395	399
1	1	537	539
1	2	553	534
1	3	55	38
1	4	294	297
1	5	63	77
1	6	108	107
1	7	104	109
2	0	660	660
2	1	280	278
2	2	119	113
2	3	233	239
2	4	199	179
2	5	260	255
2	6	72	60
2	7	86	96
3	0	449	425
3	1	448	374
3	2	112	131
3	4	92	94
3	5	264	277
3	6	142	166
3	7	108	104
4	0	485	476
4	1	230	222
4	3	226	237
4	4	168	166
4	5	177	177
4	6	138	155
4	7	136	105
5	0	197	193
5	1	199	215
5	2	457	481
5	3	92	84
5	4	267	273
5	5	165	167
5	6	187	169
5	7	93	101
6	0	184	185
6	1	476	488
6	2	137	153
6	3	349	365
6	4	155	152
6	5	142	147
7	0	129	141
7	1	215	212
7	2	387	401
7	3	141	136
7	4	229	230
7	6	114	112
8	0	257	261
8	1	182	179
8	2	108	105
8	3	170	174
8	4	126	135
8	5	157	155
8	6	97	108
9	0	113	116
9	1	177	182
9	2	91	83
9	3	66	71
9	4	108	110
9	5	138	131
10	0	208	218
10	1	121	127
10	2	46	46
10	3	150	153
10	4	92	91
11	0	90	84
11	2	231	242
11	3	60	45
12	0	78	46
12	1	105	102
12	3	137	119
****************			
H = 3			
0	0	662	667
0	1	356	371
0	2	143	137
0	3	110	96
0	4	129	128
0	5	183	181
0	6	70	64
0	7	159	149
1	0	109	124
1	1	440	471
1	3	414	445
1	4	172	182
1	5	92	84
1	6	227	234
1	7	61	67
2	0	363	371
2	1	77	95
2	2	246	256
2	3	223	237
2	4	296	305
2	5	103	101
2	6	108	105
2	7	79	82
3	0	376	329
3	1	358	375
3	2	74	101
3	3	206	244
3	4	102	85
3	5	264	217
4	0	202	206
4	1	223	230
4	2	150	162
4	3	225	239
4	4	171	183
4	5	52	46
4	6	79	89
4	7	111	95
5	1	291	317
5	2	101	101
5	3	141	141
5	4	109	119
5	5	102	128
5	6	134	134
6	0	350	347
6	1	160	174
6	2	244	260
6	4	132	122
6	5	66	59
6	6	53	18
7	1	254	268
7	2	65	68
7	3	131	130
7	6	132	132
8	0	133	135
8	1	91	96
8	2	92	101
8	3	128	156
8	4	162	165
8	5	103	101
9	0	95	99
9	1	137	137
9	2	75	72
9	3	154	142
9	4	71	59
10	0	102	123
10	1	48	42
10	2	149	161
10	3	53	46
10	4	100	105
11	0	57	11
11	1	154	153
11	3	91	101
12	0	227	130
13	1	114	101
****************			
H = 4			
0	0	371	334
0	1	65	53
0	2	79	59
0	3	210	210
0	4	374	316
0	5	73	82
0	6	82	87
1	0	251	277
1	1	118	117
1	2	284	298
1	3	151	147
1	4	134	132
1	5	274	273
1	6	140	132
2	0	153	145
2	1	295	313
2	2	192	198
2	3	249	236
2	4	129	142
2	5	105	93
2	6	79	64
3	0	358	344
3	1	107	111
3	2	424	392
3	3	88	74
3	4	128	135
3	5	56	10
4	0	243	237
4	1	330	340
4	2	102	94
4	3	82	87
4	4	121	106
4	6	129	122
5	0	108	97
5	1	142	152
5	2	134	130
5	3	223	238
5	4	93	98
5	5	152	151
5	6	77	52
6	0	58	55
6	1	95	103
6	2	69	77
6	3	70	76
6	4	144	154
7	0	124	143
7	1	65	55
7	2	79	82
7	3	97	95
7	4	50	38
7	5	135	139
8	0	139	119
8	1	101	89
8	2	69	75
8	3	138	140
8	4	92	88
9	0	127	127
9	1	76	72
9	2	188	195
10	1	134	112
11	0	121	116
11	1	61	64
****************			
H = 5			
0	0	208	180
0	1	159	177
0	2	121	122
0	3	242	235
0	5	127	97
1	0	91	59
1	1	142	137
1	2	173	165
1	3	115	93
1	4	182	181
1	5	81	63
2	0	312	314
2	1	91	99
2	2	194	120
2	3	179	154
2	5	135	120
3	0	106	94
3	1	231	248
3	2	125	122
3	4	72	55
3	5	88	47
4	0	253	227
4	3	141	133
4	4	96	37
4	5	115	112
5	0	135	127
5	1	130	113
5	2	226	238
5	3	73	87
5	4	127	131
5	5	93	55
6	0	101	106
6	1	144	146
6	2	82	81
6	3	141	155
6	4	91	93
7	0	58	68
7	1	152	144
7	2	354	184
7	3	94	102
7	4	127	131
8	0	129	132
8	1	61	74
8	2	122	119
8	3	104	104
9	0	70	52
9	1	134	141
****************			
H = 6			
0	0	222	216
0	1	111	84
0	2	61	67
1	0	79	37
1	1	154	149
1	3	84	76
2	0	159	142
2	1	121	131
2	2	156	130
2	3	92	17
2	4	171	147
3	0	101	100
3	3	168	136
3	4	86	40
4	0	59	43
4	1	61	69
4	2	146	153
4	3	103	31
5	0	142	133
5	1	165	175
5	2	110	112
5	3	119	105
6	0	128	127
6	1	171	162
6	2	90	94
7	0	104	96
7	1	135	152
****************			
H = 7			
0	0	180	164
1	0	112	109
1	2	112	84
2	0	77	57
2	1	119	123
3	0	137	128
4	0	83	64
8	0	79	52
8	0	79	52

[a] The table shows k, l, $10|F_o|$, $10|F_c|$ in blocks of constant h.

Symmetry-equivalent reflections within a level were averaged and all data were merged to a common scale by a least-squares analysis of common reflections.[24] The "R factor" for scaling was 7.3%, based on F^2. The resulting 813 independent, nonzero reflections were placed on an approximately absolute scale by means of a Wilson plot.[25]

Solution and Refinement of Structure

All crystallographic calculations were, unless otherwise stated, carried out under the CRYRM system[26] using the Harvard University IBM 7094 computer. Scattering factors for sulfur, fluorine, oxygen, carbon, boron, and hydrogen were taken from the compilation of Ibers.[27a] The Thomas–Fermi–Dirac values for neutral iron[27b] were adjusted for the real part of the dispersion correction ($\Delta f' = +0.4\ e^-$).[27c]

Discrepancy indices referred to below are $R_F = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$ and $R_{wF^2} = \Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^4$, where $w = [\sigma\{F^2(hkl)\}]^{-2}$, and $\sigma\{F^2(hkl)\}$ is derived from $\sigma\{I(hkl)\}$ by appropriate adjustment for Lorentz, polarization, transmission, and scale factors.

A three-dimensional Patterson map revealed an iron atom at $x = 0.191$, $z = 0.209$ (y arbitrarily set at 0). A Fourier synthesis, phased only by the iron atom ($R_F = 37.4\%$), showed that the sulfur atom had a y coordinate different from the iron (thus strongly suggesting that the true space group was $P2_1$) and also gave coordinates for oxygen atoms of the three carbonyl groups. A second Fourier synthesis, phased by iron, sulfur, and three oxygen atoms ($R_F = 29.6\%$) now revealed the positions of all remaining nonhydrogen atoms. Three cycles of full-matrix least-squares refinement of positional and individual isotropic thermal parameters (with $y_{Fe} = 0$, not refined) led to convergence at $R_F = 8.61\%$, and $R_{wF^2} = 3.42\%$. A difference-Fourier map

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[24] The least-squares process minimizes the sum of residuals linear in the logarithms of the individual scale factors: A. D. Rae, *Acta Crystallogr.*, **19**, 683 (1965).

[25] A. J. C. Wilson, *Nature (London)*, **150**, 152 (1942).

[26] CRYRM is an integrated sequence of crystallographic routines written in machine language for the IBM 7094 under the direction of Dr. R. E. Marsh at the California Institute of Technology.

[27] "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962: (a) p 202; (b) p 211; (c) p 216.

TABLE II

FINAL ATOMIC COORDINATES[a] AND THERMAL PARAMETERS[b] (WITH ESD'S)[c] FOR $C_4H_6Fe(CO)_3 \cdot SO_2 \cdot BF_3$

Atom	x	y	z
Fe	0.18869 (32)	0	0.21135 (28)
S	0.50362 (65)	0.16873 (36)	0.35983 (57)
F(1)	0.7774 (17)	0.0164 (10)	0.5673 (14)
F(2)	0.6141 (20)	0.0522 (13)	0.8226 (14)
F(3)	0.7870 (19)	0.1865 (10)	0.6872 (18)
O(1)	0.4648 (15)	0.0716 (9)	0.2318 (14)
O(2)	0.4803 (16)	0.1261 (11)	0.5546 (15)
O(3)	0.3824 (22)	−0.1749 (12)	−0.0056 (18)
O(4)	−0.1929 (20)	−0.1234 (12)	0.1825 (22)
O(5)	0.2282 (23)	−0.0905 (11)	0.5809 (20)
C(1)	0.1486 (28)	0.1124 (15)	−0.0239 (25)
C(2)	0.0170 (24)	0.1397 (13)	0.1206 (26)
C(3)	0.0864 (28)	0.1685 (13)	0.2991 (23)
C(4)	0.2631 (27)	0.2446 (13)	0.3317 (27)
C(5)	0.3068 (31)	−0.1095 (12)	0.0781 (23)
C(6)	−0.0427 (29)	−0.0757 (18)	0.1886 (26)
C(7)	0.2166 (27)	−0.0542 (13)	0.4429 (23)
B	0.6690 (28)	0.0950 (15)	0.6648 (26)
H(1)	0.3109	0.1148	0.0000
H(2)	0.0859	0.0896	−0.1580
H(3)	−0.1492	0.1347	0.0923
H(4)	0.0111	0.1342	0.4149
H(5)	0.2815	0.3001	0.2145
H(6)	0.2338	0.2937	0.4510

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Fe	153.8 (5.7)	47.5 (1.5)	111.5 (4.2)	15.1 (6.7)	48.5 (7.3)	−44.2 (5.3)
S	162.8 (11.0)	55.4 (3.0)	152.0 (9.0)	−14.6 (9.3)	20.1 (16.6)	5.3 (8.5)
F(1)	318 (32)	88 (9)	255 (27)	126 (33)	115 (46)	4 (29)
F(2)	350 (38)	204 (16)	117 (23)	0 (40)	20 (44)	134 (42)
F(3)	315 (37)	81 (9)	339 (34)	−93 (33)	−239 (55)	16 (30)
O(1)	131 (26)	70 (8)	84 (22)	−28 (26)	17 (36)	−39 (22)
O(2)	112 (28)	101 (11)	119 (24)	−4 (29)	−25 (43)	−8 (26)
O(3)	388 (47)	73 (10)	210 (31)	33 (39)	171 (65)	−91 (34)
O(4)	162 (36)	119 (14)	324 (41)	−102 (38)	35 (60)	−88 (36)
O(5)	375 (45)	71 (9)	210 (34)	−81 (36)	6 (65)	31 (33)
C(1)	230 (52)	72 (14)	159 (43)	55 (44)	−160 (79)	29 (37)
C(2)	112 (42)	54 (13)	232 (44)	43 (39)	56 (76)	61 (39)
C(3)	219 (47)	41 (10)	180 (40)	3 (38)	−42 (72)	47 (36)
C(4)	187 (50)	37 (11)	314 (54)	−20 (37)	−23 (86)	−1 (42)
C(5)	353 (63)	43 (11)	112 (36)	−18 (46)	4 (83)	14 (35)
C(6)	182 (54)	86 (17)	171 (43)	34 (53)	−53 (78)	27 (45)
C(7)	225 (52)	45 (10)	95 (34)	11 (39)	62 (65)	35 (33)
B	130 (44)	57 (13)	126 (42)	2 (44)	−1 (74)	−65 (37)

[a] H(1) and H(2) are bonded to C(1); H(3) is bonded to C(2); H(4) is bonded to C(3); H(5) and H(6) are bonded to C(4). [b] Hydrogen atoms were each assigned isotropic thermal parameters of $B = 4.0$ Å^2. The anisotropic thermal parameter (T) used for all other atoms is defined as $T = \exp[-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - \beta_{12}hk - \beta_{13}hl - \beta_{23}kl]$. [c] Esd's, shown in parentheses, are right-adjusted to the last digit of the preceding number.

failed to indicate positions for any hydrogen atoms and showed no features above 1.0 e$^-$ Å^{-3}. The six hydrogen atoms were therefore placed in calculated positions[28] and given isotropic thermal parameters of 4.0 Å^2; their positional and thermal parameters were kept fixed while refinement of positional and anisotropic thermal parameters for all other atoms converged ($\Delta/\sigma \leqslant 0.15$) to $R_F = 6.60\%$, $R_{wF^2} = 2.01\%$ after three cycles of full-matrix refinement. The standard error in an observation of unit weight was 1.28.

Refinement of the structure omitting hydrogen atom contributions gave $R_F = 6.98\%$. Hamilton R-factor ratio tests[29] indicate that improvements on the model effected by anisotropic refinement and inclusion of hydrogen atoms are significant to the 99.5 and 95% confidence levels, respectively.

Finally, it should be noted that systematic errors on iron–light atom bond lengths, which are introduced by failing to apply the imaginary part of the iron dispersion correction ($\Delta f''(\mathrm{Fe}) = +1.0$ e$^-$), are estimated[30] as less than 0.01 Å.

Observed and calculated structure factors are shown in Table I; final positional and thermal parameters, with estimated standared deviations (esd's), are collected in Table II.

The Molecular Structure

The molecular geometry, atomic numbering scheme, and thermal vibration ellipsoids[31] are displayed in

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[28] With d(C–H) = 1.08 Å and the appropriate idealized sp^2 or sp^3 geometry.

[29] W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

[30] D. W. J. Cruickshank and W. S. McDonald, *ibid.*, **23**, 9 (1967).

[31] This diagram was constructed using OTLIPS (an IBM 1620/CALCOMP program, written by Dr. P. H. Bird).

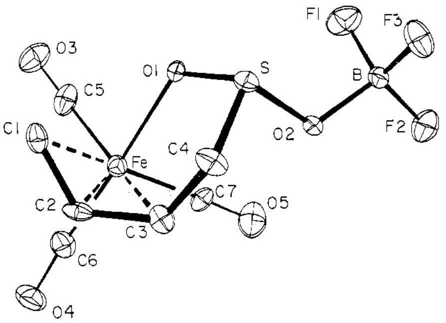

Figure 1.—Numbering of atoms in the $C_4H_6Fe(CO)_3\cdot SO_2\cdot BF_3$ molecule. The molecule is projected onto the plane of the carbonyl oxygen atoms and shows the 68% probability envelopes for the atomic vibration ellipsoids (OTLIPS[31] diagram).

Figure 1. (Hydrogen atoms have been omitted from this diagram for the sake of clarity.) Bond lengths are collected in Table III; bond angles are shown in Table IV.

TABLE III

INTERATOMIC DISTANCES (WITH ESD'S) WITHIN THE $C_4H_6Fe(CO)_3\cdot SO_2\cdot BF_3$ MOLECULE[a]

Atoms	Dist, Å	Atoms	Dist, Å
(a) Distances from Iron Atom			
Fe–O(1)	2.004 (10)	Fe–C(5)	1.818 (17)
Fe–C(1)	2.194 (18)	Fe–C(6)	1.767 (20)
Fe–C(2)	2.091 (16)	Fe–C(7)	1.830 (16)
Fe–C(3)	2.202 (17)	Fe···S	3.044 (04)
Fe···C(4)	3.050 (18)		
(b) Distances within $C_4H_6\cdot SO_2\cdot BF_3$ Moiety			
C(1)–C(2)	1.440 (24)	S–O(2)	1.540 (12)
C(2)–C(3)	1.420 (23)	O(2)–B	1.502 (21)
C(3)–C(4)	1.481 (24)	B–F(1)	1.389 (21)
C(4)–S	1.822 (18)	B–F(2)	1.335 (22)
S–O(1)	1.500 (11)	B–F(3)	1.335 (22)
(c) Distances within Carbonyl Ligands			
C(5)–O(3)	1.118 (22)	C(7)–O(5)	1.106 (21)
C(6)–O(4)	1.136 (24)		

[a] Esd's, shown in parentheses, are right-adjusted to the last digit of the preceding number.

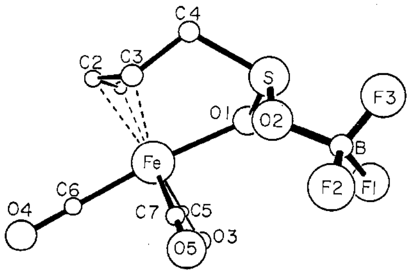

Figure 2.—$C_4H_6Fe(CO)_3\cdot SO_2\cdot BF_3$, showing the coordination sphere of the iron atom.

The integrity of the butadieneiron tricarbonyl moiety is essentially conserved; however, as shown in Figure 2, only *three carbon atoms* of the C_4H_6 fragment are bonded to the $Fe(CO)_3$ group (*i.e.*, there is now a π-allyl→ metal linkage). Individual iron–carbon distances, Fe–C(1) = 2.194 (18), Fe–C(2) = 2.091 (16), and Fe–C(3) = 2.202 (17) Å, may be compared with distances of 2.200, 2.050, and 2.142 (each ±0.008) Å for the π-allyl→iron linkage in azulenediiron pentacarbonyl.[32] The Fe···C(4) distance of 3.050 (18) Å in the present compound is essentially nonbonding.

TABLE IV

BOND ANGLES IN THE $C_4H_6Fe(CO)_3\cdot SO_2\cdot BF_3$ MOLECULE

Atoms	Angle, deg	Atoms	Angle, deg
(a) Angles around Iron Atom			
O(1)–Fe–C(1)	83.4 (0.6)	C(2)–Fe–C(3)	38.5 (0.6)
O(1)–Fe–C(2)	99.7 (0.6)	C(2)–Fe–C(5)	128.5 (0.7)
O(1)–Fe–C(3)	83.4 (0.5)	C(2)–Fe–C(6)	85.1 (0.8)
O(1)–Fe–C(5)	86.2 (0.6)	C(2)–Fe–C(7)	127.4 (0.8)
O(1)–Fe–C(6)	174.4 (0.7)	C(3)–Fe–C(5)	160.5 (0.7)
O(1)–Fe–C(7)	91.2 (0.6)	C(3)–Fe–C(6)	102.1 (0.8)
C(1)–Fe–C(2)	39.2 (0.6)	C(3)–Fe–C(7)	93.3 (0.7)
C(1)–Fe–C(3)	70.2 (0.5)	C(5)–Fe–C(6)	88.6 (0.9)
C(1)–Fe–C(5)	92.2 (0.7)	C(5)–Fe–C(7)	103.4 (0.8)
C(1)–Fe–C(6)	98.9 (0.8)	C(6)–Fe–C(7)	88.0 (0.8)
C(1)–Fe–C(7)	163.2 (0.7)		
(b) Angles in $C_4H_6\cdot SO_2\cdot BF_3$ Moiety			
C(1)–C(2)–C(3)	124.3 (1.6)	S–O(2)–B	118.3 (1.0)
C(2)–C(3)–C(4)	121.1 (1.5)	O(2)–B–F(1)	108.2 (1.3)
C(3)–C(4)–S	113.2 (1.3)	O(2)–B–F(2)	108.6 (1.4)
C(4)–S–O(1)	100.2 (0.7)	O(2)–B–F(3)	109.5 (1.4)
C(4)–S–O(2)	98.4 (0.7)	F(1)–B–F(2)	111.4 (1.5)
O(1)–S–O(2)	108.8 (0.6)	F(1)–B–F(3)	107.1 (1.4)
S–O(1)–Fe	119.9 (0.6)	F(2)–B–F(3)	111.9 (1.5)
(c) Angles within Carbonyl Groups			
Fe–C(5)–O(3)	178.3 (1.6)	Fe–C(7)–O(5)	177.1 (1.6)
Fe–C(6)–O(4)	176.7 (1.8)		

The most striking feature in the structure of $C_4H_6Fe(CO)_3\cdot SO_2\cdot BF_3$ is the mode of incorporation of SO_2 into the molecular framework. In contrast to previous observations on SO_2 insertion compounds,[4–13] the SO_2 moiety within the present molecule is linked to the metal atom *via* an *oxygen*→iron (rather than a *sulfur*→iron) linkage. This bond would appear to be of approximately unit bond order since (using the Pauling[33] covalent radii of 0.66 Å for O and 0.77 Å for C) the present Fe–O(1) distance of 2.004 (10) Å is consistent with the iron–alkyl distance of ~2.11Å in π-$C_5H_5Fe(CO)_2R$ (R = alkyl) and related complexes in suggesting a covalent radius for Fe(II) of 1.34 Å.[34]

The sulfur atom of the SO_2 fragment is bonded to one of the terminal methylene groups of the former butadiene ligand *via* a linkage (S–C(4) = 1.822 (18) Å) whose distance is in good agreement with the accepted carbon–sulfur single-bond distance of 1.817 ± 0.005 Å.[35]

The other oxygen atom of the SO_2 moiety, O(2), donates a pair of electrons to a BF_3 molecule, the O(2)–B distance of 1.502 (21) Å being comparable to the mean value of 1.48 Å found from B–O distances in tetrahedral borates;[36] this linkage, again, is of approximately unit bond order.

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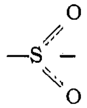
The sulfur atom lies at the apex of a trigonal pyramid, in which the angles O(1)–S–C(4) = 100.2 (0.7), O(2)–S–C(4) = 98.4 (0.7), and O(1)–S–O(2) = 108.8 (0.6)° suggest sp^3 hybridization of the sulfur atom. Bond angles about O(1) and O(2), S–O(1)–Fe = 119.9 (0.6) and S–O(2)–B = 118.3 (1.0)°, are consistent with sp^2 hybridization of the two oxygen atoms.

Sulfur–oxygen bond distances are S–O(1) = 1.500 (11) and S–O(2) = 1.540 (12) Å; the difference of 0.040 (16) Å is significant only to the 2.5σ level. The mean sulfur–oxygen distance of 1.520 Å is similar to the value of 1.513 (6) Å observed for the corresponding bonds in the



system of sodium hydroxymethanesulfinate dihydrate, $Na^+[HOCH_2SO_2^-] \cdot 2H_2O$.[37,38] We suggest, therefore, that each of the S–O linkages in $C_4H_6Fe(CO)_3 \cdot SO_2 \cdot BF_3$ has a bond order of ~1.5. The observed S–O distances in the present complex are significantly longer than those observed in other S^{IV}–O linkages of bond order 1.5—*viz.*, gaseous SO_2 (1.4321[39] or 1.4308 (2) Å[40] from microwave spectra or 1.431 (1) Å by electron diffraction[41]), or solid SO_2 (1.430 (15) Å),[42] or the SO_2 adducts [*trans*-$Ru(NH_3)_4(SO_2)Cl^+$][Cl^-] (S–O = 1.462 (10) and 1.394 (10) Å),[3a] $Ir[P(C_6H_5)_3]_2(SO_2)(CO)Cl$ (S–O = 1.411 (23) and 1.467 (25) Å)[3b] and $Rh[P(C_6H_5)_3]_2(SO_2)(CO)Cl$ (S–O = 1.446 (4) and 1.456 (4) Å).[3c] However, Truter[37] has pointed out the "covalent radius" for sulfur is rather dependent on the nature of the ligands in its coordination sphere.

Carbon–carbon distances within the C_4H_6 system are consistent with recognized values—the C(1)–C(2) and C(2)–C(3) distances of 1.440 (24) and 1.420 (23) Å are each indistinguishable from the accepted C–C(π-allyl) distance of ~1.43 Å, and the C(3)–C(4) distance of 1.481 (24) Å is in good agreement with the recognized value of 1.510 ± 0.005 Å for a C(sp^2)–C(sp^3) single bond.[35]

The $Fe(CO)_3$ Group

As should be expected from the low symmetry of the iron coordination sphere (see Figure 2), the $Fe(CO)_3$ group has only C_s (rather than the possible C_{3v}) symmetry. The "unique" carbonyl group, C(6)–O(4), which lies in the same plane as the iron atom and O(1), passes directly below the central carbon of the π-allyl residue, interatomic contacts being C(2)···C(6) = 2.621 (21) and C(2)···O(4) = 3.432 (22) Å. Other close contacts between C_4H_6 and $Fe(CO)_3$ groups are C(1)···C(5) = 2.903 (23) and C(3)···C(7) = 2.945 (20) Å.

Within the $Fe(CO)_3$ group, the angles C(6)–Fe–C(5) = 88.6 (0.9) and C(6)–Fe–C(7) = 88.0 (0.8)° are approximately equal and are appreciably smaller than the C(5)–Fe–C(7) angle of 103.4 (0.8)°. Similar patterns of distortion from C_{3v} symmetry have been observed and discussed for the $Fe(CO)_3$ fragment in (*cis*-1,3-diene)$Fe(CO)_3$ complexes.[43,44]

Finally, it may be noted that the mean Fe–CO and C–O distances of 1.805 and 1.120 Å are in good agreement with values found in other $Fe(CO)_3$-containing complexes.[44]

Packing of Molecules

The crystal is composed of distinct molecular units of $C_4H_6Fe(CO)_3 \cdot SO_2 \cdot BF_3$, separated by normal van der Waals distances. The packing is illustrated in Figure 3. Intermolecular contacts (to 3.3 Å) are collected in Table V.

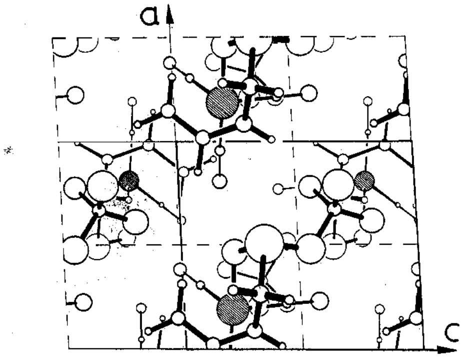


Figure 3.—Packing of molecules within the crystal, viewed down *b*.

Table V

Intermolecular Contacts (to 3.3 Å) within the $C_4H_6Fe(CO)_3 \cdot SO_2 \cdot BF_3$ Crystal

Atoms	Trans[a]	Dist, Å	Atoms	Trans[a]	Dist, Å
$F_1 \cdots H_4$	I	2.39	$F_2 \cdots H_5$	VII	3.06
$F_3 \cdots H_1$	III	2.51	$F_3 \cdots H_3$	III	3.07
$F_2 \cdots H_2$	III	2.54	$O_4 \cdots H_5$	IV	3.10
$F_3 \cdots H_4$	I	2.62	$O_3 \cdots F_3$	VII	3.11
$F_2 \cdots H_3$	III	2.66	$S \cdots H_3$	I	3.11
$O_3 \cdots H_5$	V	2.77	$O_3 \cdots O_4$	I	3.13
$O_3 \cdots H_3$	IV	2.78	$F_2 \cdots H_1$	III	3.13
$O_1 \cdots H_3$	I	2.88	$F_1 \cdots C_7$	I	3.18
$O_4 \cdots H_6$	VI	2.91	$O_3 \cdots H_2$	V	3.19
$F_1 \cdots H_1$	III	2.94	$C_7 \cdots F_3$	VII	3.20
$B \cdots H_1$	III	2.99	$F_1 \cdots O_5$	I	3.22
$B \cdots H_4$	I	3.01	$F_2 \cdots O_1$	II	3.23
$C_5 \cdots F_3$	VII	3.04	$O_1 \cdots O_4$	I	3.25
$O_5 \cdots H_1$	II	3.04	$F_3 \cdots C_1$	III	3.25
$F_1 \cdots H_5$	VII	3.05	$F_1 \cdots C_6$	I	3.27
$F_1 \cdots H_6$	VII	3.06	$O_5 \cdots F_3$	VII	3.29

[a] Transformations: (I) $1 + x, y, z$; (II) $x, y, 1 + z$; (III) $1 + x, y, 1 + z$; (IV) $-x, -1/2 + y, -z$; (V) $1 - x, -1/2 + y, -z$; (VI) $-x, -1/2 + y, 1 - z$; (VII) $1 - x, -1/2 + y, 1 - z$.

Discussion

The present molecule represents a kind of molecular iron sulfinate derivative in which butadieneiron tri-

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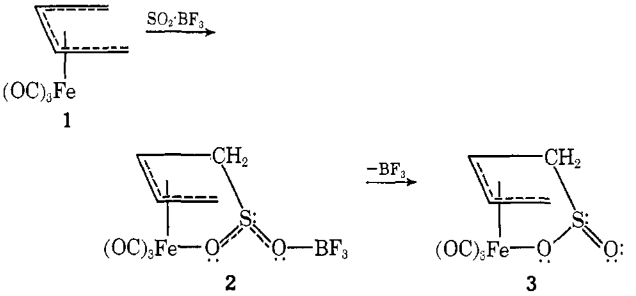
carbonyl has been the subject of electrophilic attack (either by SO_2 itself or by the $SO_2 \cdot BF_3$ adduct, which is stable below ambient temperatures[45]). The product is probably best considered as an intermediate (2) in the hypothetical Friedel–Crafts sulfination reaction **1** → **3**. [It should be emphasized that complexes of type **3** have yet to be reported. However, a complex of type **2** containing the Lewis acid SbF_5, rather than BF_3, has been prepared by Kaesz and coworkers.[18]]



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An Electron Diffraction Study of the Molecular Structure of Tetrakis(trimethylsilyl)silane[1]

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Gas-phase $Si[Si(CH_3)_3]_4$ possesses Si–Si and Si–C bond lengths of 2.361 ± 0.003 and 1.889 ± 0.003 Å, including estimated standard errors, respectively, and Si–Si–C and Si–C–H angles of 110.9 ± 0.6 and 109.3 ± 1.7°. The $(CH_3)_3Si$ groups appear to undergo cooperative torsional displacements of about 14° from T_d symmetry in order to relieve nonbonded interactions between methyl groups.

Introduction

The first successful preparation of tetrakis(trimethylsilyl)silane, $Si[Si(CH_3)_3]_4$, was reported in 1964 by Gilman and Smith.[3] Quite stable and unreactive, the yellow solid melts at 261–263°. The proton nmr exhibits a sharp singlet at τ 9.79, indicating that all protons are equivalent. Tetrakis(trimethylsilyl)silane presented a favorable opportunity to extend studies of the influence of nonbonded repulsions on molecular structure[4] to an analog of tetrakis(*t*-butyl)methane.

Experimental Section

The electron diffraction apparatus employed has been described elsewhere.[5] Except for the special heated nozzle assembly necessitated by the relatively nonvolatile sample, diffraction patterns were recorded and measured by the usual techniques.[6] Least-squares structure refinements upon the experimental leveled intensity were based on the elastic scattering factors of Cox and Bonham[7] and the inelastic scattering factors of Tavard[8] and did not differ significantly from procedures described elsewhere.[9] Comparison between experimental and theoretical points was carried out utilizing a weighting function proportional to the scattering variable for the composite reduced molecular intensity curve, $M(s)$. Asymmetry constants a were estimated[10] to be 2.5 Å^{-1} for C–H distances and 2.0 Å^{-1} for Si–Si and Si–C distances and were taken to be 1.0 Å^{-1} for all nonbonded distances. No correction was made for shrinkage effects.[11]

Results

Figure 1 shows the molecular intensity curve determined for $Si[Si(CH_3)_3]_4$ by blending together data from the individual camera distances. The index of resolution was 0.95 for each of the three experimental camera ranges. Fourier inversion of the molecular intensity produced the radial distribution function illustrated in Figure 2. The results of our structural refinement are summarized in Table I. Experimental data were analyzed by least-squares fittings of the molecular intensity, and a representation of the error matrix determined during the final runs is reproduced in Table II. Listings of the experimental leveled intensity and the background used in data analysis at regular intervals of the scattering variable are given in Table III. Table

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[1] This work was supported by a grant from the National Science Foundation.

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