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Studies on Indole Derivatives. XV.[1] Synthesis of Indoxyl Derivatives. (1). Crystal and Molecular Structure of Anhydro-2-benzyl-1-mercapto-3-methyl-9-oxo-(9H)-imidazo[1,5-*a*]indolium Hydroxide

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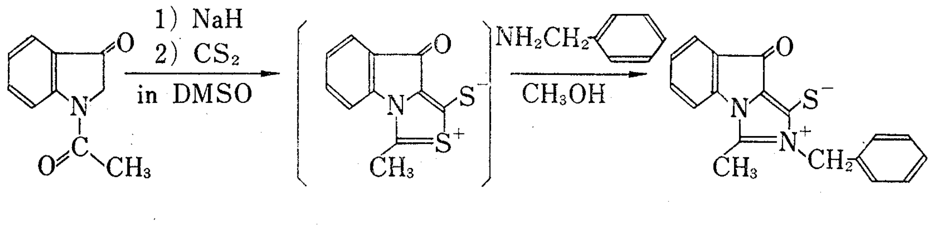
The new mesoionic compound, anhydro-2-benzyl-1-mercapto-3-methyl-9-oxo-(9H)-imidazo[1,5-*a*]indolium hydroxide, was synthesized by the reaction of 1-acetyl-3-indolinone, carbon disulfide, and benzylamine. The structure has been determined by an X-ray analysis. The crystals are monoclinic, $a=11.58$, $b=8.52$, $c=15.50$ Å, $\beta=102.7°$, and the space group is $P2_1/c$. The intensities of all independent reflections were measured with a Rigaku auto differactometer and a total of 887 were collected and employed for structure determination by the heavy atom method. The final R factor is down to 0.067 by a block diagnal least-squares refinement. The mesoionic imidazolium ring system is almost planar. The C–S bond of 1.678 Å agrees well with the accepted value of 1.78 Å, methyl group of 1.449 Å attached with an imidazolium ring indicates some double bond character.

Mesoionic compounds have received considerable interest because of their lack of bond valency. X-Ray crystal structure analysis of this type of compounds, which referes to the sydnone,[3] was first done by Schmidt and more detailed structural analyses of 3-(*p*-brom)-sydnone[4,5] and 4,4-dichloro-3,3-ethylene-bis(sydnone)[6] were published by Barnighausen and Thiessen. Other mesoionic compounds have been investigated by Newton[7] and Isaksson.[8] These compounds have a thiazolium ring system in the main structure. Here, could obtain to a mesoionic compound consisting of the imidazolium ring, it has become great interest in its molecular plane and the conjugation system. We can obtain the mesoionic compound having the imidazolium ring system by treatment of 1-acetyl-3-indolinone, carbon disulfide, and benzylamines which gives anhydro-2-benzyl-1-mercapto-3-methyl-9-oxo-(9H)-



I II III

Chart 1

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[1] Part XIV: G. Kobayashi, Y. Matsuda, R. Natsuki, and Y. Tominaga, *Yakugaku Zasshi*, **92**, 1468 (1972).

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[3] G.M.J. Schmidt, *Bull. Res. Council Israel.*, **1**, 123 (1951) [*C.A.*, **46**, 2871 (1952)].

[4] H. Barnighausen, F. Jellinek, and A. Vos, *Proc. Chem. Soc.*, **1961**, 120.

[5] H. Barnighausen, F. Jellinek, J. Munnik, and A. Vos, *Acta Cryst.*, **16**, 471 (1963) [*C.A.*, **59**, 8215 (1964)].

[6] W.E. Thiessen and H. Hope, *J. Am. Chem. Soc.*, **89**, 5977 (1967).

[7] M. Gary Newton, M.C. Mcdaniel, J.E. Baldwin, and I.C. Paul, *J. Chem. Soc.* (*B*), **1967**, 1117.

[8] H.G. Isaksson and J. Sandstron, *Acta Chem. Scand.*, **21**, 142 (1967).

imidazo[1,5-*a*]indolium hydroxide (III), whose structure was proposed from physicochemical data.[9]

In order to confirm the detailed structure, the compound (III) was subjected to an X-ray structural analysis.

Table I. Observed and Calculated Structure Factors (X10)

L	FO	FC
K= 0,H= 0		
2	478	476
4	468	466
6	216	205
8	245	253
12	116	104
K= 1,H= 0		
2	913	932
3	859	896
4	211	220
5	101	132
6	348	368
9	193	200
13	134	138
K= 2,H= 0		
1	457	476
2	764	800
3	253	249
4	110	57
5	240	260
7	339	323
8	245	245
9	371	367
15	140	135
K= 3,H= 0		
2	126	152
3	686	686
4	163	140
5	195	209
6	227	217
7	242	239
9	111	40
12	155	154
K= 4,H= 0		
1	118	118
2	180	176
3	448	430
4	320	306
5	215	214
7	187	183
10	180	162
K= 5,H= 0		
1	230	219
3	285	284
4	277	257
6	132	145
12	173	139
13	168	133
K= 6,H= 0		
1	112	130
2	108	113
3	238	221
7	240	215
9	222	238
K= 7,H= 0		
1	213	212
3	119	106
4	349	352
6	127	149
K= 8,H= 0		
7	142	84
K= 9,H= 0		
4	144	147
K= 0,H= 1		
-16	234	238
-12	144	138
-10	193	176
-8	723	690
-6	165	185
-4	1573	1612
-2	459	486
0	1080	992
4	732	716
6	275	272
8	582	479
10	203	200
12	274	297
K= 1,H= 1		
-14	118	111
-9	225	242
-8	229	204
-7	151	135
-5	134	114
-4	203	205
-3	305	302
-2	824	820
-1	203	209
1	437	443
2	421	428
3	180	171
4	307	311
5	604	610
7	143	128
10	164	161
11	116	135
13	120	110
K= 2,H= 1		
-13	155	113
-12	152	131
-8	102	52
-7	259	265
-6	263	261
-5	476	444
-4	183	166
-2	372	378
-1	667	637
0	439	432
1	838	852
2	383	383
3	249	258
4	493	511
9	144	184
10	204	211
K= 3,H= 1		
-15	143	110
-13	131	113
-11	221	253
-8	152	154
-6	121	92
-5	605	592
-3	303	320
-2	400	395
-1	446	452
0	281	273
1	803	739
2	175	173
3	195	215
4	260	254
5	111	100
7	395	390
8	183	203
10	131	150
K= 4,H= 1		
-12	169	108
-9	177	182
-6	94	116
-3	324	323
-2	99	80
-1	534	503
0	420	397
1	213	171
2	404	407
3	224	223
4	301	286
5	270	250
7	187	193
8	291	280
K= 5,H= 1		
-8	143	154
-7	191	193
-4	274	272
-3	138	133
-1	181	227
0	142	151
1	96	92
2	234	261
3	368	371
4	417	422
5	124	147
6	227	241
13	140	145
K= 6,H= 1		
-10	140	93
-7	193	206
-6	123	146
-5	151	180
0	164	148
1	155	141
2	193	194
3	111	90
4	121	71
K= 7,H= 1		
-9	140	164
-8	210	191
-7	113	93
-4	230	249
-3	246	249
-2	293	283
-1	257	234
0	198	204
4	161	150
8	103	126
K= 8,H= 1		
-7	114	115
3	154	184
K= 9,H= 1		
5	128	126
6	123	121
K= 0,H= 2		
-14	154	149
-12	286	277
-10	131	167
-8	132	158
-4	3304	3128
-2	847	832
2	801	793
4	620	632
6	257	258
8	173	147
10	295	296
12	200	234
K= 1,H= 2		
-13	138	92
-11	140	136
-10	99	132
-8	154	115
-7	527	497
-6	592	552
-5	400	399
-2	575	603
-1	435	437
0	243	234
1	258	276
2	364	311
3	259	267
4	222	215
5	365	384
6	208	211
8	142	116
9	327	318
10	166	149
11	118	93
13	100	111
K= 2,H= 2		
-13	137	99
-8	177	156
-7	213	222
-6	128	78
-4	130	132
-2	163	199
-1	321	320
0	640	625
1	635	637
2	421	388
3	506	523
5	423	420
6	182	160
7	133	125
K= 3,H= 2		
-11	124	152
-10	141	104
-9	171	175
-8	123	95
-7	295	274
-2	191	173
-1	565	551
0	427	440
2	296	267
3	267	268
4	274	250
5	91	101
6	150	100
7	226	237
9	139	143
K= 4,H= 2		
-14	170	155
-7	118	108
-6	268	280
-4	418	408
-2	195	215
-1	292	283
0	268	223
1	120	93
2	133	170
3	103	124
4	94	23
6	122	128
8	293	288
12	229	245
K= 5,H= 2		
-10	183	153
-9	104	68
-8	225	223
-4	163	145
-3	233	241
-2	123	119
-1	249	246
0	423	404
2	244	246
4	93	101
9	201	222
10	164	131
K= 6,H= 2		
-11	113	103
-7	156	182
-5	107	94
-4	313	309
0	105	146
1	263	277
3	334	347
5	301	305
7	172	210
10	132	134
K= 7,H= 2		
-9	236	234
-6	124	117
-3	248	239
0	346	340
4	177	173
6	170	159
9	196	210
K= 8,H= 2		
3	116	129
4	151	104
5	145	136
K= 9,H= 2		
-8	118	98
4	109	71
K= 0,H= 3		
-12	284	258
-8	649	646
-6	408	402
-4	1449	1478
-2	520	522
0	607	603
2	314	316
4	353	367
6	222	269
8	418	420
K= 1,H= 3		
-10	127	146
-8	184	210
-7	362	368
-6	455	455
-5	105	118
-4	91	73
-3	129	115
-2	151	178
-1	225	223
0	351	372
1	657	664
2	347	333
3	571	570
4	214	217
6	297	292
7	235	228
9	181	188
K= 2,H= 3		
-13	114	125
-11	196	184
-9	135	144
-6	93	110
-5	144	119
-3	441	457
-1	293	278
0	106	95
2	129	162
3	104	128
4	201	202
5	296	320
6	186	172
9	224	227
11	140	165
13	207	221
K= 3,H= 3		
-10	136	131
-9	259	271
-5	128	130
-3	115	98
0	193	179
3	515	512
4	155	152
5	106	74
8	256	276
10	138	145
11	182	173
K= 4,H= 3		
-10	95	52
-7	260	271
-5	358	324
-4	432	413
0	167	162
1	375	371
2	282	300
3	249	234
4	543	531
5	90	53
6	200	208
K= 5,H= 3		
-8	271	260
-7	190	223
-5	243	256
-4	122	141
-1	404	385
0	303	294
2	94	100
4	122	53
5	169	162
8	150	169
9	195	166
K= 6,H= 3		
-13	143	128
-3	194	184
1	112	115
3	171	163
4	128	163
5	292	286
6	186	199
9	202	261
K= 7,H= 3		
-7	126	170
-5	146	117
0	251	260
1	185	190
4	205	209
8	184	143
K= 8,H= 3		
-1	210	195
K= 0,H= 4		
-8	1284	1248
-6	398	403
-4	246	259
-2	961	960
0	446	459
4	177	169
6	521	535
8	150	136
12	167	154
14	130	127
K= 1,H= 4		
-13	116	101
-12	156	147
-11	169	183
-10	253	253
-9	296	298
-8	85	31
-7	100	138
-6	406	386
-5	427	416
-4	234	222
-3	175	166
-1	432	454
0	142	157
1	498	488
3	216	190
4	92	89
5	321	315
6	407	412
7	222	248
10	263	293
12	167	188
14	146	146
K= 2,H= 4		
-11	193	197
-9	103	133
-4	338	363
-3	404	389
-1	147	133
0	115	111
1	259	236
3	255	231
6	111	121
7	243	250
8	193	184
13	283	321
K= 3,H= 4		
-9	166	168
-7	259	264
-6	146	133
-5	405	481
-4	140	76
-3	93	47
-1	325	333
	318	321
1	288	283
3	333	343
4	259	252
5	164	176
6	144	93
7	211	192
11	187	173
K= 4,H= 4		
-11	113	118
-8	241	249
-6	119	86
-5	92	137
-4	317	315
-2	127	116
	234	283
1	145	146
2	189	151
3	173	147
4	353	357
5	114	118
7	126	125
8	178	192
10	133	146
K= 5,H= 4		
-12	147	162
-8	98	72
-5	136	136
-4	168	161
0	252	264
1	162	139
4	114	117
5	145	133
6	191	173
8	177	208
K= 6,H= 4		
-11	134	159
-8	147	156
-3	244	248
-2	229	221
-1	149	164
1	184	200
3	320	306
4	147	171
5	152	150
K= 7,H= 4		
-7	232	200
-6	171	158
-4	287	274
4	171	155
5	183	196
K= 0,H= 5		
-10	391	369
-8	777	748
-6	407	434
-4	485	440
0	256	263
2	440	455
4	491	470
8	150	177
12	195	251
K= 1,H= 5		
-13	137	125
-11	178	155
-10	273	228
-9	179	176
-6	229	216
-4	253	277
-3	393	413
-1	447	419
0	147	115
1	117	96
2	559	599
3	306	327
4	175	141
5	209	223
7	133	111
K= 2,H= 5		
-13	113	88
-9	234	231
-7	237	227
-6	163	157
-3	400	416
-1	381	400
0	159	124
1	203	191
2	175	134
3	110	126
4	284	266
5	337	353
7	174	185
9	283	313
K= 3,H= 5		
-13	224	189
-10	123	96
-4	246	252
-1	463	45
1	145	164
4	175	157
5	130	136
13	112	113
K= 4,H= 5		
-11	205	174
-10	136	114
-9	136	81
-8	213	234
-6	121	62
-3	359	350
-1	256	269
0	379	370
5	185	202
5	151	161
7	220	210
8	234	248
9	205	169
K= 5,H= 5		
-12	117	111
-6	149	147
-5	243	198
-4	255	249
0	182	178
1	214	195
2	165	168
4	143	161
5	314	321
6	123	101
9	129	89
K= 6,H= 5		
-7	184	153
-5	215	214
-3	137	45
-1	238	245
1	282	292
2	103	73
3	176	174
4	145	171
K= 7,H= 5		
-4	252	264
-3	161	148
3	168	159
5	110	123
K= 0,H= 6		
-16	116	90
-12	703	660
-10	102	78
-8	186	155
-6	290	303
-4	215	159
-2	194	217
0	139	151
2	375	374
8	313	341
K= 1,H= 6		
-14	195	176
-13	209	178
-11	111	122
-10	213	203
-9	207	190
-8	143	127
-5	365	362
-4	176	184
-3	103	132
-2	190	208
1	105	84
2	353	355
3	288	227
6	200	196
7	134	148
K= 2,H= 6		
-12	109	94
-11	119	104
-10	155	136
-7	285	282
-5	213	213
-3	295	275
-2	179	143
-1	233	285
1	164	215
2	123	99
3	240	250
4	121	141
6	146	131
9	325	374
K= 3,H= 6		
-13	99	88
-11	137	183
-9	191	216
-5	171	171
-4	282	290
-3	93	130
-2	107	113
0	246	236
4	134	89
5	114	103
6	206	230
7	160	173
8	125	110
K= 4,H= 6		
-12	121	104
-9	173	158
-8	277	277
-7	155	151
-6	114	86
-4	115	81
-1	123	121
0	288	374
1	114	88
3	109	124
4	213	214
6	174	174
K= 5,H= 6		
-13	129	58
-11	114	114
-4	296	322
0	139	124
1	128	141
2	187	174
5	186	176
K= 6,H= 6		
-3	168	160
-1	314	319
1	183	198
K= 7,H= 6		
-8	185	196
K= 8,H= 6		
2	162	132
K= 0,H= 7		
-12	250	219
-10	106	101
-5	244	214
-4	310	266
-2	165	157
2	136	126
4	276	236
8	169	230
K= 1,H= 7		
-14	106	133
-10	103	121
-7	169	173
-5	349	302
-3	126	131
-2	350	351
-1	354	372
1	140	141
2	99	78
3	175	175
4	102	135
5	110	90
K= 2,H= 7		
-9	126	104
-7	217	223
-5	191	160
-3	193	163
-2	152	150
0	233	242
1	224	207
3	97	132
4	94	98
5	275	293
6	111	136
9	175	204
K= 3,H= 7		
-8	131	133
-3	193	189
1	169	173
6	119	176
9	126	126
K= 4,H= 7		
-12	191	143
-9	96	48
-7	212	199
-6	98	110
-5	189	183
-4	233	211
-1	138	106
0	128	163
1	140	135
2	261	274
3	103	95
4	155	169
7	150	137
K= 5,H= 7		
-10	154	147
-9	154	132
-8	240	219
-3	226	220
1	213	212
2	165	167
3	141	143
K= 6,H= 7		
-6	141	125
-5	157	142
-3	200	196
-1	164	173
3	130	89
K= 7,H= 7		
-5	169	179
-1	222	198
0	107	132
K= 0,H= 8		
-16	206	184
-12	190	158
-10	145	158
-4	166	148
-2	353	347
4	329	336
6	201	214
K= 1,H= 8		
-9	175	175
-8	125	144
-2	226	226
-1	270	258
1	190	261
3	114	145
8	174	200
K= 2,H= 8		
-11	158	163
-10	109	85
-9	111	77
-6	116	57
-5	228	217
-4	119	101
0	149	141
3	104	116
5	421	453
11	111	114
K= 3,H= 8		
-5	149	165
-4	123	36
-2	142	176
1	170	165
2	194	185
3	182	173
K= 4,H= 8		
-4	299	282
-2	236	256
0	206	201
2	196	207
3	153	173
5	209	201
K= 5,H= 8		
-8	145	139
-3	137	154
-2	254	229
1	136	176
K= 6,H= 8		
-5	283	250
-1	148	130
K= 8,H= 8		
-5	104	35
K= 0,H= 9		
0	188	171
4	264	251
K= 1,H= 9		
-9	162	193
-7	123	90
-6	143	147
-5	124	143
-4	156	127
-2	235	295
0	364	384
2	175	198
4	153	161
K= 2,H= 9		
-8	113	66
-5	127	132
-4	153	127
-3	291	271
-2	172	153
1	190	179
2	130	129
5	201	220
K= 3,H= 9		
-4	202	179
-3	193	168
3	194	215
7	130	133
K= 4,H= 9		
-5	132	112
-4	97	37
1	95	100
3	118	101
6	143	144
7	113	64
K= 5,H= 9		
-5	108	99
-2	113	157
-1	155	164
0	151	138
1	106	117
2	121	65
K= 6,H= 9		
-5	176	182
K= 0,H= 10		
-6	173	142
-4	103	77
0	113	138
2	310	330
K= 1,H= 10		
-6	237	222
-5	132	130
-4	136	114
-3	136	114
-2	195	199
-1	255	256
2	115	81
4	130	169
K= 2,H= 10		
-9	129	111
-6	131	113
-4	139	126
-1	144	155
1	455	448
K= 3,H= 10		
-1	279	284
2	161	166
K= 4,H= 10		
-2	204	204
-1	106	143
K= 5,H= 10		
-5	128	136
K= 0,H= 11		
-2	168	151
0	319	319
K= 1,H= 11		
-10	131	121
-5	151	103
-4	115	119
-3	136	100
K= 2,H= 11		
-7	127	131
K= 3,H= 11		
-2	155	139
3	121	132

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[9] Details of the prepared mesoionic compounds will be published in a separate paper.

Experimental

Synthesis——To a suspension of 0.72 g of NaH in 20 ml abs. Me_2SO 1.75 g of 1-acetyl-3-indolinone was added, followed by 1.1 g CS_2 with vigorous stirring, during 30 min, while the temperature of the reaction mixture was maintained about 10°. After the reaction mixture was stirred for 30 min at about 10°, it was poured into ice–water and made acidic with 10% hydrochloride. The precipitate was collected on a filter and washed with MeOH. A solution of 2 g of this product and 1 g of $BzNH_2$ in 50 ml of MeOH was refluxed for 1 hr. After cooling, the precipitate was again collected by filtration, washed with MeOH, and recrystallized from dimethyl formamide to yellow crystals, mp 305°.

From the systematic absence of the reflections in the Osillation and Weissenberg photographs, the space group and cell constants were determined to be $P2_1/c$, and $a=11.58$, $b=8.52$, $c=15.50$ Å, $\beta=102.7°$. The observed density was 1.36 $g \cdot cm^{-3}$ measured by the floatation method while the calculated value was 1.30 $g \cdot cm^{-3}$ which was obtained by taking into acount that four molecules of $C_{18}H_{14}ON_2S$, are contained in the unit cell dimension. Intensity data were collected using the Zr-filtered Mo$K\alpha$ radiation. All independent reflections for which $2\theta \leq 60°$ were scanned by the ω-2θ technique at the rate of 2.0°/min.

Structure Analysis

The usual heavy atom method was applied for phase determination using the S atom. From the vectors in the Patterson map, the positional parameters of the heavy atom were uniqly determined to be

Table II. The Final Atomic Coordinates

Atom	x	y	z
S	0.5929	−0.1314	0.6877
O (1)	0.2982	0.0014	0.5456
C (2)	0.3585	0.1229	0.5602
C (3)	0.4761	0.1406	0.6141
C (4)	0.5682	0.0606	0.6675
N (5)	0.6485	0.1799	0.7053
C (6)	0.7581	0.1521	0.7695
C (7)	0.6069	0.3229	0.6772
C (8)	0.6619	0.4721	0.7065
N (9)	0.5046	0.2987	0.6209
C (10)	0.4092	0.3903	0.5736
C (11)	0.3958	0.5452	0.5644
C (12)	0.2856	0.5975	0.5143
C (13)	0.1951	0.5014	0.4765
C (14)	0.2111	0.3410	0.4862
C (15)	0.3180	0.2870	0.5351
C (16)	0.8640	0.1652	0.7273
C (17)	0.8645	0.1077	0.6434
C (18)	0.9658	0.1188	0.6081
C (19)	1.0647	0.1836	0.6591
C (20)	1.0724	0.2402	0.7406
C (21)	0.9699	0.2323	0.7760
H-C (6)	0.7517	0.0353	0.8011
H-C (6)	0.7614	0.2310	0.8160
H-C (8)	0.7366	0.4386	0.7482
H-C (8)	0.6134	0.5341	0.7417
H-C (8)	0.6708	0.5159	0.6569
H-C (11)	0.4443	0.6512	0.5871
H-C (12)	0.2742	0.7199	0.5026
H-C (13)	0.1195	0.5446	0.4279
H-C (14)	0.1497	0.2578	0.4453
H-C (17)	0.7875	0.0503	0.6103
H-C (18)	0.9645	0.0761	0.5457
H-C (19)	1.1275	0.1706	0.6221
H-C (20)	1.1398	0.2609	0.7868
H-C (21)	0.9631	0.2570	0.8275

$x/a=0.594$, $y/b=0.108$, $z/c=0.684$. The first Fourier synthesis was calculated with phases derived from the contribution of the S atom alone (R=0.58). This Fourier map showed chemically recognisable structural fragments which were allowed the positions of 1 oxygen, 2 nitrogen, and 18 carbon atoms. By including these atoms in the next structure factor calculation, R was reduced to 0.38. The values of the temperature factor in the early stages of the structure factor calculation, 3.5 Å for sulfur and 4.0 Å for all remaining light atoms, were used. The whole atomic coordinates of the molecule were determined in the next cycle of Fourier calculation and refined by means the block diagonal-squares procedures. After 3

TABLE III. Final Thermal Parameters as exp-$[\beta_{11}h^2+\beta_{22}k^2+\beta_{33}]^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl]$, with Estimated Standard Deviations in Brackets

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S	0.0070	0.0094	0.0053	0.0007	0.0011	0.0001
O (1)	0.0085	0.0146	0.0057	−0.0017	0.0000	−0.0010
C (2)	0.0073	0.0122	0.0034	−0.0010	0.0004	−0.0002
C (3)	0.0056	0.0082	0.0041	0.0004	0.0005	0.0003
C (4)	0.0063	0.0094	0.0052	0.0015	0.0022	−0.0008
N (5)	0.0054	0.0078	0.0044	−0.0006	0.0002	0.0004
C (6)	0.0058	0.0128	0.0044	−0.0004	0.0013	−0.0009
C (7)	0.0060	0.0102	0.0035	0.0016	0.0014	−0.0001
C (8)	0.0065	0.0100	0.0057	0.0008	0.0011	−0.0007
N (9)	0.0056	0.0108	0.0028	0.0018	0.0008	0.0001
C (10)	0.0049	0.0125	0.0041	0.0003	0.0013	0.0006
C (11)	0.0090	0.0121	0.0046	−0.0004	0.0023	0.0001
C (12)	0.0099	0.0113	0.0045	0.0015	0.0022	0.0010
C (13)	0.0084	0.0173	0.0040	0.0047	0.0013	0.0019
C (14)	0.0093	0.0171	0.0041	0.0015	−0.0010	0.0010
C (15)	0.0065	0.0101	0.0039	−0.0007	0.0016	−0.0007
C (16)	0.0033	0.0066	0.0044	−0.0006	−0.0001	0.0003
C (17)	0.0063	0.0138	0.0050	0.0005	0.0009	−0.0013
C (18)	0.0123	0.0240	0.0054	0.0063	0.0025	0.0027
C (19)	0.0082	0.0196	0.0071	0.0022	0.0030	0.0056
C (20)	0.0083	0.0213	0.0065	0.0001	0.0008	0.0010
C (21)	0.0063	0.0162	0.0065	0.0018	0.0010	−0.0022

TABLE IV. Bond Distances with Standard Deviations

Bond	Length	σ	Bond	Length	σ
S -C(4)	1.6784 A	0.0115 A	C (16)-C (21)	1.4121	0.0151
O(1)-C(2)	1.2406	0.0146	C (17)-C (18)	1.4038	0.0206
C(2)-C(3)	1.4400	0.0142	C (18)-C (19)	1.3569	0.0186
C(2)-C (15)	1.4986	0.0167	C (19)-C (20)	1.3371	0.0214
C(3)-C(4)	1.3777	0.0146	C (20)-C (21)	1.4153	0.0210
C(3)-N(9)	1.3852	0.0148	H(1)-C(6)	1.1185	0.1238
C(4)-N(5)	1.4150	0.0137	H(2)-C(6)	0.9803	0.1049
N(5)-C(6)	1.4494	0.0131	H(3)-C(8)	1.0008	0.0927
N(5)-C(7)	1.3465	0.0141	H(4)-C(8)	1.0137	0.1369
C(6)-C (16)	1.5161	0.0171	H(5)-C(8)	0.8805	0.1050
C(7)-C(8)	1.4492	0.0164	H(6)-C (11)	1.0806	0.1238
C(7)-N(9)	1.3234	0.0129	H(7)-C (12)	1.0610	0.1064
N(9)-C (10)	1.4177	0.0135	H(8)-C (13)	1.0852	0.0993
C (10)-C (11)	1.3322	0.0177	H(9)-C (14)	1.0998	0.1035
C (10)-C (15)	1.4035	0.0154	H (10)-C (17)	1.0464	0.1022
C (11)-C (12)	1.4118	0.0166	H (11)-C (18)	1.0303	0.1347
C (12)-C (13)	1.3574	0.0173	H (12)-C (19)	1.0269	0.1279
C (13)-C (14)	1.3830	0.0194	H (13)-C (20)	0.9526	0.1085
C (14)-C (15)	1.3800	0.0160	H (14)-C (21)	0.8445	0.1253
C (16)-C (17)	1.3908	0.0176			

cycles of refinements with isotropic temperature parameters for whole atoms except hydrogen atoms the R factor was reduced to 0.12. In order to obtain the positions of the hydrogen atoms, the difference Fourier synthesis was computed. These hydrogen atoms were included in the subsequent refinements, in fixed positions, with thermal parameters taken from those of associated atom. The apparent C–H distance ranged from 0.89 to 1.10 Å. Using parameter of these hydrogen, the whole atomic coordinates of the molecule were further refined by means of block diagonal least-squares technique with anisotropic thermal parameters for all atoms except hydrogen atoms. The final conventional R was reduced to 0.067. The final observed and calculated structure factor amplitudes, atomic coordinates, and anisotropic thermal parameters are listed in Tables I, II, and III, respectively.

Table V. Bond Angles with Standard Deviations

Angle	θ	σ	Angle	θ	σ
O(1)-C(2)-C(3)	127.99	1.07	N(9)-C(10)-C(11)	131.28	1.01
O(1)-C(2)-C(15)	126.81	0.97	N(9)-C(10)-C(15)	107.62	0.99
C(3)-C(2)-C(15)	104.78	0.95	C(11)-C(10)-C(15)	121.06	1.00
C(2)-C(3)-C(4)	143.58	1.10	C(10)-C(11)-C(12)	116.22	1.09
C(2)-C(3)-N(9)	108.98	0.91	C(11)-C(12)-C(13)	124.44	1.20
C(4)-C(3)-N(9)	107.15	0.87	C(12)-C(13)-C(14)	118.47	1.11
S -C(4)-C(3)	132.20	0.87	C(13)-C(14)-C(15)	118.13	1.13
S -C(4)-N(5)	123.60	0.78	C(2)-C(15)-C(10)	108.12	0.91
C(3)-C(4)-N(5)	104.18	0.91	C(2)-C(15)-C(14)	130.17	1.07
C(4)-N(5)-C(6)	124.31	0.90	C(10)-C(15)-C(14)	121.67	1.11
C(4)-N(5)-C(7)	111.10	0.82	C(6)-C(16)-C(17)	123.20	0.92
C(6)-N(5)-C(7)	124.52	0.90	C(6)-C(16)-C(21)	119.30	1.07
N(5)-C(6)-C(16)	111.25	0.96	C(17)-C(16)-C(21)	117.44	1.10
N(5)-C(7)-C(8)	126.18	0.92	C(16)-C(17)-C(18)	121.10	1.06
N(5)-C(7)-N(9)	106.08	0.93	C(17)-C(18)-C(19)	118.16	1.34
C(8)-C(7)-N(9)	127.69	1.01	C(18)-C(19)-C(20)	124.66	1.46
C(3)-N(9)-C(7)	111.45	0.88	C(19)-C(20)-C(21)	117.56	1.23
C(3)-N(9)-C(10)	110.50	0.83	C(16)-C(21)-C(20)	121.06	1.25
C(7)-N(9)-C(10)	137.51	1.00			

Table VI. Deviation of Atoms from the Best Plane through Five Atoms of the Imidazolium Ring

C(3)	−0.0070	C(2)	−0.1376
C(4)	0.0006	S	0.0312
N(5)	0.0059	C(6)	−0.0356
C(7)	−0.0105	C(8)	−0.0956
N(9)	0.0109	C(10)	−0.1122

The equation of the plane is $0.6453X-0.0749Y-0.7603Z=-4.9381$

Table VII. Deviation of Atoms from the Best Plane through Eleven Atoms of the Imidazo[1,5-*a*]indolium Ring

C(2)	0.0090	C(13)	−0.0623
C(3)	0.0478	C(14)	−0.0326
C(4)	−0.0479	C(15)	0.0280
N(5)	−0.0763	O(1)	−0.1526
C(7)	−0.0146	S	−0.0949
N(9)	0.0888	C(6)	−0.2224
C(10)	0.0713	C(8)	−0.1058
C(12)	−0.0111		

The equation of the plane is $0.5933X-0.0425Y-0.8039Z=-5.5366$

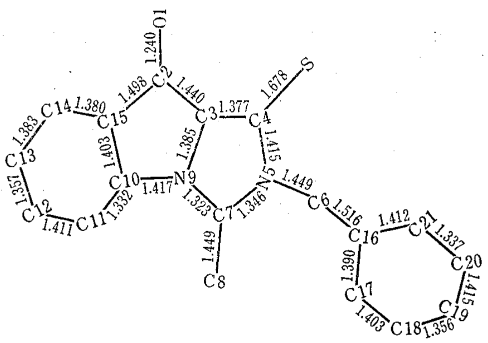

Fig. 1. Bond Distances

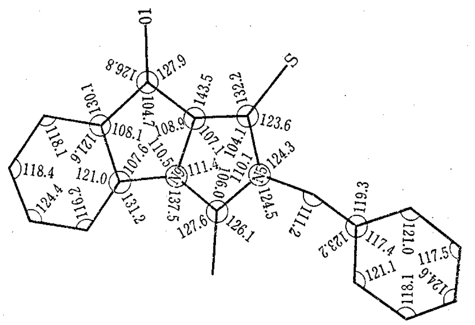

Fig. 2. Bond Angles

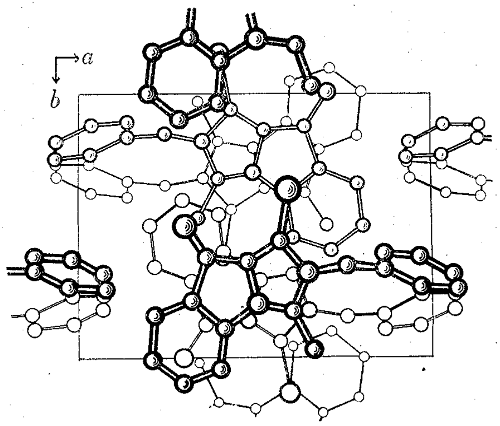

Fig. 3. Projection of the Crystal Structure along *c* Axis

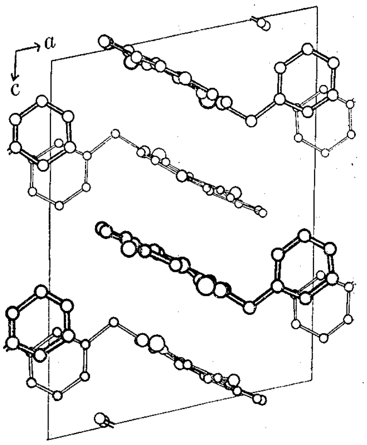

Fig. 4. Projection of the Crystal Strucuture along *b* Axis

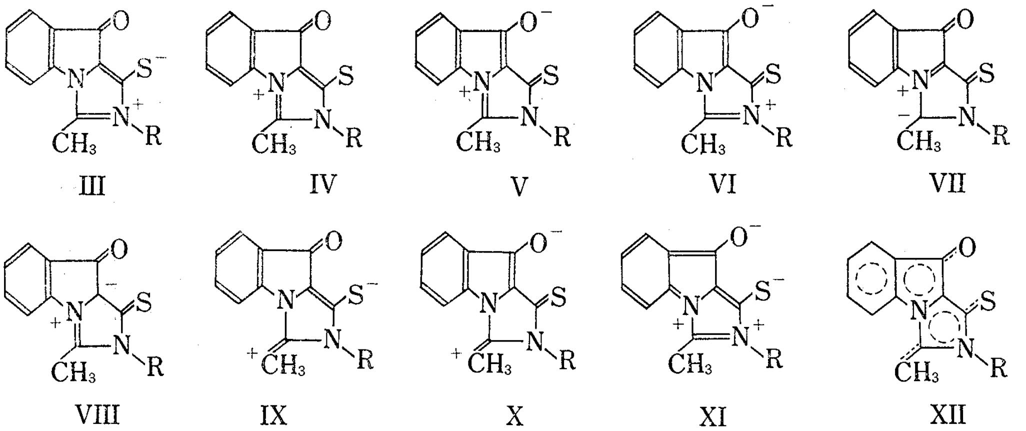

Chart 2

Result and Discussion

The bond distance and angles are shown in Fig. 1 and in Tables I and II. The C(2)-O bond distance of 1.241 Å is slightly longer than the values for C=O found in benzoquinone (1.222 Å),[10] chloranil (1.195 Å),[11] 2,6-dimethyl-1,4-benzoquinone (1.224, 1.229 Å),[12]

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[10] J. Trotter, *Acta Cryst.*, **13**, 86 (1960).

[11] S.S. Chu, G.A. Jeffreg, and T. Sakurai, *Acta Cryst.*, **15**, 661 (1962).

[12] D. Rabinovich and G.M.J. Schmidt, *J. Chem. Soc.* (*B*), **1967**, 127.

2,3-dimethylbenzoquinone (1.213 Å),[13] and dibromonaphthoquinone (1.19, 1.17 Å).[14] In zwitterion form of amino acids, the distance of C=O carbonyl group is about 1.25 Å.[15] Therefore, from this C(2)-O bond distance in this molecule, the molecule seems to take more ionized form than theusual C=O double bond. There are some reports of mesoionic compounds which contain carbonyl group; rhodanine (1.33 Å)[8] and sydnone (1.22 Å).[5] The distance of 1.678 Å for S=C double bond agrees well with the expected value of the mean S=C double bond of 1.678 Å.[16]

The C(7)-C(8) bond distance of 1.449 Å is half between the usual Csp^2-Csp^3 single bond of 1.508 Å which lies between mean value for those methylated quinone derivatives[12,13] and the aromatic C-C bond distance of 1.395 Å found in many compounds containing a benzene ring. Shortening of this particular methyl group may reflect the up-field shift (3.1 ppm (3H, singlet) in pyridine) in nuclear magnetic resonance spectrum of III. These results may be explained by the fact that there is some nature of hyperconjugated system in the C(8)-C(7) bonding.

The mean C-N bond distance in both five-membered rings is 1.337 Å which dose not significantly differ from a conjugated double bond.[17-19] The best mean plane consists of eight atoms in these rings, C(2), C(3), C(4), C(5), C(7), N(9), C(10), and C(13) is almost planar. The deviations from the least squares plane are given in Tables VI and VII in which even the largest deviation is only 0.089 Å at N(9). The mean bond angle in five-membered rings is 107.8° which corresponds to the theoretical value of 108°, indicating that each five-membered ring is very planar.

The bond angle of 132.2° of S-C(4)-C(3) is significantly larger than the opposite side bond angle of 123.6° for S-C(4)-N(5). This phenomenone is thought to be due to the mutual atomic repulsion between the sulfur and oxygen atoms instead of attraction which is observed in thio-thiophthene.[20] Together with the bond lengths and planarity in five-membered rings, it would be concluded that the π-electrons in this ring system are considerably delocarized. Thus, the cannonical forms may be written in the form of (III), (IV), (V), ……(XI) contributed to the resonance hybrid.

The molecules are stacked over along the c-axis by their π-π interaction force. The shortest intermolecular contact is 3.25 Å for O……C (17) which would refer to the distance of charge transfer complex in chloranyltetramethyl *p*-phenylenediamine (3.26 Å).[21] The S……N(9), S……C(8), and S……C(7) distances of intermolecules are 3.45, 3.47, and 3.47 Å, respectively, which are slightly more than the sum of Van der Waals radii of S and C by Pauling.[21]

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13) D. Rabinovich, *J. Chem. Soc.* (*B*), **1967**, 140.
14) M. Breton-Lacowbe, *Acta Cryst.*, **23**, 1031 (1967).
15) G.V. Gurskaya, "The Molecular Structure of Amino Acids," Translated from Russian Consultants Bureau, New York, 1968.
16) C. Tamura, *Yuki Gosei Kagaku Kyokaishi*, **29**, 977 (1971).
17) P.J. Wheatly, *Acta Cryst.*, **8**, 224 (1955).
18) P.J. Wheatly, *Acta Cryst.*, **10**, 182 (1957).
19) F. Bertiontti, G. Giacowello, and A.M. Liquori, *Acta Cryst.*, **9**, 510 (1956).
20) M. Mammi, R. Bardi, G. Traverso, and S. Bezzi, *Nature.*, **192**, 1282.
21) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, New York, 1960.