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Crystal and Molecular Structure of 3-Phenylisoxazolin-5-one

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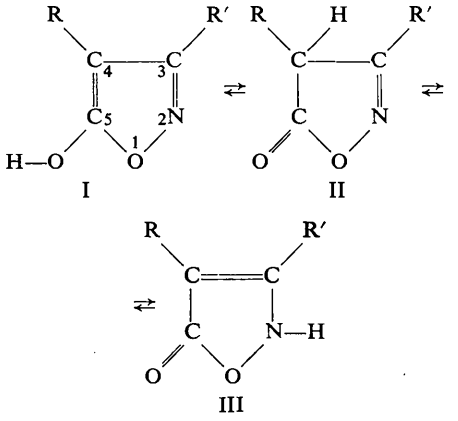
The crystal structure of 3-phenylisoxazolin-5-one has been determined from three-dimensional X-ray data. The crystals are monoclinic, space group $P2_1/c$ with four molecules in the unit cell. The cell dimensions are $a=10{\cdot}084$, $b=5{\cdot}367$, $c=18{\cdot}096$ Å, $\beta=127{\cdot}4°$. The structure was refined by the block-diagonal least-squares method to a final R value of 0·108 for 1156 observed reflexions. Bond lengths and angles in the isoxazolin-5-one ring are very close to those in 3,3′-bi-2-isoxazoline, except the C–O bond, which is significantly shorter. The ring is planar and makes an angle of 2·45° with the plane of the phenyl ring.

Introduction

The derivatives of 5-hydroxisoxazole may exist in the following three tautomeric forms:



Many investigations have been performed in order to assign the stable tautomeric form to each derivative and to understand the factors which influence the equilibrium between the above three forms. After the earlier investigations (Uhlenhuth, 1897; Moureu & Lazennec, 1907; Kohler & Blatt, 1928) by chemical methods, studies with more advanced physical techniques (comparison of ultraviolet, infrared and Raman spectra and dipole moments with those of a compound of known structure) were carried out by Brown, Hukins, Le Fèvre, Northcott & Wilson (1949), Angyal & Le Fèvre (1953) and Califano, Speroni, Tafuri & Vitale (1958). Afterwards Speroni (1962) suggested that the three tautomeric forms should be energetically very close, and that the equilibrium should be determined mainly by two factors: (i) the influence of the substituents in positions 3 and 4; (ii) the interactions with the solvent molecules in solution and with the nearest neighbour molecules in the solid state. From ultraviolet and infrared investigations of fifteen compounds of the series it was deduced (Boulton & Katritzky, 1961; Katritzky, Oksne & Boulton, 1962) that the 3-monosubstituted derivatives exist mainly in form II in the solid state and in low dielectric constant media; in aqueous solution a significant percentage of form III is also found to be present. Form III is, however, generally exhibited by bisubstituted derivatives.

3-Phenylisoxazolin-5-one, which was first synthesized by Claisen & Zedel (1891) and has been extensively studied. The determination of its structure by X-ray diffraction was undertaken as a part of a program on the bi-isoxazoles and some phenyl derivatives of isoxazole (Cannas & Mocci, 1965; Cannas & Marongiu, 1967, 1968).

Experimental

3-Phenylisoxazoline-5-one was prepared from hydroxylamine and the ethyl ester of benzoylacetic acid, according to Moureu & Lazennec (1907). Crystals suitable for X-ray analysis were grown by slow evaporation of an ethyl alcohol solution. The crystals are colourless prisms elongated along **b**; they turn to orange-yellow after a few days of exposure to X-rays. This phenomenon does not produce any detectable variation in the position and intensity of the diffraction spots. Cell dimensions were determined from zero layer Weissenberg photographs around [100] and [010].

Crystal data:

3-Phenylisoxazoline-5-one $C_9H_7NO_2$.

M.W. 161·06, m.p. 150–52 °C.

$a=10{\cdot}084\pm0{\cdot}025$ Å, $b=5{\cdot}367\pm0{\cdot}015$ Å,

$c=18{\cdot}096\pm0{\cdot}030$ Å, $\beta=127{\cdot}4\pm0{\cdot}5°$.

$V=778{\cdot}0$ Å^3. $D_m=1{\cdot}36$ g.cm^{-3},

D_c(for $Z=4$) $=1{\cdot}37$ g.cm^{-3}.

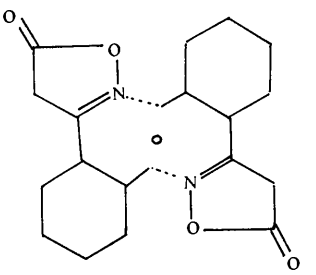
Space group $P2_1/c$ from systematic absences.

A crystal of dimensions $0{\cdot}35\times0{\cdot}50\times0{\cdot}35$ mm was mounted along the b axis and reflexions of the type $h0l$ to $h4l$ were obtained from equi-inclination Weissenberg photographs, using Ni-filtered Cu $K\alpha$ radiation. Each layer was recorded twice with a four film multipack and average exposure times of 100 and 2·5

hours respectively. The range of intensities, estimated visually by comparison with a standard scale, is between 10000 and 1·0. The intensities for layers $h=0$ through 5 were also recorded with an average exposure of 50 hours to provide cross-correlation terms. Of the 1634 reflexions which should appear on the films examined, the intensities of 1093 were estimated, 70, just barely detectable, were assigned $I_{min}/2$ and the remaining 471 were assigned $I_{min}/4$. Intensities were reduced to structure amplitudes with an IBM 1620/II program which takes into account Lorentz, polarization and spot-shape factors and incipient but incomplete α_1–α_2 splitting. A standard deviation for each F_o was estimated according to five intensity ranges; a percentage error was assumed in the range of top intense reflexions and a constant error in the following three. The reflexions which appeared in the fifth range were too weak to be estimated with any accuracy; they were given a code to exclude them from the rescaling and refinement procedures. Reflexions were put on a common relative scale by the least-squares procedure of Rae (1965). The atomic scattering factors were interpolated from the values given in *International Tables for X-ray Crystallography* (1962).

Structure determination and refinement

The structure was solved by trial and error methods using the *h*0*l* reflexions. The high intensity of the 004 reflexion suggested a packing of molecules parallel to the *a* axis. Moreover, the value of the 002 structure factor suggested that the intercept of the molecular plane with the *c* axis should be near to $\frac{1}{8}$ and not $\frac{1}{4}$. According to the spectroscopic studies, a model of tautomeric form II was assumed, with bond distances and angles derived from the literature. To simplify and limit the possible trials, we assumed a centrosymmetric unit where two molecules are connected through C–H···N contacts.



The centre of symmetry of this dimer was located at $\frac{1}{2},0,0$ and the molecular axis through C(10) and the mid point of the C(5)–O(1) bond was kept close to parallel to the *a* axis. Systematic trial packings were obtained for the two different orientations of the molecule with respect to the *a* axis and for slightly different rotations of the molecule about the molecular axis defined above; the length of the *b* axis suggested a rotation of approximately 50°. All the trials were checked by the values of intermolecular distances and and by structure factor graphs. In this way a molecular disposition was obtained, giving a fair agreement between observed and calculated structure factors for the *h*0*l* reflexions. All the atoms were located in an electron density projection, and after two successive

Table 1. *Final positional and thermal parameters*

The estimated standard deviations given in parentheses refer to the last decimal position.

	x	*y*	*z*
O(6)	0·0190 (4)	0·3289 (6)	0·1890 (2)
O(1)	0·8411 (4)	0·6454 (5)	0·1120 (2)
N(2)	0·6854 (5)	0·7286 (6)	0·0918 (3)
C(3)	0·6409 (5)	0·5735 (5)	0·1270 (2)
C(4)	0·7633 (6)	0·3638 (6)	0·1769 (3)
C(5)	0·8906 (6)	0·4304 (7)	0·1633 (3)
C(7)	0·4849 (5)	0·6096 (6)	0·1163 (2)
C(8)	0·4415 (6)	0·4402 (7)	0·1574 (3)
C(9)	0·2927 (6)	0·4690 (8)	0·1458 (3)
C(10)	0·1849 (6)	0·6657 (9)	0·0931 (3)
C(11)	0·2298 (7)	0·8364 (8)	0·0531 (3)
C(12)	0·3783 (6)	0·8092 (7)	0·0643 (3)

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
O(6)	0·01585 (68)	0·06309 (141)	0·00757 (20)	0·01044 (149)	0·01492 (64)	0·00568 (82)
O(1)	0·01796 (66)	0·04354 (110)	0·00710 (17)	0·00045 (127)	0·01656 (59)	0·00472 (66)
N(2)	0·01873 (74)	0·03573 (119)	0·00656 (20)	0·00283 (142)	0·01569 (66)	0·00537 (65)
C(3)	0·01520 (79)	0·02543 (111)	0·00440 (17)	−0·00518 (133)	0·00988 (63)	−0·00105 (61)
C(4)	0·01543 (85)	0·03293 (127)	0·00579 (21)	0·00398 (152)	0·01325 (75)	0·00443 (76)
C(5)	0·01457 (87)	0·03880 (149)	0·00516 (21)	0·00279 (154)	0·01089 (74)	0·00068 (75)
C(7)	0·01309 (76)	0·03002 (118)	0·00415 (18)	−0·00058 (142)	0·00880 (65)	−0·00114 (65)
C(8)	0·01653 (88)	0·03646 (133)	0·00561 (21)	−0·00011 (164)	0·01320 (75)	0·00076 (76)
C(9)	0·01845 (107)	0·04554 (163)	0·00666 (25)	−0·00258 (191)	0·01542 (90)	−0·00067 (98)
C(10)	0·01309 (83)	0·05354 (177)	0·00607 (24)	−0·00001 (188)	0·01170 (77)	−0·00571 (98)
C(11)	0·01699 (99)	0·04691 (163)	0·00626 (25)	0·01019 (188)	0·01187 (84)	0·00165 (98)
C(12)	0·01728 (91)	0·03581 (138)	0·00499 (20)	0·00054 (163)	0·01118 (74)	0·00192 (77)

Table 2. *Observed and calculated structure factors*

Columns are: $h, l, 10F_o, 10F_c$. * For unobserved reflexions, ** for reflexions assumed to be affected by extinction.

K=0			
1	0	139	-128
2	0	337	-333
3	0	45	-42
4	0	95	73
5	0	65	64
6	0	137	137
7	0	19	2
8	0	47	40
9	0	16 *	16
10	0	10 *	10
0	2	4 *	-29
1	2	90	-81
2	2	69	-60
3	2	105	-100
4	2	34	4
5	2	196	-189
6	2	18 *	-12
7	2	119	-106
8	2	45	-32
9	2	13 *	-14
-1	2	395	-438
-2	2	563	-584
-3	2	63	-63
-4	2	461	-392
-5	2	403	377
-6	2	88	87
-7	2	16 *	9
-8	2	19 *	9
-9	2	75	-56
-10	2	31	-26
0	4	884 **	-1122
1	4	48	-54
2	4	22	-20
3	4	136	141
4	4	162	161
5	4	81	73
6	4	175	-142
7	4	125	87
8	4	64	48
-1	4	504 **	616
-2	4	404	425
-3	4	7 *	30
-4	4	205	-170
-5	4	171	140
-6	4	40	-51
-7	4	294	-274
-8	4	133	-110
-9	4	58	46
-10	4	37	-35
-11	4	12 *	-16
0	6	50	55
1	6	118	-116
2	6	120	117
3	6	22	-9
4	6	42	33
5	6	47	41
6	6	149	-126
7	6	57	47
-1	6	434	463
-2	6	353	312
-3	6	275	278
-4	6	325	294
-5	6	369	-330
-6	6	13 *	-23
-7	6	134	114
-8	6	169	149
-9	6	222	199
-10	6	19 *	17
-11	6	15 *	-11
0	8	74	-81
1	8	190	-191
2	8	114	126
3	8	47	-47
4	8	64	-59
5	8	69	-68
6	8	104	69
-1	8	62	-62
-2	8	304	-283
-3	8	326	-328
-4	8	199	-199
-5	8	260	-250
-6	8	46	36
-7	8	171	151
-8	8	16 *	3
-9	8	183	-160
-10	8	19 *	10
-11	8	16 *	-20
-12	8	11 *	-24
0	10	14 *	25
1	10	101	100
2	10	18 *	-16
3	10	20 *	21
4	10	18 *	6
5	10	14 *	-29
-1	10	77	78
-2	10	101	105
-3	10	204	-209
-4	10	166	169
-5	10	234	228
-6	10	146	143
-7	10	64	-61
-8	10	167	-163
-9	10	151	-123
-10	10	54	60
-11	10	17 *	19
-12	10	13 *	-1
0	12	29	27
1	12	160	126
2	12	69	-63
3	12	17 *	-25
4	12	13 *	-12
-1	12	92	-95
-2	12	32	32
-3	12	78	84
-4	12	26	18
-5	12	13 *	-10
-6	12	34	-34
-7	12	143	137
-8	12	133	-125
-9	12	126	124
-10	12	90	50
-11	12	92	66
-12	12	81	56
0	14	49	-47
1	14	22	-20
2	14	16 *	10
3	14	11 *	28
-1	14	72	-67
-2	14	33	-24
-3	14	138	136
-4	14	183	-197
-5	14	113	-100
-6	14	69	-71
-7	14	57	60
-8	14	19 *	-2
-9	14	34	-47
-10	14	72	-59
-11	14	79	-54
-12	14	13 *	-10
0	16	17 *	21
1	16	37 *	-36
-1	16	19 *	16
-2	16	75	67
-3	16	42	37
-4	16	28	30
-5	16	60	55
-6	16	19 *	7
-7	16	132	-122
-8	16	298	260
-9	16	54	-44
-10	16	79	-49
-11	16	29	-26
-12	16	13 *	17
0	18	38	32
-1	18	37	-37
-2	18	16 *	14
-3	18	60	-49
-4	18	25	26
-5	18	23 *	-26
-6	18	63	-48
-7	18	28	-26
-8	18	102	80
-9	18	12 *	4
-10	18	34	-32
-11	18	63	39
-12	18	11 *	-12
-2	20	64	-57
-3	20	13 *	-
-4	20	16 *	8
-5	20	22 *	18
-6	20	17 *	8
-7	20	75	52
-8	20	175	-128
-9	20	16 *	14
-10	20	31	28
-11	20	12 *	-2
-5	22	13	12
-6	22	25	21
-7	22	30	-28
-8	22	39	-32
-9	22	41	39
-10	22	24	24
K=1			
1	0	122	143
2	0	104	111
3	0	119	-111
4	0	194	-220
5	0	106	95
6	0	84	83
7	0	151	-113
8	0	100	-76
9	0	10 *	2
10	0	7 *	-22
0	1	522 **	-686
1	1	110	-125
2	1	181	-200
3	1	84	85
4	1	7 *	8
5	1	187	181
6	1	117	-115
7	1	87	70
8	1	51	42
9	1	10 *	-14
-1	1	213	239
-2	1	140	181
-3	1	99	105
-4	1	7 *	4
-5	1	97	-97
-6	1	26	-31
-7	1	145	-125
-8	1	41	-34
-9	1	28	26
-10	1	7 *	5
0	2	455	508
1	2	144	-170
2	2	262	-273
3	2	61	-68
4	2	175	-182
5	2	32	31
6	2	170	170
7	2	52	-40
8	2	12 *	-7
9	2	7 *	-27
-1	2	320	-357
-2	2	279	-284
-3	2	260	-283
-4	2	172	-185
-5	2	63	-63
-6	2	54	55
-7	2	101	-80
-8	2	69	-54
-9	2	96	-80
-10	2	10 *	9
0	3	942 **	1054
1	3	176	-185
2	3	10 *	13
3	3	75	-72
4	3	9 *	-7
5	3	44	41
6	3	57	-46
7	3	37	29
8	3	10 *	15
-1	3	70	85
-2	3	58	-67
-3	3	43	42
-4	3	77	81
-5	3	144	-158
-6	3	80	76
-7	3	10 *	-2
-8	3	51	51
-9	3	89	71
-10	3	10 *	13
-11	3	16	-6
0	4	843 **	1003
1	4	242	255
2	4	147	-158
3	4	56	56
4	4	82	88
5	4	12 *	14
6	4	14 *	8
7	4	12 *	-1
8	4	9 *	29
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-4	4	99	113
-5	4	301	301
-6	4	101	111
-7	4	49	-40
-8	4	13 *	-6
-9	4	37	32
-10	4	11 *	-
-11	4	28	22
0	5	118	137
1	5	141	-153
2	5	90	96
3	5	54	-53
4	5	10 *	-16
5	5	98	-89
6	5	106	83
7	5	58	-44
8	5	24	-19
-1	5	60	-77
-2	5	348	-379
-3	5	260	-286
-4	5	166	-207
-5	5	174	158
-6	5	104	99
-7	5	43	50
-8	5	12 *	15
-9	5	119 *	-95
-10	5	12 *	-5
-11	5	25	21
0	6	209	-250
1	6	44	-39
2	6	51	-50
3	6	23	-26
4	6	38	34
5	6	14 *	-4
6	6	123	-98
7	6	10 *	-19
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-3	6	216	221
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-6	6	76	-70
-7	6	20	-21
-8	6	24	27
-9	6	50	44
-10	6	31	-35
-11	6	19	20
0	7	254	-272
1	7	83	107
2	7	39	-39
3	7	31	30
4	7	37	37
5	7	13 *	-3
6	7	11 *	17
7	7	15	22
-1	7	198	206
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-4	7	34	31
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-6	7	50	50
-7	7	139	-129
-8	7	140	-134
-9	7	33	-29
-10	7	13 *	5
-11	7	10 *	16
0	8	247	-279
1	8	151	-155
2	8	60	66
3	8	45	47
4	8	40	37
5	8	41	40
6	8	49	-43
-1	8	232	259
-2	8	105	116
-3	8	20	9
-4	8	99	-89
-5	8	55	-57
-6	8	46	-60
-7	8	190	-184
-8	8	40	48
-9	8	25	22
-10	8	59	-46
-11	8	63	-47
-12	8	36	-34
0	9	41	-38
1	9	53	57
2	9	19	-19
3	9	13 *	-10
4	9	13 *	-5
5	9	11 *	11
6	9	60	-55
-1	9	41	40
-2	9	103	115
-3	9	151	153
-4	9	34	29
-5	9	181	-183
-6	9	43	-45
-7	9	110	114
-8	9	43	-37
-9	9	154	145
-10	9	31	18
-11	9	11 *	6
-12	9	7 *	13
0	10	85	98
1	10	40	-42
2	10	34	34
3	10	27	-25
4	10	12 *	-
5	10	9 *	-2
-1	10	164	177
-2	10	78	63
-3	10	93	-100
-4	10	214	215
-5	10	49	-46
-6	10	75	75
-7	10	45	38
-8	10	151	136
-9	10	61	66
-10	10	24	24
-11	10	11 *	5
-12	10	7 *	-2
0	11	28	-32
1	11	64	-69
2	11	49	50
3	11	32	30
4	11	10 *	-10
5	11	7 *	-7
-1	11	64	-62
-2	11	52	-50
-3	11	83	75
-4	11	124	-130
-5	11	151	-151
-6	11	18	-24
-7	11	90	95
-8	11	62	60
-9	11	69	-66
-10	11	24	-16
-11	11	56	-44
-12	11	9 *	-11
0	12	12 *	-6
1	12	13 *	12
2	12	26	26
3	12	11 *	-29
4	12	7 *	-10
-1	12	56	-63
-2	12	119	-120
-3	12	143	-151
-4	12	13	-17
-5	12	65	-64
-6	12	16	27
-7	12	95	103
-8	12	179	-179
-9	12	113	-83
-10	12	51	41
-11	12	29	19
-12	12	9 *	-19
0	13	13 *	18
1	13	13 *	-6
2	13	12 *	-14
3	13	10 *	5
-1	13	12 *	-1
-2	13	87	88
-3	13	43	-43
-4	13	57	53
-5	13	94	90
-6	13	26	32
-7	13	102	-104
-8	13	121	111
-9	13	116	-86
-10	13	24	-3
-11	13	11 *	-3
-12	13	9 *	5
0	14	36	-34
1	14	25	30
2	14	10 *	-10
3	14	7 *	23
-1	14	37	38
-2	14	13 *	-1
-3	14	16 *	13
-4	14	24	26
-5	14	81	78
-6	14	53	56
-7	14	24	21
-8	14	216	-181
-9	14	28	-9
-10	14	84	62
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-12	14	9 *	5
0	15	33	29
1	15	57	46
2	15	7 *	-9
-1	15	44	-44
-2	15	13 *	17
-3	15	50	-46
-4	15	18 *	14
-5	15	12 *	6
-6	15	46	-44
-7	15	30	25
-8	15	37	-32
-9	15	52	39
-10	15	13 *	6
-11	15	67	50
-12	15	9 *	5
0	16	13 *	-9
1	16	9 *	13
-1	16	20	-11
-2	16	51	46
-3	16	58	51
-4	16	27	-23
-5	16	24	-23
-6	16	13 *	-20
-7	16	13 *	7
-8	16	58	49
-9	16	90	57
-10	16	13 *	-6
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- 7 3	57	46	2 10	54	- 53	- 4 18	12	- 17	- 8 5	8 *	6	- 5 13	39	- 38	2 6	34	30	- 5 4	10 *	- 9
- 8 3	84	- 83	3 10	9 *	- 11	- 5 18	40	- 37	- 9 5	6 *	- 13	- 6 13	25	34	3 6	21	- 22	0 5	23	- 18
- 9 3	21	- 23	4 10	7 *	- 16	- 6 18	26	36	0 6	8 *	- 6	- 7 13	80	- 94	4 6	32	29	1 5	8 *	3
-10 3	5 *	- 7	- 1 10	101	-110	- 7 18	18	18	1 6	21	23	- 8 13	21	- 24	- 1 6	26	26	2 5	7 *	8
0 4	74	78	- 2 10	105	120	- 8 18	8 *	9	2 6	37	38	- 9 13	7 *	13	- 2 6	11 *		- 1 5	13	4
1 4	60	66	- 3 10	8 *	- 4	- 9 18	7 *	8	3 6	30	- 32	-10 13	5 *	- 1	3 6	29	- 65	- 2 5	53	- 45
2 4	37	- 39	- 4 10	68	- 67	-10 18	6 *	15	4 6	8 *	2	0 14	25	36	- 4 6	25	- 19	- 3 5	37	32
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6 4	10 *	- 6	- 8 10	47	52	- 6 19	13	- 19	- 3 6	71	- 77	- 4 14	8 *	14	2 7	26	23	1 6	7 *	2
7 4	7 *	3	- 9 10	38	39	- 7 19	7 *	9	- 4 6	30	- 23	- 5 14	47	45	3 7	9 *	- 11	2 6	21	- 24
- 1 4	21	- 17	-10 10	9 *	- 12	- 8 19	15	- 20	- 5 6	37	41	- 6 14	13	8	- 1 7	10 *	- 6	- 1 6	10 *	- 7
- 2 4	93	96	-11 10	6 *	- 7	- 9 19	40	- 53	- 6 6	18	19	- 7 14	13	- 17	- 2 7	12 *	6	- 2 6	19	17
- 3 4	153	-177	0 11	109	115	-10 19	4 *	2	- 7 6	23	- 22	- 8 14	7 *	6	- 3 7	12 *	-	- 3 6	37	27
- 4 4	67	67	1 11	15	- 17	- 5 20	5 *	16	- 8 6	43	- 51	- 9 14	6 *	- 4	- 4 7	14 *	- 15	- 4 6	11 *	4
- 5 4	29	21	2 11	10 *	3	- 6 20	6 *	8	- 9 6	35	- 41	-10 14	4 *	- 4	- 5 7	52	- 52	0 7	7 *	8
- 6 4	122	-113	3 11	7 *	6	- 7 20	6 *	- 7	0 7	20	- 20	- 1 15	22	- 17	0 8	30	- 22	1 7	7 *	1
- 7 4	19	15	4 11	4 *	18	- 8 20	5 *	- 2	1 7	9 *	- 12	- 2 15	7 *	- 9	1 8	34	25	- 1 7	9 *	4
- 8 4	10 *	- 13	- 1 11	71	62	- 9 20	17	- 24	2 7	51	- 54	- 3 15	15 *	12	2 8	10 *	10	- 2 7	10 *	10
- 9 4	9 *	9	- 2 11	149	-160		K=4		3 7	9 *	4	- 4 15	26	- 25	3 8	37	- 36	- 3 7	49	45
-10 4	6 *	- 4	- 3 11	27	26	0 0	122	-148	4 7	7 *	- 15	- 5 15	29	29	- 1 8	10 *	1	- 4 7	25	- 23
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1 5	19	22	- 5 11	125	134	2 0	18	- 12	- 1 7	122	-141	- 7 15	7 *		- 3 8	12 *	- 5	0 8	46	- 37
2 5	8 *	10	- 6 11	61	64	3 0	132	140	- 2 7	160	195	- 8 15	13	15	- 4 8	56	49	- 1 8	25	18
3 5	137	135	- 7 11	11 *	- 15	4 0	35	- 39	- 3 7	25	- 22	- 9 15	21	28	- 5 8	40	34	- 2 8	18	16
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6 5	9 *	-	-10 11	15	18	7 0	30	35	- 6 7	67	- 67	- 4 16	16	- 13	2 9	8 *	- 7	- 5 8	31	- 23
7 5	12	- 13	-11 11	27	30	8 0	26	- 38	- 7 7	16	- 16	- 5 16	33	31	- 1 9	34	- 32	- 1 9	7 *	10
- 1 5	22	21	0 12	37	39	0 1	22	18	- 8 7	8 *	12	- 6 16	19	- 25	- 2 9	75	71	- 2 9	28	- 19
- 2 5	103	120	1 12	25	24	1 1	22	- 23	- 9 7	7 *	- 3	- 7 16	7 *	16	- 3 9	21	- 19	- 3 9	12	- 4
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- 5 5	68	69	- 1 12	72	- 77	4 1	49	- 47	1 8	9 *	- 8	- 3 17	5 *	- 1	0 10	9 *	3	- 2 10	7 *	- 6
- 6 5	169	-165	- 2 12	49	47	5 1	42	- 41	2 8	22	- 19	- 4 17	6 *	5	1 10	8 *	- 2	- 3 10	29	- 25
- 7 5	26	24	- 3 12	51	- 52	6 1	24	- 24	3 8	52	35	- 5 17	6 *	1	2 10	6 *	2	- 4 10	9 *	- 8
- 8 5	104	107	- 4 12	102	- 97	7 1	43	54	4 8	6 *	6	- 6 17	6 *	- 8	- 1 10	36	- 28	- 5 10	16	15
- 9 5	10 *	16	- 5 12	87	86	- 1 1	45	43	- 1 8	93	90	- 7 17	6 *	5	- 2 10	29	28	- 3 11	6 *	- 8
-10 5	13	- 14	- 6 12	10 *	- 4	- 2 1	61	- 59	- 2 8	96	-101	- 8 17	5 *	5	- 3 10	21	17	- 4 11	21	20
0 6	89	- 95	- 7 12	61	65	- 3 1	84	- 76	- 3 8	31	31	- 9 17	10	- 19	- 4 10	28	- 24	- 5 11	21	- 22
1 6	39	42	- 8 12	25	27															

Fourier syntheses the R value dropped to 0·24 for the observed $h0l$ reflexions.

The y coordinates of the trial model were introduced in an $hk0$ structure factor calculation, and the results were considered satisfactory enough to start a three-dimensional refinement.

Refinement was carried out by the block-diagonal least-squares method with the programs I.C.R. No.4 (Van der Helm, 1962) and I.C.R. No.7 (Johnson & Glusker, 1967); the minimized quantity is $\Sigma w(|kF_o| - |F_c|)^2$. The weights were given values equal to $1/\sigma^2$. For the first six cycles, positional parameters and individual isotropic temperature factors of non-hydrogen atoms were refined, and the R value dropped from 0·45 to 0·19. Then the hydrogen atoms were introduced at a distance of 1·05 Å from the pertinent carbon

atoms, assuming a tetrahedral configuration for C(4) in the isoxazoline ring. Seven low θ reflexions, with F_o systematically lower than F_c, were considered affected by secondary extinction and were excluded from the following refinement cycles. After two more cycles the R index did not drop below 0·15. At this point, an attempt to localize the hydrogen atoms by a difference-Fourier synthesis failed, probably owing to thermal anisotropy of the heavy atoms. Anisotropic thermal parameters were introduced and the refinement progressed to an R value of 0·108 for observed reflexions. Maximum shifts of positional and thermal parameters were less than one half of the standard deviations during the final cycle. A second three-dimensional difference-Fourier synthesis was calculated, which showed irregular smears of density where the hydrogen atoms were expected; in addition there were a few spurious peaks of intensity comparable to those of the hydrogen atoms, but no indication for significant changes in the refined parameters. Because of the difficulty in locating the hydrogen atoms with any accuracy, their calculated positional parameters were kept for intermolecular distance calculations. Final coordinates and thermal parameters are listed in Table 1, and Table 2 shows the observed and calculated F values. The root mean square displacement along the principal axes of the thermal ellipsoids and the direction of these axes relative to the cell edges are given in Table 3 and illustrated in Fig. 1 (Johnson, 1965). The atom O(6) exhibits a marked anisotropy with the maximum thermal movement perpendicular to the C=O bond.

Discussion

The present analysis confirms the tautomeric form II for the molecule, as postulated by Boulton & Katritzky (1961). The least-squares method of Schomaker, Waser, Marsh & Bergman (1959) was used to fit a plane through all non-hydrogen atoms in the molecule and the planes through isoxazoline-5-one and through the benzene ring. The results of this analysis, given in Table 4, show the rings to be planar and their planes are twisted by 2·45°.

Table 3. *Principal axes of thermal ellipsoids*

The root mean square displacement $\bar{u}_i$ corresponds to the ith principal axis of the ellipsoids, and $\theta_{ia}, \theta_{ib}, \theta_{ic}$* are angles between the i axis and the crystallographic axes a, b, c* respectively. The B_i are equal to the corresponding $8\pi^2\bar{u}_i^2$.

		B_i	$\bar{u}_i$	θ_{ia}	θ_{ib}	θ_{ic}
O(6)	1	3·321	0·205	14·6	81·0	101·4
	2	5·915	0·274	104·4	62·3	148·2
	3	7·780	0·314	92·4	29·4	60·7
O(1)	1	3·149	0·200	157·6	70·9	101·2
	2	4·844	0·248	67·6	36·4	117·1
	3	6·288	0·282	90·4	60·3	29·7
N(2)	1	3·292	0·204	131·9	50·0	112·1
	2	4·231	0·231	42·7	49·7	101·6
	3	5·850	0·272	96·6	65·7	25·2
C(3)	1	2·749	0·187	109·6	21·3	82·0
	2	3·616	0·214	107·6	88·1	162·3
	3	4·130	0·229	26·8	68·8	105·7
C(4)	1	3·111	0·199	153·6	68·3	104·4
	2	3·525	0·211	63·9	35·5	112·2
	3	5·142	0·255	93·6	63·4	26·9
C(5)	1	3·519	0·211	17·0	76·1	99·6
	2	4·264	0·232	103·0	76·2	160·9
	3	4·323	0·240	100·8	19·8	73·6
C(7)	1	3·267	0·203	91·7	47·8	42·6
	2	3·386	0·207	23·3	71·9	104·2
	3	3·663	0·215	113·2	47·7	128·8
C(8)	1	3·489	0·210	162·1	79·8	104·6
	2	4·209	0·231	77·7	14·3	97·1
	3	4·724	0·245	102·8	80·1	16·3
C(9)	1	3·822	0·220	168·9	82·7	98·3
	2	5·219	0·257	86·4	23·0	67·3
	3	5·599	0·266	79·5	68·3	155·6
C(10)	1	2·896	0·192	12·3	80·6	97·8
	2	4·544	0·240	87·7	60·7	29·4
	3	6·820	0·294	102·1	31·0	118·1
C(11)	1	3·821	0·220	39·5	59·7	112·8
	2	5·408	0·262	75·1	71·8	23·8
	3	6·028	0·276	125·6	36·4	96·4
C(12)	1	3·783	0·219	104·5	45·6	132·0
	2	4·398	0·236	111·7	55·3	42·8
	3	4·552	0·240	26·6	64·4	83·3

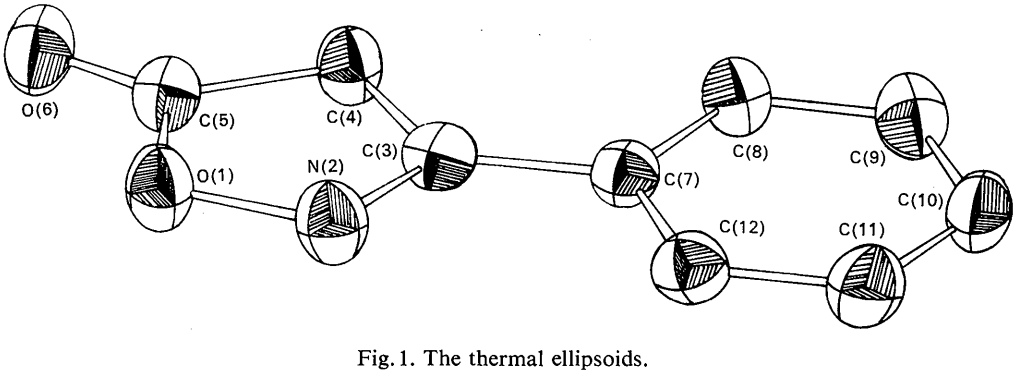

Fig. 1. The thermal ellipsoids.

Table 4. *Molecular least-squares planes*

Description of plane;

I Complete 3-phenylisoxazolin-5-one molecule
II Phenyl ring
III Isoxazolin-5-one

I $-0{\cdot}207X+2{\cdot}947Y+12{\cdot}237Z=3{\cdot}096$
II $-0{\cdot}378X+3{\cdot}030Y+12{\cdot}265Z=3{\cdot}095$
III $-0{\cdot}155X+2{\cdot}868Y+12{\cdot}317Z=3{\cdot}109$

Angle between II and III, 2·45°.

	Distances from planes		
	I	II	III
O(1)	−0·0025		0·0080
N(1)	−0·0327		−0·0059
C(3)	−0·0156		−0·0015
C(4)	0·0171		0·0042
C(5)	0·0136		0·0004
O(6)	0·0249		−0·0052
C(7)	−0·0234	0·0050	
C(8)	−0·0361	−0·0022	
C(9)	−0·0098	−0·0034	
C(10)	0·0331	0·0062	
C(11)	0·0288	−0·0034	
C(12)	0·0026	−0·0022	

The bond lengths and angles with their estimated standard deviations are diagrammatically shown in Fig. 2. Molecular parameters in the isoxazoline ring are very close to those found by Bednowitz, Fankuchen, Okaya & Soffer (1966) in 3,3′-bi-2-isoxazoline. The only significant difference is the value of the C(5)–O(1) bond, which was reported as 1·46 Å in 3,3′-bi-2-isoxazoline and was found to be 1·371 Å in the present analysis. The double bond character in 3-phenylisoxazolin-5-one might be attributed to the presence of the adjacent C(5)=O(6) bond. All the other bond lengths did not differ significantly from the values expected for the pertinent single and double bonds, which is in agreement with a negligible conjugation effect in the ring. This consideration, together with the hexagonal symmetry of the benzene ring and the value of the C(3)–C(7) bond (1·476 Å), corresponding to a C(sp^2)–C(sp^2) bond, suggests that there is no significant conjugation between the rings. The structure viewed along the *b* axis is shown in Fig. 3. The packing of the molecules in the cell does not appear very compact. The only close contacts are those between C(8)–H(8) $(x,y,z)\cdots$ N(2) $(1-x,2-y,\bar{z})$ (2·6 Å) and between O(6) $(x,y,z)\cdots$ C(5) $(1-x,\frac{1}{2}+y,\frac{1}{2}-z)$ (3·10 Å). Their values correspond to the van der Waals limiting contacts. The molecules connected by C–H···N contacts lie approximately on a plane which is very close to (014); the crystal structure can thus be described as consisting of molecular planes coinciding with (014) and the equivalent $(01\bar{4})$.

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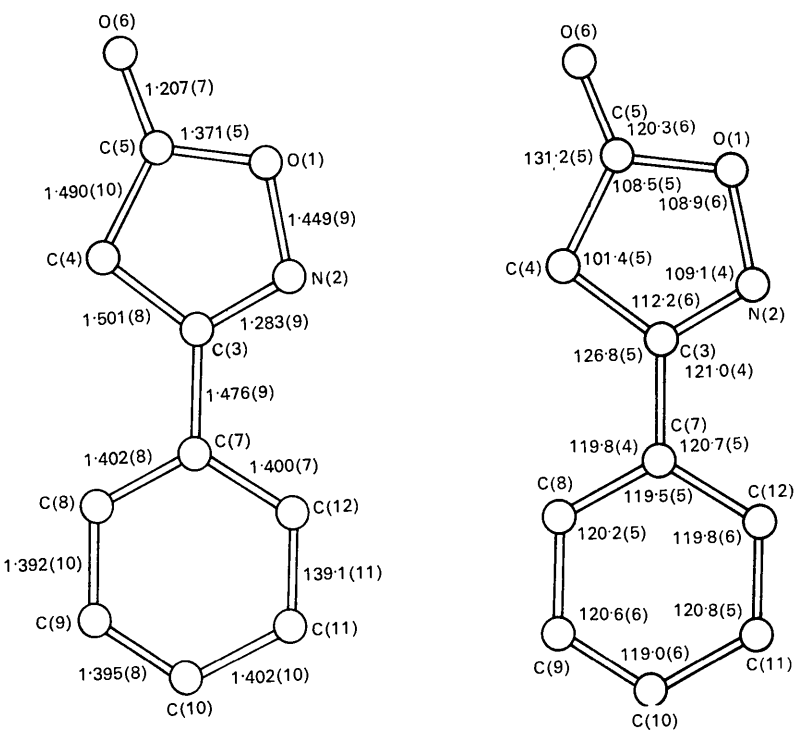

Fig. 2. Bond lengths and angles.

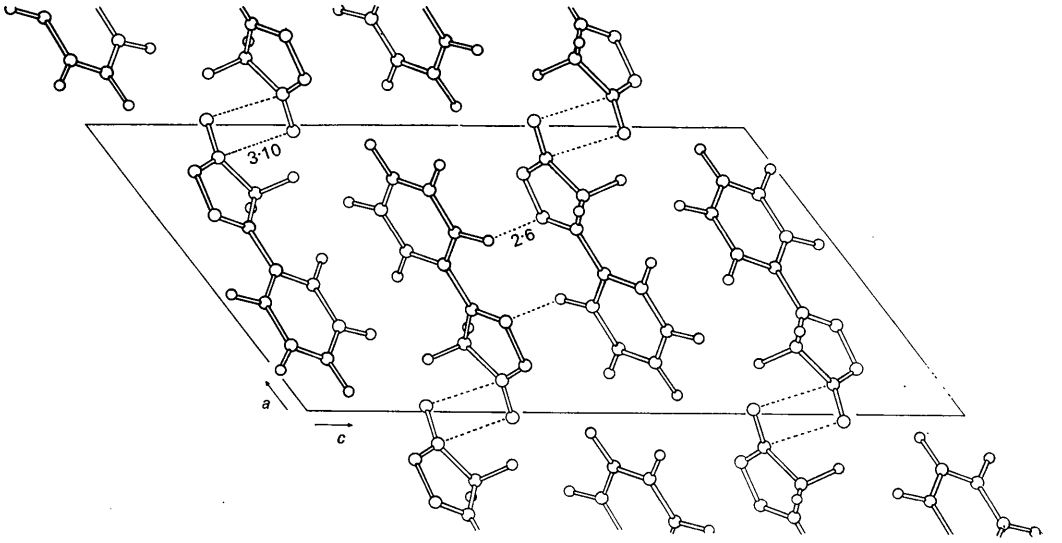

Fig. 3. Projection of the structure along the *b* axis.

References

ANGYAL, C. L. & LE FÈVRE, R. J. W. (1953). *J. Chem. Soc.* p. 2181.

BEDNOWITZ, A. L., FANKUCHEN, I., OKAYA, Y. & SOFFER, M. D. (1966). *Acta Cryst.* **20**, 100.

BOULTON, A. J. & KATRITZKY, A. R. (1961). *Tetrahedron*, **12**, 41.

BROWN, R. D., HUKINS, A. A., LE FÈVRE, R. J. W., NORTHCOTT, J. & WILSON, I. R. (1949). *J. Chem. Soc.* p. 2812.

CALIFANO, S., DEL RE, G., SPERONI, G., TAFURI, F. & VITALE, A. (1958). Comunic. VIII Congresso Nazionale di Chimica, Torino, page 137.

CANNAS, M. & MOCCI, G. (1965). *Ric. sci.* **35**, (II–A), 467.

CANNAS, M. & MARONGIU, G. (1967). *Z. Kristallogr.* **124**, 143.

CANNAS, M. & MARONGIU, G. (1968). *Z. Kristallogr.* **127**, 388.

CLAISEN, L. & ZEDEL, W. (1891). *Chem. Ber.* **24**, 140.

HELM, D. VAN DER (1961). I.C.R. No. 4. *Structure Factor Program and Least-Squares Sum Maker*. The Institute for Cancer Research. Philadelphia, Pa.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP: A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations*. ORNL–3794, Revised. Oak Ridge National Laboratory, Oak Ridge, Tennessee.

JOHNSON, C. K. & GLUSKER, J. P. (1966). *I.C.R.* 7 *Least-Squares Sums Solver Program* (*Part* 1) *and Parameter Shifter Program* (*Part* 2). The Institute for Cancer Research. Philadelphia, Pa.

KATRITZKY, A. R., OKSNE, S. & BOULTON, A. J. (1962). *Tetrahedron*, **18**, 777.

KOHLER, E. P. & BLATT, A. H. (1928). *J. Amer. Chem. Soc.* **50**, 504.

MOUREAU, C. & LAZENNEC, I. (1907). *Bull. Soc. chim. Fr.* (4) **1**, 1092.

RAE, A. D. (1965). *Acta Cryst.* **19**, 683.

SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMAN, G. (1959). *Acta Cryst.* **12**, 600.

SPERONI, G. (1962). In *The Chemistry of Heterocyclic Compounds*. Vol. 17. *Five and Six-Membered Compounds With Nitrogen and Oxygen*. New York: Interscience.

UHLENHUTH, R. (1897). *Liebigs Ann.* **296**, 33.