The Crystal Structure of *N*-Methyl-3-phenyl-4-bromoisoxazolin-5-one

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N-Methyl-3-phenyl-4-bromoisoxazolin-5-one, $C_{10}H_8NO_2Br$, crystallizes in the monoclinic space group $P2_1/n$ with cell dimensions $a=7\cdot551$, $b=18\cdot310$, $c=7\cdot626$ Å and $\beta=100\cdot85°$. There are four molecules in the unit cell. The structure, solved with the 'heavy atom' method after localization of the bromine atom from Patterson maps, was refined by three-dimensional anisotropic full-matrix least-squares analysis. A final R index of $0\cdot065$ for 1008 observed reflexions was obtained. Bond lengths and angles are normal; the planes of the phenyl and isoxazolinone rings contain a dihedral angle of $50\cdot4°$. The results are compared with those for *N*-methyl-4-phenylisoxazolin-5-one in order to explain the differences found in the solid phase between 3-aryl and 4-aryl derivatives of *N*-methylisoxazolin-5-one.

Introduction

In the solid phase the 4-aryl derivatives of *N*-methyl-isoxazolin-5-one exhibit different physical properties from those of the 3-aryl derivatives. In the preceding paper (Sabelli & Zanazzi, 1969) the crystal structure of *N*-methyl-4-phenylisoxazolin-5-one, a member of the former group of compounds, is reported. The main purpose of the present investigation is to obtain information on the crystal structure of 3-aryl substituted *N*-methylisoxazolin-5-ones, in order to give an interpretation of the differences found.

The crystal structure of *N*-methyl-3-phenyl-4-bromo-isoxazolin-5-one, which has been briefly described elsewhere (Cialdi & Sabelli, 1967), was therefore refined, and the results, as well as the general conclusions, are reported in this paper.

Experimental and structure determination

Suitable crystals for X-ray investigation were obtained by recrystallizing from alcohol the material kindly supplied by Dr De Sarlo of the Istituto di Chimica Organica of Florence University. The crystals are monoclinic, with:

$$a= 7\cdot551 \pm 0\cdot001 \text{ Å}$$
$$b=18\cdot310 \pm 0\cdot009$$
$$c= 7\cdot626 \pm 0\cdot005$$
$$\beta=100\cdot85 \pm 0\cdot07°$$

Space group: $P2_1/n$
Cell contents: $4C_{10}H_8NO_2Br$
$D_m=1\cdot61$ g.cm^{-3}, $D_x=1\cdot63$ g.cm^{-3}.

The lattice parameters were determined at room temperature. 1431 reflexions from $hk0$ to $hk4$ were collected by the Weissenberg method, with [001] as rotation axis (Cu $K\alpha$ radiation); of these, 423 were too weak to be measured. These unobserved reflexions were given an intensity value just below the minimum observed and they were included in least-squares refinement, as indicated later. The layer lines were put on the same scale by the method used in the previous paper.

Table 1. *Fractional coordinates of non-hydrogen atoms and thermal parameters*

The estimated standard deviations are given in parenthesis and refer to the last decimal places of the respective values. The temperature factors are in the form:

$$T=\exp [-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)].$$

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	0·6731 (1)	0·3827 (1)	0·6544 (2)	0·0164 (1)	0·0035 (1)	0·0272 (4)	0·0010 (1)	0·0096 (2)	−0·0017 (1)
O(1)	0·6972 (6)	0·5596 (3)	0·7463 (9)	0·0131 (9)	0·0034 (2)	0·0183 (19)	−0·0026 (3)	0·0055 (9)	−0·0007 (4)
O(2)	0·4207 (6)	0·5562 (2)	0·8155 (8)	0·0136 (8)	0·0022 (1)	0·0149 (18)	−0·0014 (3)	0·0066 (9)	−0·0014 (3)
N	0·2905 (6)	0·5006 (3)	0·8212 (9)	0·0107 (10)	0·0022 (2)	0·0129 (23)	−0·0009 (3)	0·0049 (10)	−0·0007 (4)
C(1)	0·2058 (12)	0·3336 (4)	0·5746 (15)	0·0250 (18)	0·0031 (2)	0·0046 (31)	−0·0008 (5)	0·0044 (17)	−0·0015 (6)
C(2)	0·0975 (14)	0·2677 (5)	0·5717 (22)	0·0294 (22)	0·0041 (3)	0·0215 (45)	−0·0021 (7)	0·0062 (23)	−0·0062 (10)
C(3)	0·0371 (12)	0·2455 (4)	0·7176 (16)	0·0252 (18)	0·0028 (2)	0·0108 (40)	−0·0013 (5)	0·0084 (19)	0·0013 (7)
C(4)	0·0661 (11)	0·2854 (4)	0·8692 (17)	0·0181 (15)	0·0029 (2)	0·0199 (40)	−0·0018 (5)	0·0017 (16)	0·0012 (7)
C(5)	0·1639 (10)	0·3488 (4)	0·8816 (15)	0·0161 (12)	0·0023 (2)	0·0120 (35)	0·0008 (4)	0·0048 (14)	0·0015 (5)
C(6)	0·2364 (8)	0·3721 (3)	0·7389 (12)	0·0116 (10)	0·0027 (2)	0·0022 (26)	−0·0009 (3)	0·0011 (12)	0·0000 (5)
C(7)	0·3454 (8)	0·4391 (3)	0·7519 (11)	0·0109 (9)	0·0020 (2)	0·0033 (24)	0·0001 (3)	0·0023 (10)	0·0002 (4)
C(8)	0·5140 (8)	0·4503 (3)	0·7152 (11)	0·0133 (11)	0·0027 (2)	0·0042 (25)	−0·0009 (4)	0·0024 (11)	−0·0011 (5)
C(9)	0·5656 (8)	0·5238 (3)	0·7536 (10)	0·0146 (11)	0·0022 (2)	0·0064 (25)	−0·0009 (3)	0·0056 (12)	0·0000 (4)
C(10)	0·1107 (8)	0·5332 (5)	0·7736 (17)	0·0108 (12)	0·0036 (3)	0·0264 (35)	0·0009 (4)	0·0094 (14)	−0·0008 (7)

The positions of the bromine atoms in the cell were readily found from a three-dimensional Patterson function. Oxygen, nitrogen and carbon atoms in the structure were then located by means of subsequent Fourier syntheses. After the improvement of atomic coordinates by a final more detailed electron density map, the R index, defined as $\Sigma \, ||F_o| - |F_c|| / \Sigma \, |F_o|$, was 0·17.

Refinement of the structure

The crystal structure of N-methyl-3-phenyl-4-bromo-isoxazolin-5-one was refined three-dimensionally by the least-squares method on the IBM 7090 computer* with the program of Busing & Levy adapted by Stewart (1964). The function minimized was $\Sigma \, w(|F_o| - |F_c|)^2$, where $\sqrt{w} = 1$ for observed reflexions with $F < 4F_{min}$ and for unobserved reflexions for which $F_c > F_{min}$; $\sqrt{w} = 4F_{min}/F$ for observed reflexions with $F \geq 4F_{min}$ and $\sqrt{w} = 0$ for unobserved reflexions with $F_c < F_{min}$ and for some strong reflexions with low value of $\sin \theta/\lambda$, which showed extinction. Two cycles of full-matrix least-squares refinement using individual isotropic temperature factors, each followed by a proper rescaling of F_o's, reduced the R index to 0·15. Individual anisotropic thermal parameters were then applied and R dropped to 0·076 in two cycles. At this stage a difference Fourier synthesis was computed. On the maps small peaks were found at, or very close to, the positions expected for hydrogen atoms. With the contribution of these atoms, to which an overall isotropic thermal parameter of 5 Å^2 was assigned, R reached the value 0·065 for all the observed reflexions included in the refinement. The atomic coordinates and thermal parameters for non-hydrogen atoms are listed in Table 1. The positional parameters of hydrogen atoms are given in Table 2. The observed and calculated structure factors are shown in Table 3. The atomic scattering factors used for Br, O, N, C and H were those from *International Tables for X-ray Crystallography* (1962).

Discussion

Fig. 1 shows the structure of N-methyl-3-phenyl-4-bromoisoxazolin-5-one projected along the c axis. The bond lengths and angles with their e.s.d.'s are listed in Table 4.

The equations of the best planes through the six carbon atoms of the phenyl group and through the five atoms of the isoxazolinone ring are respectively:

$$5\cdot961x - 9\cdot617y + 1\cdot246z + 1\cdot264 = 0$$
$$1\cdot952x - 4\cdot821y + 6\cdot590z - 3\cdot537 = 0$$

where x, y, and z are fractional atomic coordinates referred to the monoclinic axes. The deviations of the atoms from these planes appear in Table 5. As in the

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* The calculations were carried out at the Centro Nazionale Universitario di Calcolo Elettronico of Pisa University.

Table 2. *Fractional coordinates of hydrogen atoms*

	x	y	z
H(1)	0·260	0·345	0·440
H(2)	0·070	0·255	0·420
H(3)	−0·040	0·200	0·730
H(4)	0·015	0·270	0·960
H(5)	0·160	0·375	0·980
H(6)	0·070	0·565	0·880
H(7)	0·095	0·545	0·630
H(8)	0·000	0·500	0·810

case of N-methyl-4-phenylisoxazolin-5-one (Sabelli & Zanazzi, 1969), both rings are planar within the experimental limits. A significant difference was found for the dihedral angle between phenyl and isoxazolinone planes. This angle is 50·4°.

The phenyl ring has a mean observed C–C bond distance of 1·385 Å. The interatomic distances in the isoxazolinone ring are similar to those found for the 4-phenyl derivative: the bond lengths lie between the corresponding single and double bond values, so confirming the presence of resonance in the ring.

The bond length between the bromine atom and C(8) is 1·843 Å, in agreement with the value of 1·85 Å given by *International Tables* (1962) for bromine bound to the aromatic ring. The displacement of Br from the isoxazolinone plane (0·24 Å) has to be attributed to the steric hindrance of the phenyl group: the resultant distances between bromine and C(1) and H(1) are 3·58 and 3·31 Å respectively.

It is worth pointing out that the distance between the nitrogen atom and the carbon atom of the methyl group, which has a value of 1·464 Å, nearly the normal value for the single N–C bond, is somewhat longer than the corresponding distance found in the 4-phenyl compound, 1·421 Å. This carbon atom, C(10), shows a considerable deviation (0·79 Å) from the mean isoxazolinone plane. Most likely this displacement is a consequence of the steric hindrance between the methyl and phenyl groups: the interatomic distances are 3·48 Å for C(10)–C(5), 3·28 Å for C(10)–H(5), 3·04 Å for H(8)–C(5) and 2·79 Å for H(8)–H(5). This strained position of the methyl group could account for the exceptional behaviour of the compound when heated in alkaline solution: the reaction yields 3-phenylisoxazolin-5-one, thus showing that a demethylation occurs at the N atom (De Sarlo & Renzi, 1966).

The C=O bond, 1·200 Å long, is somewhat shorter than that (1·217 Å) in the 4-phenyl derivative, and this feature agrees with the higher value of the infrared C=O stretching frequency.

The interatomic C(6)–C(7) distance between the two rings is 1·470 Å, greater than the corresponding distance in the 4-phenyl compound (1·455 Å). This difference was expected, because of the higher value of the tilt angle between phenyl and isoxazolinone rings in N-methyl-3-phenyl-4-bromoisoxazolin-5-one, which does not allow the two rings to be conjugated in the same way as in the 4-phenyl derivative. However, the

Table 3. Observed and calculated structure factors

The columns are h, $10F_o$ and $10F_c$. Unobserved reflexions are indicated with * and have been given F_o values just below the estimated minimum observable intensity. The letter E indicates reflexions affected by extinction.

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H,0,0              H,12,0              3   65  -59     H,9,1             H,16,1            6   74*  -73     3  251  248     5   56*  41
2 597E -650      0  553 -527         -3   60  -13                                       -6  156  131    -3   96  -97    -5  111  120
4 229 -240       1  499 -452          4  450  468    0  338  338      3   82*  -67     7   70*  10     4   91  -87     6   68  -73
6 376  377       2  114  106         -4  364 -331    1  118 -128     -3   99  -90     -7  242 -211    -4  235  227    -6   53* -56
8 232 -247       3  153  161          5  102  -81   -1  117   83      4  121 -123     -8   68*  30     5  175  174    -7   32*  35
                 4  130  126         -5  151  126    2  571 -561     -4  114  100     -9  212  256    -5  277 -252
H,1,0            5  232  236         -6  130  126   -2  369  339      5  154  166                      6   71*   3     H,17,2
1 740E  940      6  127 -133          7   82* -70    3  223  217     -5  134 -113     H,3,2            7  146 -130     0   73*  12
2 905E-1117      7  107 -114         -7  184  173   -3  190  175      6  124  116                     -7  255  247     1  292 -303
3 452 -723       8   41   45          8   70*  10    4   77* -37     -6   75   71    0  797 -929      8   38*  46    -1   73*  68
4 324  322                           -8  191  193   -4  361 -363     -7   99  113    1  179  222     -8   56* -52     2   71*  -6
5 423  452       H,13,0              -9   57*   3    5   83*  72                     -1  364 -399                    -2   73* -49
6 178 -151       1  312 -282                        -5  142 -141     H,17,1          2  239  236     H,10,2           3  138  148
7  76*  -27      2  131  114          H,3,1          6  150  154                     -2  276  262                    -3  123  125
8 101  -97       3  314  317                         7  157  147    0  195  183      3  104  -93    0  226  209      4   61*   5
9 144 -142       4  167  144         0  493 -578    -7   88 -108     1   83*  42     -3  272 -246     1   77  -50    -4   92   67
                 5  173 -169         1  964 -1135    8   78* -23    -1   83*  24      4  129  117    -1  491 -453     5   50*  11
H,2,0            6   68*  -18        -1  161 -151   -8  130 -122      2  121  117    -4  203  201     2   63*   1    -5  135 -156
0 570E  760      7   59  -56          2  780  859   -9   62*  28     -2   83* -30     5  265 -259    -2  339  323    -6   46*  15
1 284E -316                          -2  204 -208                     3   79*  39    -5  354  314     3  345  356
2 276 -265       H,14,0               3  377  407    H,10,1          -3   81*  42     6  170 -149    -3  391  401     H,18,2
3 248 -222                           -3  314  337                     4  134  126    -6  334 -307     4  302  304
4  56*  -29      0  171 -165          4  415 -417    0  523 -506     -4  133 -131     7  199  200    -4  384 -381    0   79  -75
5 369  391       1  274  287         -4  584  573    1  129 -106      5  272 -266    -7  144 -131     5  331 -355     1   71*  -9
6  74*  43       2   73*  24          5   75*  18    2  401  402     -5  133 -109     8   72   86    -5   73* -11    -1   71* -16
7 256 -263       3  155  151         -5  507 -494   -2   68   72      6   44*  41    -8  180  171     7   56*  51     2   82  -86
8  68*  -38      4   76*  19          6   82*  12    3  595  613     -6  140  127    -9   50* -27    -7  150 -156    -2  226  239
9  81   64       5  124 -127         -6  232 -212    4  267 -249                                     -8   68   79     3   77   84
                 6   97  -89          7  278 -288   -3   94   77     H,18,1           H,4,2                          -3   83   84
H,3,0            7  122  114         -7   83* -20    5  207  210                                     H,11,2           4   89  116
1 344  315                            8   92  104   -4  131 -121    0  106  -98     0   64*  -55                    -4  127 -143
2 224 -242       H,15,0              -8   75* -18    5  157  143     1   81* -46     1  380 -374    0  389 -389      5   41*  -38
3 250  261                           -9   78   93   -5  123 -109    -1  122  107     2  120  110     1  295  281    -5   52*  -2
4 498  511       1  132  117                        6  149 -145      2   79*  14    -2  140  142    -1   86   69    -6   35*   4
5  66*  -10      2  297  273          H,4,1         -6  237 -227      3   75*  19     3  230  230     2  411  408
6  99  -80       3  187 -189                         7   75  -64    -3  130 -129    -3  105  -77    -2  289  244     H,19,2
7 173 -181       4  139 -128         0  463  467    -7   75*  31      4   70   83     4  440 -426     3   89   90
8  87  -99       5   70*  -3          1  363  391    8   48*  23     -4   70*   3    -4  423  441    -3  142 -137    0  174 -187
9  77   75       6   67   69         -1 100TE-1260  -8  130  158      5   81   81     5   70*   2     4  179 -189     1  110 -108
                 7   41*  18          2   72  -47                    -5   60* -22    -5  191 -159    -4  524  538    -1   67*  67
H,4,0                                -2  444   53    H,11,1           6   51  -51     6  126  119     5   73* -15     2  100  124
0 415 -447       H,16,0               3  582  602                                   -6   85   90    -5  104  103    -2   91  101
1 397 -386                           -3  417  513   0   66* -41      H,19,1          7   69* -30     6  152 -173     3   57*  14
2 983 1100       0  377  350          4   67*  -3   1  598 -604                     -7  112  118    -6  335 -355    -3   61*  38
3 301 -304       1  208  207         -4  195 -169  -1  101   74     0   78* -23     8   56   83     7   53   70     4   47*  21
4 237  221       2  203 -187          5  465 -481   2  232  211      1  119 -114    -8  186 -194    -7   64* -15    -4   89   92
5  74  -72       3   75*   4         -5  164  153  -2  166 -155     -1   78*   4    -9   48*  -2    -8   51   52    -5   43* -24
6 441 -485       4   72* -15          6  212 -204   3  424  426      2   79* -32
7  75*   7       5   65* -43         -6  229 -217  -3  420  480     -2   80  180     H,5,2           H,12,2          H,20,2
8 123  121       6  107  124          7  180  178   4  137 -133      3  113  117
9  45*  23                           -7  337 -331  -4  220  190     -3  124  133    0   99  103    0  310  298    0   62*  10
                 H,17,0               8   82  -85   5  100  -90      4   59*  46    1  556  565     1  135  109     1   68  -75
H,5,0                                -8   74*   3  -5  335 -306     -4   63* -13    -1  485 -510    -1  144 -144    -1   79  -86
1 587 -614       1  264  244         -9  183  178   6   95  -90      5   43* -27    2  633 -633     2  111  103     2   56*   8
2 645  649       2   78   64                       -6  105 -108     -5  134 -134    -2   42* -32    -2  364 -367    -2   95  -97
3 675  717       3  296 -311         H,5,1          7  105 -108                     3  266 -265     3   72*  16     3   52   59
4 743 -778       4   69*   0                       -7  108   93     H,20,1         -3  224 -206    -3  380  379    -3  115  137
5 244 -206       5  125  141         0  527 -572   -8   53* -13                     4  231  217     4  221  210     4   69  -93
6  75*  27       6   49   41          1  636  667                   0  125 -120    -4  399 -379    -4  199 -200    -4   46*  39
7  98  -99                           -1   42*  26   H,12,1           1   71*  70    5  225 -222     5   74* -23    -5   47  -57
8  80   88       H,18,0               2  540  579                  -1  105 -116    -5  476  448    -5   63*   7
9 134  141                           -2  143 -137  0  125 -120      2   67*   4    6  129  139     6   81   71     H,21,2
                 0  324  312          3  594  -53   1  130 -133     -2   86   94   -6  205  191    -6   47*  16
H,6,0            1   87  -93         -3  389 -399  -1  195  177      3   63   71    7   47*  16     7   60* -45    0   54* -27
0 393 -381       2  156 -157          4  544 -538   2  544 -532     -3   63* -17   -7  212  219    -7  112 -128     1   53   66
1 708  797       3   70* -11         -4  766  792  -2   67*   4      4  109  113    8   52* -49                    -1   55  -58
2 225 -195       4   63* -25          5   80  -76   3  371  365     -4   54* -43   -8  177 -169     H,13,2          2   47*  -3
3  75 -187       5   62   77         -5  276  257  -3  120  122     -5   35*  47   -9   46* -10                    -2   51*  11
4 133  119       6   75   90          6   83* -21   4  329  322                                    0   68*   0     3   37* -24
5 389 -408                           -6  380 -379  -4  114  112      H,21,1         H,6,2           1  303  283    -3   61  -73
6 133 -114       H,19,0               7   80* -46   5  151 -143                                    -1  261 -264    -4   52  -74
7 317  350                           -7  206 -203  -5  244 -258     0   90  -93    0  252  257     2   71* -29
8  63*  53       1   71*  38          8  117  137   6  105  -96      1   63*  -5    1  110  -91    -2   90   83     H,22,2
9  81  -77       2  142 -137         -8   73*  20  -6   79* -40     -1   63   46   -1  441  451     3   73*  -9
                 3   69  -51         -9  105  -97   7  125  152      2  165  192    2  190  191    -3   72*  -7    0   45*  45
H,7,0            4   88   94                       -7  213 -210     -2   75  -64   -2  336 -333     4  103 -115     1   42* -26
                 5   58   53         H,6,1          8  132  122      3   50*  25    3  527 -534    -4   74*  34    -1   44*  39
1  45*  25                                                         -3   54*   2   -3  945 -951     5  270  259     2   49   51
2 794  842       H,20,0              0 1085 1243    H,13,1          -4   71   70    4   65* -39    -5   59*   7    -2   41* -39
3 109 -117                           1  429  402                                   -4  146   68     6   67*  25    -3   30* -36
4 456 -464       0   67* -38        -1  377 -370   0  289 -285      H,22,1         5  380  410    -6   91  106
5  71*  21       1   75  -70         2  238 -194   1  140  135                     -5  110   95     7  109 -122     H,23,2
6 100   82       2   63  -68        -2  888 -983  -1   75*   4      0   71   72    6   59*   7    -7   32*  -8
7  73* -10       3   57*  31         3  253 -220   2  456  461      1   53*  51   -6   45   66                    0   53   62
8  77   82       4   74   60        -3  563  570  -2  186 -169     -1  106 -124    7   67*  25     H,14,2
9  34* -44                           4  379 -385   3   82*   5      2   67*   4   -7  141  135                     H,0,3
                 H,21,0             -4   67*  34  -3   81*  -0     -2   79  -67    8   50*  27    0  317 -365
H,8,0                                5  266 -252   4  195 -182     -3   88   85   -8   95 -111     1  223  203     1  317 -365
                 1   59* -28        -5   76* -32  -4  324  323                    -9  190 -199    -1  195  187    -1  293 -347
0 665  677       2   55* -32         6  185  183   5   83*  56      H,23,1                         2  279  276     3  565  549
1 384  379       3  139  126        -6  105   93  -5   72* -52                     H,7,2           -2  119 -117    -3  736  696
2 492 -475                           7  114  114   6  249 -242     0   41* -17                     3  256 -273     5  128 -119
3 306 -280       H,22,0             -7   82* -62   7   88  112      1   57   58   0  568  590     -3  110 -106    -5  523 -522
4  76  -81                           8   71  -72  -7   93   92     -1   40* -12    1  158 -155     4  103 -106    -7  239 -244
5 157 -133       0  128 -122        -8  236 -240                   -2   30*  -3   -1  279  276     5   66*  72    -9  259  265
6 238  238       1   50*  49        -9   68   54   H,14,1                          2  629 -655    -5   71*  53
7 158  156       2   46*  39                                       H,0,2         -2  119 -117     6   88* -40     H,1,3
8  85  -95                           H,7,1         0  316  293                     3  256 -273
                 H,0,1                             1  230  218     -2  599 -621   -3  110 -106     H,15,2          0  193 -250
H,9,0                               0  190  176   -1  306 -280     -2 1042 1091    4  103 -106                    1  468  535
                 1  178  167         1  584  621   2   81*  -4      4  475  477   -4  162  149    0  452  457    -1  390 -500
1  88    5      -1  323  364        -1  283 -272  -2  212 -189     -4  738 -693    5   66*  72     1  125 -129     2  139  129
2 274 -249       3  123 -122         2  339 -327   3   83*  62      6  245 -228   -5   71*  53    -1   73*  28    -2  370  392
3 423 -633      -3  719 -806        -2  360  347  -3  204  189     -6   96   73    6   88* -40     2  227 -227     3   61  -52
4 280  277       5  520  535         3  611 -626   4  140 -139     -8  211  215   -6   64* -56    -2   73*  17    -3   49   73
5 306  311      -5  195 -175        -3  481 -493  -4  117 -106                     7   85   86    -3  161  153     4  194  170
6  76* -29       7  196 -204         4   73*  55   5  104 -109      H,1,2                          4   81  -95    -4  127 -103
7  49*  51      -7  497  528        -4  154 -147  -5   81* -20                     H,8,2           5   62* -12     5  262 -227
8  88  -99      -9  177 -203         5   80*  66   6  107  114     0 564E -767                     6   68* -16    -5  271  242
                                    -5  446  439  -6  145  151     1 1226E-1511   0  102 -105                     6  146 -164
H,10,0           H,1,1               6  104  108   7   78   69     -1  255  304    1   51*  49     H,16,2         -6  527 -492
                                    -6   83* -56  -7   79  -93      2  329  339   -1  126  133                    -7  264 -245
0 242 -203       0  270  314         7   78   69                    -2  354  312    2  235 -225    0  276 -275    -8  198  207
1 539 -557       1   67  -95        -7  235 -209   H,15,1           3  255  255   -2  682  681     1   74*   3    -9   81   69
2 280 -257      -1  350  454         8   82 -103                    -3  466  430    3  164 -158    -1  175  178
3 165  163       2  819 -930        -8   69*  59  0  110  -97       4   67   65   -3  122  113     2  101 -107     H,2,3
4  71*   6      -2  444  470        -9   95 -107   1  300  296     -4  202  178    4  300 -343    -3  382  391
5 383  412       3  429  444                      -1   82*  36      5   69* -17   -4  616 -582     4  128 -138    0  332 -404
6  75*  71      -3  448  468         H,8,1         2  133  120     -5  632 -593    5   73*  57    -4   83  -75     1   99 -102
7 202 -224       4  326  326                      -2   83* -47      6  300 -343   -5  182  170     5   66*  76    -1  213  222
8  50* -81      -4  476 -504        0  412  408    3  275 -280     -6  141 -136    6   72  -54     6   66* -76     2  459  490
                 5   74*  20        1  157 -155   -3  218 -197      7   73*  57   -6   74*  53    -6  135 -136    -2  377 -388
H,11,0          -5  404 -417       -1  472  513    4   81*  -2     -7  350  338    7   63* -56                     3  131 -131
                 6   82*  65        2  158  140   -4   82* -47      8   68*  60   -7   71*   8     H,3,3          -3   50* -20
1 141 -122      -6  382  355       -2  202 -194    5  202 -194     -9   52*  20    8   43* -46                     4  302 -286
2 320 -313       7  240 -257        3  525 -560   -5  247  228                    -8  152  168    0  477  577    -4  858  841
3  68*  14      -7   83*  21       -3  117 -126    6   61*   3      H,2,2         -9   55  -55     1  281  339     5   80*  56
4 502  533       8  107 -110        4  222 -219   -6   67*  20                                                   -5  241 -225
5  76* -67      -8   76*  33       -4   72*  23    7   98  114     0 867E-1017     H,9,2                          6   82*  -7
6  81  -80      -9   64*  73        5  396  420   -7   49*   7      1  459 -493                                  -6  248 -211
7  69  -69                         -5  264 -243                    -1  759 -847   0  271 -266                    -7  192 -198
8  99 -103       H,2,1              6   83* -46    H,16,1           2  101 -106    1  435 -463                    -8   74* -65
                                   -6   83* -45                    -2  300  327   -1  640  626                   -9   55*   1
                 0 916E-1223        7  111  -96   0  204  175      3  726  762    2   59*  27
                 1   38   18       -7  217  217    1  116  117     -3  623  625   -2   56* -30
                -1  122   88        8   58* -42   -1   83*  59      4  102  620
                 2  262  257       -8  121 -124   -2  236 -210     -4   68   30
                -2 912E 1128       -9  120 -122                     5  337 -325
                                                                   -5  219 -192
```

Table 3 (cont.)

C(6)–C(7) bond length is shortened in relation to a single C–C bond, and this is indicative of a small double bond character.

The mean C–H bond length is 1·06 Å.

The intermolecular distances are listed in Table 6. The shortest contact involving a bromine atom is Br–H(8) (a) with a value of 3·07 Å.

Because of the type of data rescaling, anisotropic thermal parameters are only of semiquantitative value. In Table 7 the axes of thermal ellipsoids, with angles relative to the cell edges, are listed. All the atoms were found to vibrate with marked anisotropy, but the thermal motion is lower than that in N-methyl-4-phenylisoxazolin-5-one (previous paper) and the rigid body molecular displacement is not so evident.

Conclusions

In the preceding paper and in the Introduction to the present one, it was pointed out that the 3-aryl and 4-aryl derivatives of N-methylisoxazolin-5-one have similar physical properties in solution, but some differences arise in the crystalline state, as can be seen in the following table (after De Sarlo, Fabbrini & Renzi, 1966):

Compound				Solubility in ether at 18°C	$\nu_{C=O}$ (cm^{-1})		Dipole moments in benzene
No.	R	R'	m.p.	(mg.ml^{-1})	Solid	CCl$_4$ soln.	solution
1	C$_6$H$_5$	H	43–45°	160	1743	1751	6·00 Debyes
2	C$_6$H$_5$	CH$_3$	67–69°	130	1730	1745	5·73
3	C$_6$H$_5$	Br	108–109°	26	1745	1760	6·20
4	H	C$_6$H$_5$	144–146°	1·5	1700	1758	5·40
5	CH$_3$	C$_6$H$_5$	112–113°	4·2	1706	1742	5·65
6	H	p-Br-C$_6$H$_4$	173–174°	1·4	1680	1760	5·83

(R is the substituent in position 3 and R' the substituent in position 4 in the isoxazolinone ring).

Table 4. *Bond distances and angles with their standard deviations*

C(7)–C(8)	1·369 (8) Å	C(7)–C(8)—Br	128·7 (4)°
C(8)–Br	1·843 (6)	C(9)–C(8)—Br	121·5 (4)
C(8)–C(9)	1·416 (7)	C(7)–C(8)—C(9)	109·3 (5)
C(9)–O(1)	1·200 (7)	C(8)–C(9)—O(1)	135·0 (6)
C(9)–O(2)	1·402 (7)	O(2)–C(9)—O(1)	119·3 (5)
O(2)–N	1·421 (6)	C(8)–C(9)—O(2)	105·7 (5)
N—C(10)	1·464 (8)	C(9)–O(2)—N	107·2 (4)
N—C(7)	1·342 (8)	O(2)–N—C(10)	108·3 (5)
C(7)–C(6)	1·470 (7)	C(7)–N—C(10)	125·8 (6)
C(6)–C(1)	1·418 (11)	C(7)–N—O(2)	108·8 (5)
C(1)–C(2)	1·455 (12)	C(8)–C(7)—N	108·8 (5)
C(2)–C(3)	1·342 (17)	C(8)–C(7)—C(6)	129·9 (5)
C(3)–C(4)	1·350 (14)	N—C(7)—C(6)	121·1 (6)
C(4)–C(5)	1·369 (10)	C(7)–C(6)—C(1)	118·1 (7)
C(5)–C(6)	1·374 (12)	C(6)–C(1)—C(2)	115·0 (9)
		C(1)–C(2)—C(3)	121·1 (1·1)
		C(2)–C(3)—C(4)	121·3 (8)
		C(3)–C(4)—C(5)	121·1 (1·0)
		C(4)–C(5)—C(6)	119·9 (9)
		C(5)–C(6)—C(1)	121·5 (6)
		C(5)–C(6)—C(7)	120·5 (7)
C(1)–H(1)	1·19	C(6)–C(1)—H(1)	130
C(2)–H(2)	1·16	C(2)–C(1)—H(1)	115
C(3)—H(3)	1·03	C(1)–C(2)—H(2)	100
C(4)—H(4)	0·90	C(3)–C(2)—H(2)	138
C(5)—H(5)	0·90	C(2)–C(3)—H(3)	127
C(10)–H(6)	1·09	C(4)–C(3)—H(3)	111
C(10)–H(7)	1·10	C(3)–C(4)—H(4)	118
C(10)–H(8)	1·11	C(5)–C(4)—H(4)	121
		C(4)–C(5)—H(5)	114
		C(6)–C(5)—H(5)	125
		H(6)–C(10)–H(7)	130
		H(6)–C(10)–H(8)	77
		H(7)–C(10)–H(8)	114
		N—C(10)–H(6)	114
		N—C(10)–H(7)	104
		N—C(10)–H(8)	115

On the basis of the determination of the crystal structure of *N*-methyl-4-phenylisoxazolin-5-one (number 4 in the table) and of *N*-methyl-3-phenyl-4-bromoisoxazolin-5-one (number 3 in the table) as representative members of the two series of compounds, it is possible to make an allowances for the differences in physical behaviour.

Table 5. *Deviations from the least-squares planes*

The equations of the planes were computed with the first six and first five atoms for the phenyl and isoxazoline rings respectively.

Phenyl	C(1)	−0·001 Å
	C(2)	−0·016
	C(3)	0·019
	C(4)	−0·003
	C(5)	−0·014
	C(6)	0·016
	C(7)	0·039
	H(1)	0·04
	H(2)	−0·25
	H(3)	0·01
	H(4)	−0·05
	H(5)	−0·17
Isoxazolinone	O(2)	−0·022
	N	0·029
	C(7)	−0·024
	C(8)	0·009
	C(9)	0·008
	C(6)	0·001
	O(1)	0·05
	C(10)	−0·79
	Br	0·24

Table 6. *Shortest intermolecular distances*

Distances are less than 3·5 Å for non-hydrogen atoms; less than 3 Å for contacts involving carbon, nitrogen and oxygen atoms with hydrogen atoms; and less than 2·7 Å for contacts between hydrogen atoms.

(a)	$x-1$,	y , z
(b)	$-x+\frac{1}{2}$,	$y-\frac{1}{2}$, $-z+\frac{3}{2}$
(c)	$-x+1$,	$-y+1$, $-z+1$
(d)	$-x+1$,	$-y+1$, $-z+2$
(e)	$-x$,	$-y+1$, $-z+2$

O(2)—O(2) (d)	3·51 Å
N——O(1) (d)	3·46
N——O(2) (d)	3·35
C(1)—O(1) (c)	3·32
C(3)—O(2) (b)	3·50
C(5)—O(1) (d)	3·29
C(7)—O(2) (d)	3·44
C(8)—O(2) (d)	3·52
C(9)—N(d)	3·25
C(10)—O(1) (a)	3·13
H(1)—O(1) (c)	2·31
H(5)—O(1) (d)	2·47
H(8)—O(1) (a)	2·50
H(6)—H(5) (e)	2·42

The most significant difference between these two substances is the value of the dihedral angle between the two rings of the molecule, *i.e.* between phenyl and isoxazolinone planes. This angle is $\simeq 50°$ for compound 3 and $\simeq 12°$ for compound 4. This feature may be explained on the basis of general considerations on the thermodynamic stability of organic crystals, according to the theory of Kitajgorodskij (1965). This stability is reached when the free vibrational energy, as a sum of intra- and intermolecular energies, corresponds to a minimum. In substances such as these the energies involved are the potential energy, depending on the effects between the atoms forming the molecule, the resonance energy and the lattice energy. The first term reaches a minimum when the phenyl ring is perpendicular to the isoxazolinone ring. On the contrary, the other two energy terms attain a minimum when the two rings are coplanar.
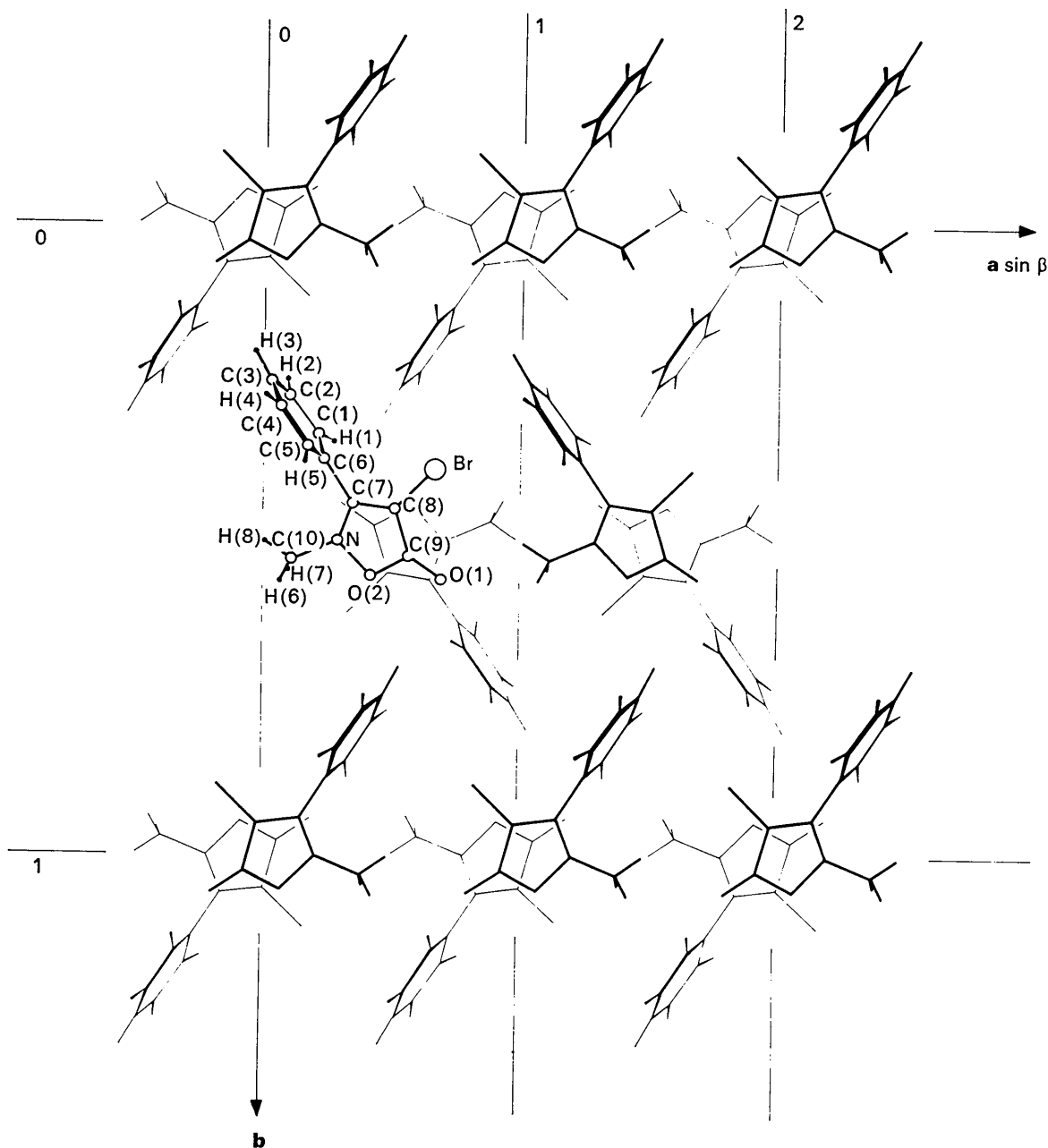

Fig. 1. Projection of the structure along the *c* axis.

Table 7. *Principal axes of thermal ellipsoids*

The root mean square displacement U_i (Å) corresponds to the ith principal axis of the ellipsoid and $\theta_{ia}, \theta_{ib}, \theta_{ic}$ are the angles (°) between the ith axis and the crystallographic axes a, b, c respectively. The B_i are equal to the corresponding $8\pi^2 U_i^2$.

	B_i	U_i	θ_{ia}	θ_{ib}	θ_{ic}
Br	4·87	0·25	60·5	32·9	82·2
	6·66	0·29	79·3	111·1	30·2
	2·37	0·17	31·6	113·9	119·0
O(1)	3·92	0·22	94·0	67·5	23·3
	5·46	0·26	117·0	35·9	106·1
	1·92	0·16	27·3	63·5	106·3
O(2)	2·35	0·17	91·8	38·2	52·2
	4·52	0·24	60·2	121·6	54·0
	2·04	0·16	29·8	70·7	121·9
N	2·60	0·18	83·2	42·5	50·8
	3·62	0·21	114·6	49·8	123·4
	1·79	0·15	25·6	78·3	123·0
C(1)	4·14	0·23	108·5	159·0	77·3
	5·62	0·27	20·6	106·3	88·0
	0·72	0·10	98·8	77·3	12·7
C(2)	6·13	0·28	16·6	77·9	111·8
	8·74	0·33	106·6	44·9	125·4
	1·74	0·15	89·8	47·5	43·5
C(3)	4·08	0·23	84·4	28·3	63·9
	5·88	0·27	24·7	105·6	81·7
	1·37	0·13	114·0	113·0	27·5
C(4)	3·96	0·22	120·2	74·3	135·2
	5·62	0·27	127·0	55·2	48·5
	2·86	0·19	51·8	39·1	103·8
C(5)	2·98	0·19	141·1	53·5	69·7
	4·16	0·23	53·8	54·2	64·1
	1·96	0·16	102·3	123·6	33·8
C(6)	2·37	0·17	156·9	112·6	84·2
	3·79	0·22	112·6	22·6	87·0
	0·48	0·08	94·3	90·5	6·5
C(7)	2·39	0·17	13·8	96·3	88·4
	2·72	0·19	84·3	6·7	87·5
	0·65	0·09	102·6	92·2	2·9
C(8)	2·69	0·18	154·7	115·1	82·4
	3·92	0·22	113·9	27·7	98·5
	0·77	0·10	97·5	78·9	11·4
C(9)	2·72	0·19	63·5	34·1	75·4
	3·69	0·22	40·2	123·3	79·1
	0·90	0·11	117·8	96·3	18·2
C(10)	4·84	0·25	75·5	17·4	83·3
	6·21	0·28	79·2	102·4	24·9
	1·50	0·14	18·1	101·9	113·9

The molecular configuration in the crystal depends, of course, on the equilibrium of these terms. In 3-aryl compounds the most important term is the potential energy of the molecule, and the steric hindrance between the methyl group linked to the nitrogen atom of the isoxazolinone ring and the phenyl group in the 3 position rules out the possibility of the molecule being planar. In 4-aryl compounds, however, the pressure exerted by the crystalline field upon the molecule gives a tendency towards planarity and, though the molecular energy is increased, the total free energy decreases in agreement with the decrease of the lattice energy, because of the possibility of a closer packing of molecules. This fact is responsible for the higher melting points and the lower solubility in ether of 4-aryl compounds in comparison with the 3-aryl ones.

As regards the shift in the keto group stretching frequency, it could be said that it is in agreement with differences in C=O bond lengths for both the compounds whose structures have been solved. However, the shift is not easily explained on the basis of the different conjugation between the phenyl and the isoxazolinone rings. It might be thought that the shift of $\nu_{C=O}$ in the 4-aryl compounds is to be attributed to crystal intermolecular interactions; this could also be ascribed to the different packing possibilities of the molecules of the two series of compounds.

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