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The Crystal Structure of *N*-Methyl-4-phenylisoxazolin-5-one

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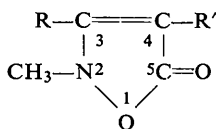
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Crystals of *N*-methyl-4-phenylisoxazolin-5-one, $C_{10}H_9NO_2$, are monoclinic, $P2_1/c$, with $a=13.716$, $b=10.925$, $c=11.333$ Å, $\beta=91.51^\circ$ and $Z=8$. X-ray analysis was based on layers 0-8 about the b axis. The structure was determined by trial-and-error methods and refined by an anisotropic least-squares analysis of 870 observed reflexions. The final R index including the contribution of hydrogen atoms was 0.053. The two independent molecules are arranged in the asymmetric unit according to a nearly orthorhombic symmetry. Bond distances and angles agree with accepted values. The phenyl and isoxazolinone rings of the two molecules are slightly tilted: the angles are 14° and 11° .

Introduction

Researches carried out (De Sarlo, Fabbrini & Renzi, 1966) on the series of aryl derivatives of 2-methylisoxazolin-5-one with the formula:



have established some differences in physical properties between the compounds with $\text{R}=\text{C}_6\text{H}_5$ and $\text{R}'=\text{H}$, CH_3 , Br and those with $\text{R}=\text{H}$, CH_3 and $\text{R}'=\text{C}_6\text{H}_5$.

N-Methyl-4-aryl isoxazolin-5-ones have higher melting points and lower solubilities in ether than the isomeric 3-aryl derivatives. Moreover, the $\nu_{\text{C}=\text{O}}$ in the infrared spectra is located before 1706 cm^{-1} for 4-aryl compounds and after 1730 cm^{-1} for all other *N*-methylisoxazolin-5-ones. It must be noted, however, that these differences are observed only in the solid phase, whereas comparable values are found in solution: e.g. the infrared spectra in carbon tetrachloride and the dipole moments in benzene solution. Analysis of the crystal structure of one compound for each of the two groups could account for these differences. In the

present paper the crystal structure of *N*-methyl-4-phenylisoxazolin-5-one is described. In the following paper (Sabelli & Zanazzi, 1969) the crystal structure of *N*-methyl-3-phenyl-4-bromoisoxazolin-5-one is reported and the relations between the two types of compound are discussed.

Experimental

A sample of *N*-methyl-4-phenylisoxazolin-5-one was kindly supplied by Dr De Sarlo of the Istituto di Chimica Organica of the Florence University. Well formed, colourless crystals were obtained by recrystallization from an alcoholic solution.

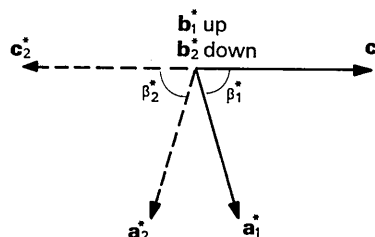


Fig. 1. Relationship between the axes in the twinned reciprocal lattices.

From a first X-ray examination these crystals were assigned to the monoclinic system and the approximate lattice parameters were determined. The refinement of the cell constants was carried out by the least-squares method, starting from the 2θ data measured on $h0l$ and $0kl$ Weissenberg photographs, after calibration with Ag powder diffraction effects. The cell dimensions at room temperature are:

$$\begin{aligned} a &= 13.716 \pm 0.009 \text{ \AA} \\ b &= 10.925 \pm 0.003 \\ c &= 11.333 \pm 0.002 \\ \beta &= 91.51 \pm 0.04^\circ. \end{aligned}$$

With these values, assuming eight molecules per unit cell, the calculated density is 1.37 g.cm^{-3} , while the observed density determined by the flotation method is 1.36 g.cm^{-3} . The systematic extinctions ($h0l$, l odd and $0k0$, k odd) indicate the space group $P2_1/c$.

Crystals of *N*-methyl-4-phenylisoxazolin-5-one are frequently twinned. This fact is manifested by the splitting of some reflexions on Weissenberg photographs. The population of spots can be explained taking into account the diffraction effects of two joined monoclinic individuals having their reciprocal axes related in the way shown in Fig. 1. According to the Friedel's (1926) notation the crystals are twinned by pseudo-merohedry, with reflexion plane (001).

Three-dimensional diffraction data were collected by the equi-inclination Weissenberg method (Cu $K\alpha$ radiation, multiple film technique) about [010], from the $h0l$ to $h8l$ layers. Unfortunately the compound slowly decomposes on exposure to X-rays, as is evident both from the colour of the crystal, which turns brown, and from the diffusion which takes place in the diffraction effects. Therefore it was necessary to use three different crystals with approximately the same shape to complete the collection of intensities. The integrated intensities were estimated with a microdensitometer.

The intensity of the spot 400 on the $h0l$ layer was too great in comparison with the intensities of the other reflexions in the layer, and it was not possible to scale this intensity directly to the others. The $K\beta$ residual intensities of the strongest reflexions were therefore measured and related to the $K\alpha$ intensities, after the proper Lorentz-polarization correction, and taking into account the different absorption coefficient of films for $K\beta$ radiation. The average F_β^2 to F_α^2 ratio (1:57) was applied to the F_α^2 of the 400 reflexion. Of course such an evaluation of the intensity is somewhat uncertain and, though the 400 reflexion was the key to the solution of the structure, as will be shown later, its contribution was omitted from the last cycles of refinement.

The nine layers of reflexions were placed approximately on the same relative scale by exposure time; further scaling was done during the structure deter-

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

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

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

Molecule A	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)	0.3990 (3)	0.5596 (3)	0.3035 (2)	0.0138 (3)	0.0177 (4)	0.0075 (3)	0.0004 (3)	0.0002 (2)	0.0015 (3)
O(2)	0.3841 (2)	0.7462 (3)	0.2264 (2)	0.0115 (3)	0.0137 (4)	0.0076 (3)	0.0010 (2)	-0.0004 (2)	0.0004 (2)
N(1)	0.3684 (3)	0.7948 (4)	0.1129 (3)	0.0113 (4)	0.0140 (5)	0.0078 (3)	0.0006 (3)	-0.0009 (3)	0.0017 (3)
C(1)	0.4092 (4)	0.3674 (5)	0.1015 (4)	0.0106 (5)	0.0146 (6)	0.0090 (4)	-0.0002 (4)	0.0007 (3)	0.0018 (4)
C(2)	0.4085 (4)	0.2525 (4)	0.0484 (4)	0.0112 (5)	0.0113 (6)	0.0128 (5)	-0.0004 (4)	0.0011 (4)	-0.0019 (4)
C(3)	0.3762 (4)	0.2376 (5)	-0.0680 (4)	0.0099 (4)	0.0150 (6)	0.0123 (5)	-0.0020 (4)	0.0010 (3)	-0.0017 (4)
C(4)	0.3430 (4)	0.3407 (5)	-0.1309 (4)	0.0101 (5)	0.0172 (7)	0.0106 (5)	-0.0004 (4)	0.0004 (3)	-0.0022 (4)
C(5)	0.3425 (4)	0.4537 (5)	-0.0795 (4)	0.0080 (4)	0.0163 (6)	0.0087 (4)	-0.0001 (4)	-0.0008 (3)	-0.0013 (4)
C(6)	0.3762 (3)	0.4715 (4)	0.0386 (3)	0.0092 (4)	0.0132 (6)	0.0078 (4)	-0.0004 (4)	0.0008 (3)	0.0000 (3)
C(7)	0.3757 (3)	0.5925 (4)	0.0919 (3)	0.0082 (4)	0.0133 (6)	0.0066 (4)	-0.0006 (3)	0.0015 (3)	-0.0002 (3)
C(8)	0.3885 (4)	0.6193 (4)	0.2143 (3)	0.0090 (4)	0.0140 (5)	0.0070 (4)	0.0001 (3)	0.0005 (3)	0.0006 (3)
C(9)	0.3668 (3)	0.7023 (4)	0.0369 (4)	0.0090 (4)	0.0104 (5)	0.0103 (4)	-0.0004 (3)	-0.0002 (3)	0.0002 (3)
C(10)	0.3813 (4)	0.9234 (4)	0.1031 (4)	0.0116 (5)	0.0118 (6)	0.0109 (5)	0.0011 (4)	-0.0007 (4)	0.0008 (4)
Molecule B									
O(3)	0.0931 (2)	0.4406 (3)	0.8072 (2)	0.0139 (3)	0.0143 (4)	0.0080 (3)	0.0012 (3)	0.0007 (2)	-0.0014 (2)
O(4)	0.1128 (2)	0.2531 (3)	0.7324 (2)	0.0114 (3)	0.0147 (4)	0.0071 (3)	0.0003 (2)	0.0005 (2)	0.0000 (2)
N(2)	0.1350 (3)	0.2039 (4)	0.6216 (3)	0.0101 (4)	0.0163 (5)	0.0082 (3)	0.0002 (3)	0.0014 (3)	-0.0006 (3)
C(11)	0.0918 (4)	0.6322 (4)	0.6048 (4)	0.0107 (5)	0.0139 (6)	0.0088 (4)	0.0002 (4)	-0.0008 (3)	-0.0010 (4)
C(12)	0.0901 (4)	0.7477 (5)	0.5530 (4)	0.0124 (5)	0.0127 (6)	0.0132 (5)	-0.0005 (4)	0.0001 (4)	0.0007 (4)
C(13)	0.1233 (4)	0.7636 (4)	0.4396 (4)	0.0102 (5)	0.0143 (6)	0.0118 (4)	-0.0010 (4)	0.0000 (3)	0.0007 (4)
C(14)	0.1555 (4)	0.6600 (5)	0.3785 (4)	0.0101 (4)	0.0193 (7)	0.0096 (4)	0.0001 (4)	0.0006 (3)	0.0030 (4)
C(15)	0.1547 (4)	0.5459 (5)	0.4287 (4)	0.0093 (4)	0.0170 (6)	0.0078 (4)	0.0004 (4)	0.0002 (3)	0.0019 (4)
C(16)	0.1222 (3)	0.5289 (4)	0.5452 (4)	0.0074 (4)	0.0148 (6)	0.0084 (4)	-0.0006 (4)	-0.0006 (3)	0.0000 (4)
C(17)	0.1229 (3)	0.4079 (4)	0.5988 (3)	0.0075 (4)	0.0153 (6)	0.0070 (4)	-0.0004 (3)	0.0004 (3)	-0.0008 (3)
C(18)	0.1077 (4)	0.3783 (4)	0.7198 (3)	0.0107 (4)	0.0128 (5)	0.0077 (4)	0.0004 (4)	-0.0004 (3)	-0.0007 (3)
C(19)	0.1369 (4)	0.2966 (4)	0.5441 (3)	0.0106 (4)	0.0126 (5)	0.0072 (4)	-0.0012 (4)	0.0003 (3)	0.0003 (3)
C(20)	0.1241 (4)	0.0755 (4)	0.6079 (4)	0.0110 (5)	0.0121 (6)	0.0117 (5)	0.0015 (4)	0.0023 (4)	-0.0020 (4)

mination by comparing ΣF_c with ΣF_o . In each layer, reflexions at high Bragg angles were too weak to be measured and were neglected. Of the 1460 intensities measured, 870 were observable above background. The remainders were given values just lower than the minimum threshold observed intensity and treated as unobserved reflexions, as described below.

Corrections for Lorentz-polarization factors were made, but no absorption correction was applied.

Structure determination and refinement

The intensity of the 400 diffraction effect, which is by far the strongest reflexion on the photographs, indicates that the *N*-methyl-4-phenylisoxazolin-5-one molecules are approximately planar and lie on equidistant planes parallel to (100) with spacings of $\frac{1}{2}a$. In accordance with the symmetry of the $P2_1/c$ space group, the possible x coordinates for the two asymmetric molecules are $\frac{1}{8}$ and $\frac{3}{8}$. From the examination of Weissenberg photographs it is evident that the structure presents a well marked orthorhombic pseudosymmetry. Indeed, the β angle is close to 90° and hkl reflexions have nearly the same intensity as $h\bar{k}l$; furthermore $0kl$ reflexions with k odd and $hk0$ with h odd are absent or very feeble, so simulating the symmetry of the *Pbca* space group. Thus the two molecules of the monoclinic asymmetric unit must be related to each other by the pseudosymmetry operations corresponding to the symmetry of this orthorhombic space group. Therefore in the first stages of structure solution, the crystals were considered as orthorhombic and a three-dimensional Patterson function was computed leaving out $h\bar{k}l$ reflexions. The orientation of the molecule was found by inspection of this synthesis; then, taking into account packing considerations, the y and z coordinates were obtained by trial to give a reasonable structure.

The atomic coordinates were refined in the $P2_1/c$ space group by successive Fourier syntheses computed with the whole set of reflexions. At this stage the index

$$R = \frac{\Sigma ||F_o| - |F_c||}{\Sigma |F_o|}$$

was 0.27.

The refinement of the structure was continued by a least-squares program written by Albano, Bellon, Pompa & Scatturin (1963) for the IBM 1620 computer, using the block-diagonal approximation and individual isotropic thermal parameters. The weighting scheme suggested by Cruickshank (1961), $\gamma/w = 1/(a + F_o + cF_o^2)$ with $a = 2F_{\min}$ and $c = 2/F_{\max}$, was employed for the structure factors and the unobserved reflexions were not included in the calculations. After four cycles the R index dropped to 0.15. At this stage the full-matrix least-squares refinement was carried out with the program of Busing & Levy, adapted for the IBM 7090 computer by Stewart (1964)*. For the observed planes a weighting scheme like that specified by Hughes (1941) was used, with $\gamma/w = 1$ for reflexions with $F_o < 4F_{\min}$; $\gamma/w = 4F_{\min}/F_o$ for $F_o \geq 4F_{\min}$. In this new series of calculations the unobserved reflexions were included (with $\gamma/w = 1$) only if the calculated value of F exceeded the observational threshold. After two isotropic full-matrix cycles, the anisotropic refinement was undertaken. Since the number of parameters exceeded the 180-variable capacity of the full-matrix least-squares program, it was necessary to refine with the block-diagonal approximation. After five cycles, each followed by a proper rescaling of F_o 's, the R index reached a value of 0.086. Three-dimensional difference

* The calculations were performed with the IBM 7090 computer of the Centro Nazionale Universitario di Calcolo Elettronico of Pisa University.

Table 2. Fractional coordinates of hydrogen atoms

The isotropic thermal parameters are those of the atoms to which the hydrogen atoms are bonded.

Molecule A	x	y	z	B
H(1)	0.435 (3)	0.383 (4)	0.183 (4)	6.48 Å ²
H(2)	0.420 (4)	0.166 (4)	0.104 (4)	6.68
H(3)	0.383 (3)	0.149 (4)	-0.094 (4)	6.57
H(4)	0.325 (4)	0.325 (4)	-0.222 (4)	6.71
H(5)	0.331 (3)	0.528 (4)	-0.115 (4)	5.73
H(11)	0.466 (3)	0.920 (4)	0.120 (4)	6.18
H(12)	0.318 (3)	0.955 (4)	0.145 (4)	6.18
H(13)	0.364 (3)	0.929 (4)	0.019 (4)	6.18
H(14)	0.376 (3)	0.741 (4)	-0.048 (3)	5.22
Molecule B				
H(6)	0.068 (3)	0.612 (4)	0.687 (4)	6.09
H(7)	0.068 (4)	0.840 (4)	0.601 (4)	6.82
H(8)	0.122 (3)	0.854 (4)	0.400 (4)	6.48
H(9)	0.177 (4)	0.674 (4)	0.299 (4)	6.70
H(10)	0.172 (3)	0.460 (4)	0.379 (4)	5.72
H(15)	0.196 (3)	0.049 (4)	0.660 (4)	6.50
H(16)	0.049 (3)	0.061 (4)	0.633 (4)	6.50
H(17)	0.137 (3)	0.073 (4)	0.529 (4)	6.50
H(18)	0.140 (3)	0.277 (4)	0.451 (4)	5.26

Table 3 (cont.)

H _{5,5} ,8	-7 43* 34 8 70 71	H _{6,5}	5 100 101 -5 71 -8*	9 48* 34 -9 30 30	-6 47* 32 -7 49* -31 -7 48* -45	-1 135 -154 -2 26* 22 -2 26* 21	8 58 56 -8 66 69								
-5 143 -134 6 93 86 -6 119 -111 7 62 57 -7 57* 31	-8 80 87 9 60 87 -9 61 -49 10 50* 7 -10 50* -5	0 48 -55 1 40* -1 -1 39* -10 2 83 91 -2 63 55 3 124 125	-6 50* -5 7 55 53 -7 85 -89 8 47* -17 -1 50* -13 2 154 -158 -2 141 155	0 25* -9 1 25 24 -1 13* 120 2 154 -158 -2 141 155	0 44* -10 1 134 120 -1 149 141 2 112 -116 -2 124 133	-4 35* 21 -5 35* 13 -5 116 122 6 46 43 -6 30 -26	0 102 95 -1 42* -4 -1 42* -12 2 43* -28 -2 43* -2								
H _{5,9}	6 57* -20 1 99 -95 -1 148 -134 2 116 -117 -2 115 116	H _{6,2}	0 93 99 1 157 170 -1 152 -154 2 27* 18	H _{6,9}	0 103 99 1 59 65 -1 50* -41 2 50* -7 -2 50* 12 3 50* 14	H _{7,6}	0 44* -10 1 134 120 -1 149 141 2 112 -116 -2 124 133	H _{8,5}	0 102 95 -1 42* -4 -1 42* -12 2 43* -28 -2 43* -2						
3 115 94 -3 87 57 4 57* -9 -4 57* 29 5 78 81 -5 118 115 6 69 66 -6 03 -99	-2 27* 18 -3 94 46 3 87 98 -3 89 -91 4 57* -9 -4 57* 29 5 78 81 -5 118 115 6 69 66 -6 03 -99	-4 83* 27 5 103 104 -5 119 -120 6 15 -119 -6 121 -121 7 100 -95 -7 75 67 -8 50* 5 9 88 -87 -9 96 101 10 65 60 -10 77 74	0 103 99 1 59 65 -1 50* -41 2 50* -7 -2 50* 12 3 50* 14 4 50* -52 -4 50* -55 5 50 -60 6 47* 41 -6 48* 5 7 45* -27 -7 46* 45 8 42* -2 -8 43* -38 9 39 38 -9 41* -28	0 44* -10 1 134 120 -1 149 141 2 112 -116 -2 124 133 3 107 -108 4 69 -74 5 88 -86 -5 84 -79 6 76 78 7 77 -79 8 45* 23 -7 45* 30 -8 78 -77 9 89 86 -9 81 85	-1 48* -19 -4 47* -14 5 96 -101 -5 110 -111 6 55 55 -6 75 -80 0 47* 15 1 48* -19 -2 184 168 -2 161 -169 3 51 57 -3 64* -48 -4 66* 38 -4 75 -67 5 72 63 -5 49* 46 -5 49* 46 6 70 -78 -6 74 78 7 48* 52 -7 53 54	8 47* 5 7 45* 5 4 74 -78 5 47* -11 9 52 46 -9 48* -49	0 119 -98 1 123 -116 1 106 90 -2 46* -32 -2 53 -46 3 118 -124 3 131 129 4 61 67 -4 59 64 5 47* 52 -5 47* -12 6 52 55 7 63 75 -7 49 -64								
H _{5,10}	0 56* -23 1 56* -5 -1 56* 22 2 145 -142 -2 137 142 3 63 54 -3 56 -58 4 54* -53 -4 91 89 5 53* 35 -5 54* 17 6 59 65 -6 52* -55	H _{6,3}	0 59 47 1 145 -159 -1 130 142 2 32* -10 -2 31* 25 3 131 -131 -3 145 161	H _{6,6}	0 205 201 1 99 -107 -1 80 71 2 45* -27 -2 44* 21 3 46* -3 -3 45* 45 4 173 -171 -4 150 -168	H _{7,3}	0 31* -12 1 202 -194 -1 221 -224 -2 132 -118 -2 119 110 -2 153 153 -3 138 129 -4 53 50 -4 53 50 5 90 97 -5 107 114 -6 44* 31 -6 43* -23 7 51 -42 -7 49* 43 8 48* 31 -8 48* -19	H _{8,2}	0 71 -67 1 27* -21 -1 32 32 2 33 30 -2 35 38 3 76 -76 -3 79 75 4 62 -63 -4 82 87 -5 85 -70 -5 84 -70 6 50 -50 -6 50 -50 -6 50 -50 7 60 58 -7 60 58 8 53 -14 9 62 -67 9 70 -72 -9 68 -74	H _{8,6}	0 119 -98 1 123 -116 1 106 90 -2 46* -32 -2 53 -46 3 118 -124 3 131 129 4 61 67 -4 59 64 5 47* 52 -5 47* -12 6 52 55 7 63 75 -7 49 -64				
H _{5,11}	0 53* 15 1 52* -16 -1 53* -33 2 67 67 -2 63 -67	H _{6,4}	0 59 47 1 145 -159 -1 130 142 2 32* -10 -2 31* 25 3 131 -131 -3 145 161	H _{6,7}	0 76 -76 1 89 -90 -1 74 64 2 46* 29 -2 48* 0 3 58 -58 -3 78 76 4 49* 46 -4 68 77 -5 50 30 -5 50* -27 6 50* -43 -6 50* -17 7 50 17 -7 50* -19 8 49* -25 -8 50* -49 9 47* 17 -9 48* -3	H _{7,4}	0 36* -1 1 117 -114 -1 130 -128 2 69 80 -2 80 72 3 56 48 -3 39* 32 4 45 51 -4 58 -57 5 67 76 -5 70 70 6 53 -55 -6 45* 46 7 52 38 -7 47* 41 8 53 -50 -8 54 62	H _{7,7}	0 49* 16 1 94 -81 -1 107 -104 2 57 51 -2 64 -53 3 62 59 -3 49* 31 4 49* 13 -4 64 -53 5 62 59 -5 42* 38 6 45* -45 -6 44* -50 7 47* -25 -7 46* 23 8 47 12 -8 47* 0 9 47* 38 -9 47* -31	H _{7,8}	0 49* 16 1 94 -81 -1 107 -104 2 57 51 -2 64 -53 3 62 59 -3 49* 31 4 49* 13 -4 64 -53 5 62 59 -5 42* 38 6 45* -45 -6 44* -50 7 47* -25 -7 46* 23 8 47 12 -8 47* 0 9 47* 38 -9 47* -31	H _{8,7}	0 72 75 -1 47 -36 -1 62 53 -2 47* -28 -2 47* -15 3 36 36 -3 40 -40 4 40 14 -4 39* 29 5 50 -46 -5 42* 38 6 45* -45 -6 44* -50 7 47* -25 -7 46* 23 8 47 12 -8 47* 0 9 47* 38 -9 47* -31		
H _{6,0}	0 115* 2 2 119 -161 3 26* -8 4 353 427 5 35* -31 6 190 211 7 43* 14 8 155 -166 9 49* 15 10 91 -89 11 50* -2 12 49* 50	H _{6,1}	0 141 -118 1 35* -15 -1 35* 1 2 36* -16 3 57 54 -3 62 -54 4 59 60 -4 60 50 5 85 78 -5 75 75 6 45* 15 -6 45* 8 7 48* -20 -7 48* 17 8 49* 31 -8 49* 29 9 62 -52 3 71 -72 -3 113 116 4 51* -11 -4 50* -51	H _{6,8}	0 95 96 1 114 -121 -1 87 96 2 50* 1 -2 50* 14 3 71 -72 -3 113 116 4 51* -11 -4 50* -51	H _{7,1}	0 117* -1 1 130 165 -2 24* -17 -2 24* 22 3 60 58 -3 62 -71 4 33* -1 -4 33* -5 2 58 61 -2 58 61 3 52 54 -3 52 54 4 45* -5 -4 45* -11 5 46* 9 -5 46* 27 6 51 -61	H _{7,5}	0 40* 23 1 41* -36 -1 47 -52 2 58 61 -2 58 61 3 52 54 -3 52 54 4 45* -5 -4 45* -11 5 46* 9 -5 46* 27 6 51 -61	H _{8,0}	0 165 150 1 120 99 -1 104 -89 2 39* -6 -2 39* 5 3 116 107 -3 127 -122 4 112 -107 -4 129 -129 5 54 -57 -5 45 53 6 46* 9 -6 46* -15 7 74 -81 -7 77 93	H _{8,4}	0 165 150 1 120 99 -1 104 -89 2 39* -6 -2 39* 5 3 116 107 -3 127 -122 4 112 -107 -4 129 -129 5 54 -57 -5 45 53 6 46* 9 -6 46* -15 7 74 -81 -7 77 93	H _{8,8}	0 72 75 -1 47 -36 -1 62 53 -2 47* -28 -2 47* -15 3 36 36 -3 40 -40 4 40 14 -4 39* 29 5 50 -46 -5 42* 38 6 45* -45 -6 44* -50 7 47* -25 -7 46* 23 8 47 12 -8 47* 0 9 47* 38 -9 47* -31

maps were then calculated, from which the hydrogen atoms were found at reasonable locations with respect to the carbon atoms. The hydrogen atoms were now included in a last cycle of refinement, their thermal parameters being set equal to the isotropic B 's of the carbon atoms to which they are bonded, but only their positional parameters were allowed to refine. The 400 diffraction effect, which appeared to be overestimated, was excluded from the refinement. After this last cycle a final $R=0.053$ was obtained with all observed reflexions included in the refinement and the positional and thermal parameters listed in Tables 1 and 2 for non-hydrogen and hydrogen atoms respectively. The observed and calculated structure factors are given in Table 3. The scattering factors from *International Tables for X-ray Crystallography* (1962) for O, N, C and H were used.

Results and discussion

Figs. 2 and 3 show the structure of *N*-methyl-4-phenylisoxazololin-5-one projected along a and c axes. The interatomic distances and angles found in the two inde-

Table 4. Bond lengths and standard deviations (in parenthesis)

Molecule A		Molecule B	
C(1)-C(6)	1.411 (7) Å	C(11)-C(16)	1.385 (7) Å
C(1)-C(2)	1.392 (7)	C(11)-C(12)	1.392 (7)
C(2)-C(3)	1.390 (6)	C(12)-C(13)	1.386 (7)
C(3)-C(4)	1.403 (7)	C(13)-C(14)	1.403 (7)
C(4)-C(5)	1.365 (7)	C(14)-C(15)	1.371 (7)
C(5)-C(6)	1.418 (6)	C(15)-C(16)	1.417 (6)
C(6)-C(7)	1.453 (6)	C(16)-C(17)	1.455 (6)
C(7)-C(8)	1.424 (5)	C(17)-C(18)	1.429 (6)
C(8)-O(2)	1.395 (6)	C(18)-O(4)	1.378 (6)
O(2)-N(1)	1.403 (4)	O(4)-N(2)	1.403 (4)
N(1)-C(9)	1.328 (6)	N(2)-C(19)	1.341 (6)
C(9)-C(7)	1.356 (6)	C(19)-C(17)	1.380 (6)
C(8)-O(1)	1.208 (5)	C(18)-O(3)	1.223 (5)
N(1)-C(10)	1.420 (6)	N(2)-C(20)	1.421 (6)
C(1)-H(1)	1.00 (4)	C(11)-H(6)	1.02 (4)
C(2)-H(2)	1.14 (5)	C(12)-H(7)	1.19 (5)
C(3)-H(3)	1.02 (5)	C(13)-H(8)	1.09 (5)
C(4)-H(4)	1.07 (4)	C(14)-H(9)	0.97 (5)
C(5)-H(5)	0.91 (4)	C(15)-H(10)	1.13 (4)
C(9)-H(14)	1.06 (4)	C(19)-H(18)	1.07 (4)
C(10)-H(11)	1.17 (5)	C(20)-H(15)	1.17 (4)
C(10)-H(12)	1.06 (5)	C(20)-H(16)	1.09 (5)
C(10)-H(13)	0.98 (4)	C(20)-H(17)	0.91 (4)

pendent molecules (*A* and *B*) are listed in Tables 4 and 5, with their e.s.d.'s. As it can be noted, the values found for chemically equivalent functions are very similar. These values, averaged from molecules *A* and *B*, are shown in Fig. 4.

The equations of the best planes through the six carbon atoms of the phenyl rings are:

$$\text{Molecule } A \quad 12.826x + 1.756y - 3.856z - 5.501 = 0$$

$$\text{Molecule } B \quad 12.628x + 1.671y + 3.793z - 4.497 = 0$$

where *x*, *y*, and *z* are the fractional atomic coordinates referred to the monoclinic cell axes. The planes through the five atoms constituting the isoxazolinone rings were found to be:

$$\text{Molecule } A \quad 13.623x + 0.630y - 1.444z - 5.370 = 0$$

$$\text{Molecule } B \quad 13.407x + 0.964y + 1.882z - 3.161 = 0.$$

The displacements Δ of the ring and extra-ring atoms from the phenyl and isoxazolinone rings are listed in Table 6. Referring to the isoxazolinone ring, the maxi-

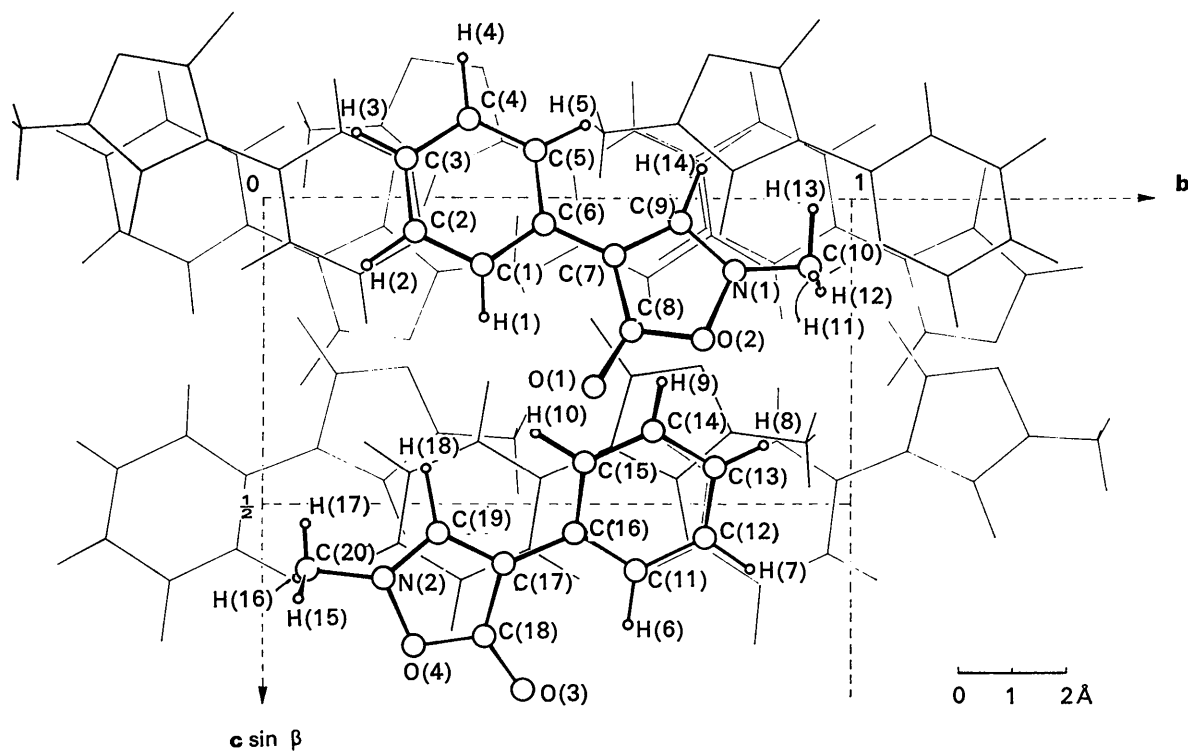


Fig. 2. Projection of the structure along the *a* axis.

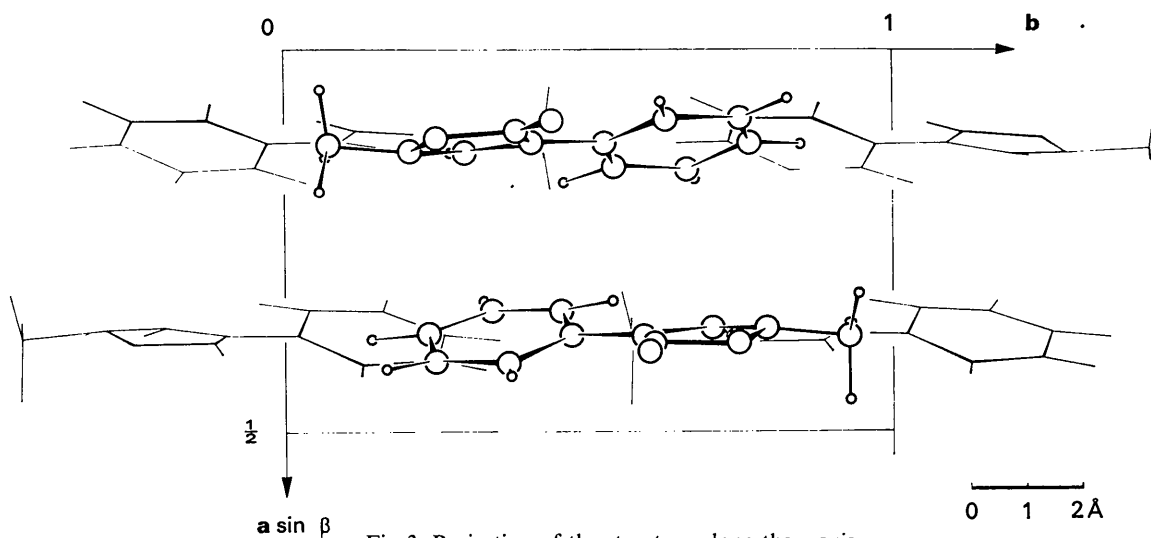
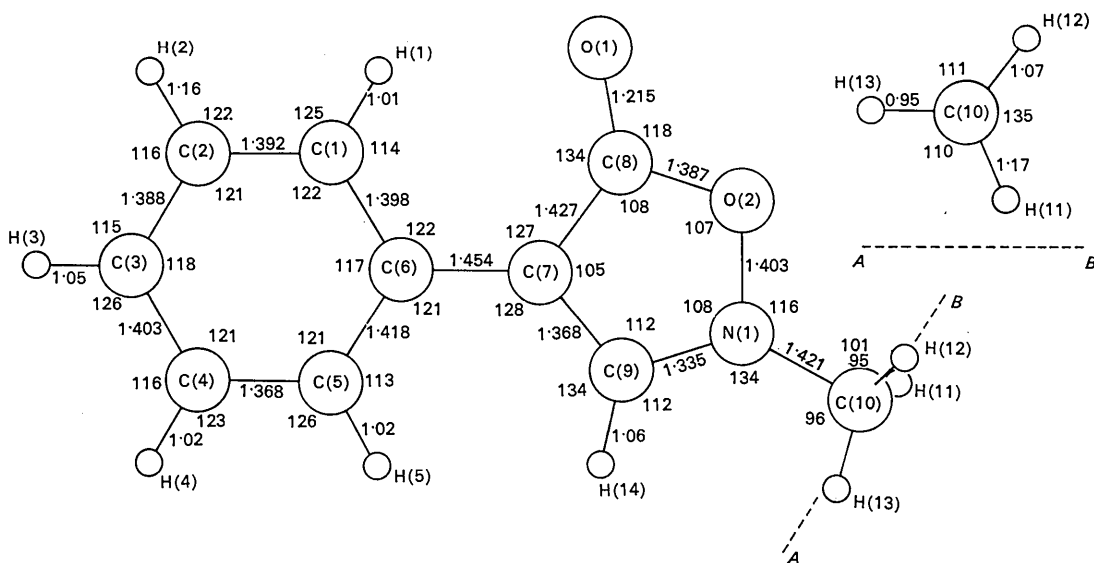


Fig. 3. Projection of the structure along the *c* axis.

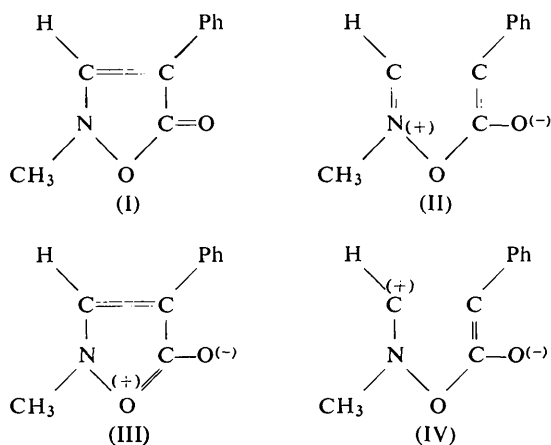
Table 5. Bond angles and standard deviations (in parenthesis)

Molecule <i>A</i>		Molecule <i>B</i>	
C(6)—C(1)—C(2)	120.7 (4)°	C(16)—C(11)—C(12)	122.4 (4)°
C(1)—C(2)—C(3)	121.0 (4)	C(11)—C(12)—C(13)	120.1 (4)
C(2)—C(3)—C(4)	118.6 (4)	C(12)—C(13)—C(14)	118.2 (4)
C(3)—C(4)—C(5)	121.0 (4)	C(13)—C(14)—C(15)	121.5 (4)
C(4)—C(5)—C(6)	121.5 (4)	C(14)—C(15)—C(16)	120.8 (4)
C(5)—C(6)—C(7)	120.8 (4)	C(15)—C(16)—C(17)	120.6 (4)
C(5)—C(6)—C(1)	117.3 (4)	C(15)—C(16)—C(11)	117.0 (4)
C(7)—C(6)—C(1)	121.9 (4)	C(17)—C(16)—C(11)	122.4 (4)
C(6)—C(7)—C(8)	126.2 (4)	C(16)—C(17)—C(18)	127.3 (4)
C(6)—C(7)—C(9)	127.9 (4)	C(16)—C(17)—C(19)	127.8 (4)
C(8)—C(7)—C(9)	105.9 (4)	C(18)—C(17)—C(19)	104.9 (4)
C(7)—C(8)—O(1)	135.5 (4)	C(17)—C(18)—O(3)	133.0 (4)
C(7)—C(8)—O(2)	107.2 (3)	C(17)—C(18)—O(4)	108.3 (3)
O(1)—C(8)—O(2)	117.3 (4)	O(3)—C(18)—O(4)	118.7 (3)
C(8)—O(2)—N(1)	107.0 (3)	C(18)—O(4)—N(1)	107.5 (3)
O(2)—N(1)—C(9)	107.9 (3)	O(4)—N(2)—C(19)	107.7 (3)
O(2)—N(1)—C(10)	115.5 (3)	O(4)—N(2)—C(20)	116.9 (3)
C(10)—N(1)—C(9)	134.6 (4)	C(20)—N(2)—C(19)	132.8 (4)
N(1)—C(9)—C(7)	112.0 (4)	N(2)—C(19)—C(17)	111.5 (4)
C(6)—C(1)—H(1)	116 (3)	C(16)—C(11)—H(6)	112 (3)
C(2)—C(1)—H(1)	124 (3)	C(12)—C(11)—H(6)	126 (3)
C(1)—C(2)—H(2)	120 (2)	C(11)—C(12)—H(7)	125 (2)
C(3)—C(2)—H(2)	118 (2)	C(13)—C(12)—H(7)	114 (2)
C(2)—C(3)—H(3)	111 (3)	C(12)—C(13)—H(8)	119 (2)
C(4)—C(3)—H(3)	130 (3)	C(14)—C(13)—H(8)	122 (2)
C(3)—C(4)—H(4)	116 (3)	C(13)—C(14)—H(9)	116 (3)
C(5)—C(4)—H(4)	123 (3)	C(15)—C(14)—H(9)	122 (3)
C(4)—C(5)—H(5)	128 (3)	C(14)—C(15)—H(10)	123 (2)
C(6)—C(5)—H(5)	110 (3)	C(16)—C(15)—H(10)	116 (2)
N(1)—C(9)—H(14)	106 (2)	N(2)—C(19)—H(18)	119 (2)
C(7)—C(9)—H(14)	139 (2)	C(17)—C(19)—H(18)	129 (2)
N(1)—C(10)—H(11)	94 (2)	N(2)—C(20)—H(15)	96 (2)
N(1)—C(10)—H(12)	100 (3)	N(2)—C(20)—H(16)	102 (3)
N(1)—C(10)—H(13)	97 (3)	N(2)—C(20)—H(17)	96 (3)
H(11)—C(10)—H(12)	140 (3)	H(15)—C(20)—H(17)	107 (3)
H(11)—C(10)—H(13)	112 (3)	H(15)—C(20)—H(16)	129 (3)
H(12)—C(10)—H(13)	104 (3)	H(16)—C(20)—H(17)	118 (3)

Fig. 4. A schematic drawing of the *N*-methyl-4-phenylisoxazolin-5-one molecule. The numbering of atoms refers to molecule *A*; bond lengths and angles are averaged from the values for molecules *A* and *B*.

mum value of Δ is 0.017 Å and the mean magnitude of deviation is 0.010 Å. Since the e.s.d. in the direction normal to the plane is 0.005 Å, the ring can be considered as planar within the limits of experimental error. The dihedral angles between phenyl and isoxazolinone ring are 14.1° for molecule *A* and 11.1° for molecule *B*. These values are probably imputable to the interactions between the atoms H(5)–H(14) (distance 2.53 Å) and H(1)–O(1) (2.42 Å) for molecule *A* and H(10)–H(18) (2.21 Å) and H(6)–O(3) (2.34 Å) for molecule *B*, which do not allow the two rings to be perfectly coplanar.

The mean length of the aromatic C–C bond is 1.394 Å, in good agreement with the normal value in the literature (*International Tables for X-ray Crystallography*, 1962). The bond lengths in the isoxazolinone rings can be accounted for by considering the hybrid structure resultant from the resonance between the forms:



Form (II) seems to make an important contribution to the mesomeric structure: the bond lengths between the nitrogen atom and the carbon atom in position 3 in the ring (1.335 Å) and between the carbon atoms in positions 4 and 5 in the ring (1.427 Å) are both sensibly shorter than the normal single bonds N–C and C–C. Furthermore the distance of 1.368 Å between the carbon atoms in positions 3 and 4 is greater than the normal double C=C bond length. The importance of form (II) in the resonance is also confirmed by the high value of the dipole moment ($\mu = 5.4$ D) (Cencioni, Franchini & Orienti, 1968).

The C=O bond is 1.215 Å; as pointed out by High & Kraut (1966), the strain of a pentatomic ring has interesting effects on the stereochemistry of the keto group, resulting in a somewhat more *s* character of orbital of the carbon atom of the C=O bond, and in a consequent shortening of the carbon–oxygen distance. Indeed these authors found a value of 1.189 Å for the C=O bond length in androsterone. This value is similar to those found in some γ -lactones, in which the ring resonance is inhibited: 1.198 Å (Jeffrey, Rosenstein & Vlasse, 1967), 1.16 Å (Glusker, Patterson, Love & Dornberg, 1963). The distance found in the present work is somewhat larger than these values, and even this feature can be attributed to the contribution of form (II) to the mesomeric structure.

The bond length between the carbon atom of the methyl group and the nitrogen atom of the isoxazolinone ring (1.421 Å) is sensibly shorter than the values found for exocyclic C–N bonds in some *N*-methyl derivatives of purine and pyrimidine (mean value 1.47 Å; Sutor, 1963), tetrazole (1.47 Å; Bryden, 1955, 1956) and pyrazolone (1.481 and 1.487 Å; Vijayan & Viswamitra, 1966, 1967). This fact could be indicative

Table 6. *Deviations from the least-squares planes*

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

Molecule <i>A</i>			Molecule <i>B</i>		
Phenyl			Phenyl		
	C(1)	0.001 Å		C(11)	0.012 Å
	C(2)	–0.005		C(12)	–0.012
	C(3)	0.004		C(13)	0.003
	C(4)	0.001		C(14)	0.005
	C(5)	–0.005		C(15)	–0.006
	C(6)	0.004		C(16)	–0.003
	C(7)	0.004		C(17)	0.007
	H(1)	0.04		H(6)	–0.01
	H(2)	–0.22		H(7)	0.52
	H(3)	0.04		H(8)	–0.01
	H(4)	0.10		H(9)	0.00
	H(5)	0.12		H(10)	–0.12
Isoxazolinone	O(2)	0.005	Isoxazolinone	O(4)	–0.012
	N(1)	–0.014		N(2)	0.017
	C(7)	–0.012		C(17)	0.007
	C(8)	0.003		C(18)	0.003
	C(9)	0.016		C(19)	–0.015
	C(6)	–0.004		C(16)	0.013
	O(1)	–0.02		O(3)	0.03
	C(10)	0.25		C(20)	–0.28
	H(14)	0.29		H(18)	–0.16

of a strong interaction of the methyl group with the resonating electronic system of the isoxazolinone ring.

The significant shortening of the C—C bond between the phenyl and isoxazolinone rings (1.454 Å) is indicative of conjugation between the two rings. This fact is confirmed by the activation of the *para* position of the phenyl group, allowing bromination with *N*-bromosuccinimide without acid catalysis.

The C—H bond lengths range from 0.91 to 1.19 Å, with an average value of 1.06 Å.

The crystal structure of *N*-methyl-4-phenylisoxazolin-5-one can be schematically described as layers of molecules on planes parallel to (100) at x about $\frac{1}{3}$ and $\frac{2}{3}$. The shortest intermolecular distances are reported in Table 7. There are no abnormally short contacts.

Table 7. *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 , $y+1$, z	(e) $-x+1$, $-y+1$, $-z$
(b) x , $-y+\frac{3}{2}$, $z+\frac{1}{2}$	(f) $-x$, $y+\frac{1}{2}$, $-z+\frac{3}{2}$
(c) x , $-y+\frac{1}{2}$, $z+\frac{1}{2}$	(g) $-x$, $-y+1$, $-z+1$
(d) $-x+1$, $y+\frac{1}{2}$, $-z+\frac{1}{2}$	(h) $-x$, $y-\frac{1}{2}$, $-z+\frac{3}{2}$

O(1)—C(10) (b)	3.42 Å	C(2)—H(14) (e)	2.96 Å
C(2)—C(9) (e)	3.29	C(3)—H(11) (e)	2.84
O(3)—C(20) (c)	3.43	C(10)—H(2) (a)	2.71
C(10)—O(1) (d)	3.50	C(16)—H(12) (b)	2.89
C(19)—C(12) (g)	3.31	H(7)—O(3) (f)	2.70
C(20)—O(3) (h)	3.48	H(7)—C(20) (a)	2.68
O(1)—H(2) (d)	2.91	H(11)—O(1) (d)	2.54
O(1)—H(3) (c)	2.57	H(15)—C(6) (c)	2.86
O(1)—H(13) (b)	2.50	H(1)—H(3) (c)	2.66
O(1)—H(14) (b)	2.78	H(2)—H(4) (c)	2.39
O(2)—H(14) (b)	2.57	H(3)—H(11) (e)	2.23
O(3)—H(8) (b)	2.50	H(6)—H(8) (b)	2.54
O(3)—H(16) (f)	2.46	H(6)—H(16) (f)	2.69
O(3)—H(17) (c)	2.58	H(7)—H(9) (b)	2.66
O(3)—H(18) (c)	2.95	H(7)—H(16) (a)	2.46
O(4)—H(10) (c)	2.96	H(11)—H(1) (d)	2.62
O(4)—H(18) (c)	2.52	H(15)—H(10) (c)	2.52
C(2)—H(4) (c)	2.99	H(16)—H(8) (g)	2.54

Because of the type of data rescaling, anisotropic thermal parameters are only of semiquantitative value; moreover, the results of thermal motion analysis seem physically significant. Thermal parameters were transformed to obtain the axes of vibration ellipsoids with their angles relative to the cell axes, with a program written by Coda (1966) and adapted by the authors for the IBM 1620 computer: the results are listed in Table 8 and a representation of thermal ellipsoids for molecule *B* is shown in Fig. 5. It is apparent that the predominant thermal motion is a rigid body molecular displacement parallel to the crystallographic a axis and normal to the molecular plane.

As has been mentioned, the two molecules in the asymmetric unit are nearly identical within experimental limits, save for slight differences in the angles of tilt between phenyl and isoxazolinone rings. Molecules *A* and *B* are nearly related within the asymmetric unit by the symmetry operation $\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z$ of the orthorhombic space group *Pbca*. Since relative atomic displacements from orthorhombic symmetry are not greater than 0.16 Å, there are no appreciable changes in the systematic absences $0kl$ with $k=2n+1$ and $hk0$ with $h=2n+1$ of the orthorhombic space group.

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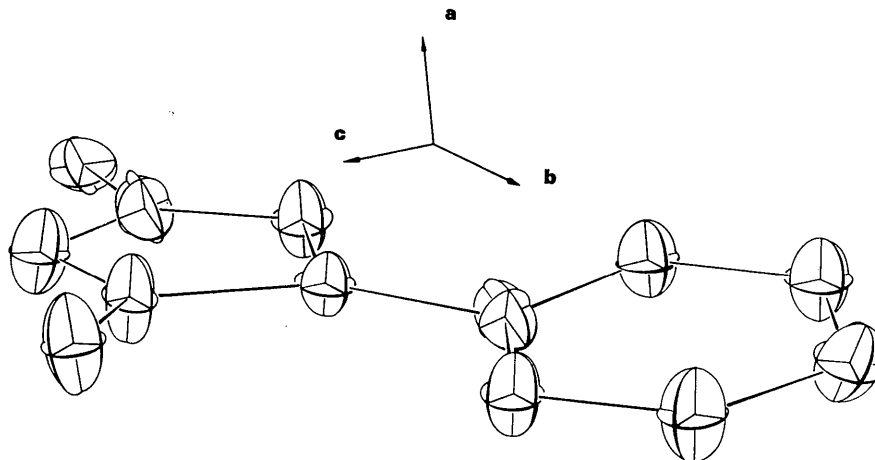


Fig. 5. A perspective drawing of molecule *B* showing the ellipsoids of thermal motion.

Table 8. *Principal axes of thermal ellipsoids*

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

	Molecule A					Molecule B					
	B_i	U_i	θ_{ia}	θ_{ib}	θ_{ic}	B_i	U_i	θ_{ia}	θ_{ib}	θ_{ic}	
O(1)	8.52 10.38 3.74	0.33 0.36 0.22	82.6 7.3 90.0	168.5 82.7 98.7	98.8 90.3 8.8	O(3)	6.87 10.62 3.90	0.29 0.37 0.22	80.1 10.7 94.1	161.8 79.3 75.4	75.1 90.0 14.8
O(2)	6.41 8.82 3.88	0.28 0.33 0.22	103.6 14.4 85.4	14.8 75.9 94.7	83.9 94.7 7.6	O(4)	7.00 8.62 3.62	0.30 0.33 0.21	83.8 6.6 92.3	173.8 83.8 89.7	89.6 89.2 0.8
N(1)	6.88 8.65 3.67	0.30 0.33 0.22	84.8 9.9 81.5	162.0 82.6 106.2	107.2 98.0 19.1	N(2)	7.67 7.82 4.02	0.31 0.31 0.23	30.8 62.1 102.0	117.5 27.9 85.4	78.5 89.0 11.5
C(1)	7.28 8.04 4.29	0.30 0.32 0.23	88.6 5.4 95.2	18.7 92.9 108.4	71.3 86.9 18.8	C(11)	6.70 8.22 4.32	0.29 0.32 0.23	79.5 14.0 80.8	165.3 81.4 78.1	80.1 102.5 16.0
C(2)	6.95 8.62 4.87	0.30 0.33 0.25	70.5 19.4 91.1	61.9 98.4 29.5	145.6 74.0 60.4	C(12)	6.91 9.35 5.88	0.30 0.34 0.27	84.9 6.4 85.9	68.5 95.6 22.1	22.4 94.7 111.9
C(3)	6.37 8.83 5.74	0.28 0.33 0.27	46.7 46.8 75.5	65.2 130.6 50.7	127.8 71.8 43.4	C(13)	6.64 8.04 5.93	0.29 0.32 0.27	60.7 29.4 93.4	38.0 118.0 113.5	68.6 99.8 23.6
C(4)	7.52 8.64 5.10	0.31 0.33 0.25	166.3 103.6 90.3	102.9 23.1 71.1	84.5 108.0 18.8	C(14)	7.64 9.70 4.42	0.31 0.35 0.24	175.0 90.6 94.9	89.1 17.5 107.5	93.4 72.4 17.8
C(5)	6.23 7.89 4.18	0.28 0.32 0.23	162.3 87.8 72.5	84.7 10.9 80.3	71.6 100.8 21.4	C(15)	6.98 8.34 3.81	0.30 0.32 0.22	170.7 80.7 89.6	81.0 15.2 102.1	86.1 78.2 12.3
C(6)	6.24 6.99 3.96	0.28 0.30 0.22	72.5 19.1 97.6	17.6 107.6 90.2	87.9 84.1 6.1	C(16)	5.67 7.17 4.13	0.27 0.30 0.23	25.0 103.9 69.7	75.8 14.3 87.9	111.6 86.6 21.9
C(7)	5.99 6.73 3.15	0.27 0.29 0.20	49.0 45.4 106.1	43.2 133.2 90.5	79.6 79.7 14.6	C(17)	5.58 7.38 3.53	0.26 0.30 0.21	9.3 98.6 93.1	80.9 10.8 84.1	89.2 96.0 6.0
C(8)	6.66 6.82 3.57	0.29 0.29 0.21	117.4 27.7 93.7	27.5 62.9 95.1	86.4 85.6 5.6	C(18)	6.14 8.15 3.90	0.28 0.32 0.22	81.1 9.8 85.7	168.5 81.8 82.0	83.0 96.9 9.8
C(9)	5.23 6.89 4.95	0.26 0.29 0.25	79.1 12.2 84.3	81.2 97.3 11.5	15.2 101.2 100.1	C(19)	5.76 8.23 3.67	0.27 0.32 0.22	71.7 18.3 91.6	18.8 108.3 94.3	85.8 91.1 4.3
C(10)	6.02 8.92 4.98	0.28 0.34 0.25	90.1 13.0 76.9	43.4 80.1 132.7	46.5 99.9 46.1	C(20)	6.86 8.91 4.29	0.29 0.33 0.23	82.5 23.1 111.7	42.8 80.6 48.6	132.1 70.4 48.5

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