Synthesis and Single Crystal X-Ray Structure of Ethyl 2-(1,3-Benzoxazol-2-yl)-5-oxo-3-(4-toluidino)-2,5-dihydro-4-isoxazolecarboxylate

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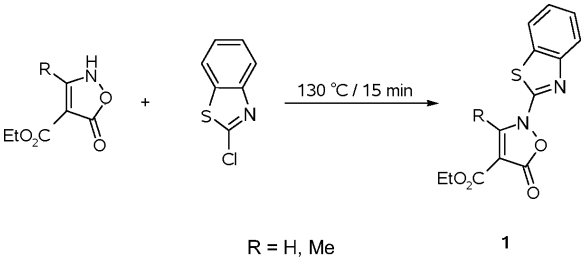
Ethyl 5-oxo-3-(4-toluidino)-2,5-dihydro-4-isoxazolecarboxylate was prepared from the reaction of diethyl 2-(4-toluidinocarbothioyl)malonate with hydroxylamine. Its reaction with 2-chlorobenzoxazole gave the corresponding *N*-substituted isoxazolone. The structure of the final product **4** was confirmed by IR, ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry, and by X-ray single crystal structure determination.

Key words: Synthesis, Hydroxylamine, 2-Chlorobenzoxazole, *N*-Substituted Isoxazolone, X-Ray Single Crystal Structure

Introduction

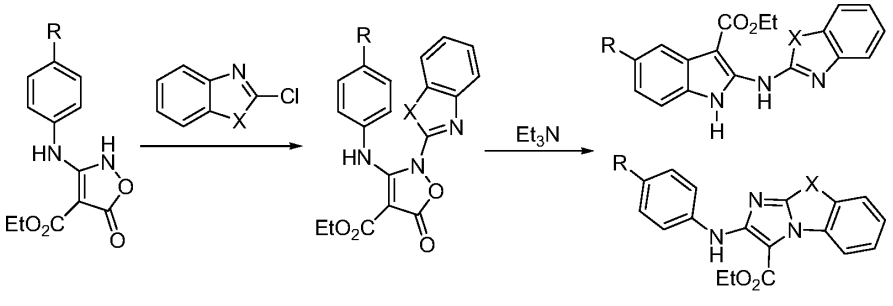
The reaction of isoxazol-5(2*H*)-ones, unsubstituted at C-3, with base is well known [1 – 5] and the various intermediates have been trapped to prepare a large number of heterocyclic systems [6 – 9]. However, the reaction of 3-substituted compounds with base is not so well known.

The synthesis of isoxazol-5(2*H*)-one **1**, bearing a benzothiazole substituent at nitrogen has been reported by Prager and co-workers [10] as shown is Scheme 1.



Scheme 1.

We have recently reported [11] the synthesis of new *N*-substituted derivatives of 3-arylaminoisoxazol-5(2*H*)-ones with benzoxazole and benzothiazole substituted at the nitrogen atom and their rearrangement in the presence of triethylamine in ethanol under reflux conditions to produce the corresponding indole and imidazobenzothiazole derivatives, respectively (Scheme 2), which are suitable synthetic intermediates for a series of new heterocycles that could be expected to have pharmaceutical applications [12, 13].

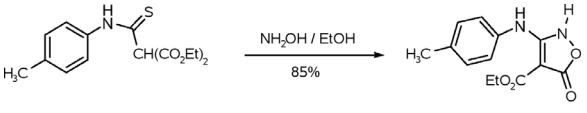


Scheme 2.

Here we report a new and efficient synthesis of ethyl 2-(1,3-benzoxazol-2-yl)-5-oxo-3-(4-toluidino)-2,5-dihydro-4-isoxazolecarboxylate (**4**) and the confirmation of its structure by single crystal X-ray diffraction.

Results and Discussion

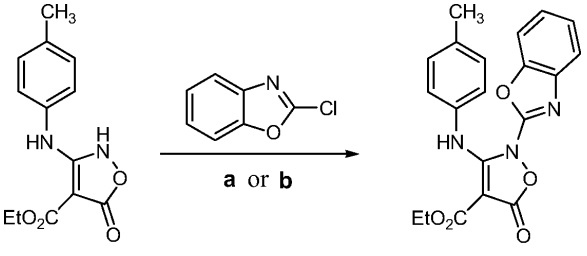
The isoxazolone **3** was prepared from the reaction of the corresponding thiocarbamate **2** with hydroxylamine by the general method of Worrall [14] (Scheme 3).



2 **3**

Scheme 3.

The reaction of isoxazolone **3** with 2-chlorobenzoxazole under nitrogen atmosphere either in chloroform under reflux conditions, or upon heating without solvent at 130 °C, afforded the corresponding *N*-benzoxazole derivative **4** in 42 and 40 % yield, respectively (Scheme 4).



3 **4**

a: in chloroform under reflux conditions;
b: heating neat at 130 °C under nitrogen atmosphere

Scheme 4.

The structure of compound **4** was confirmed by elemental analysis, IR, ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry, and by X-ray single crystal structure determination.

*Description of the crystal structure of **4***

The crystal of **4** is built up from molecules, the structure of which is shown in Fig. 1. A summary of the experimental details is given in Table 1.

Searching the Cambridge Structural Database [15] revealed eleven hits for isoxazolones of related structure, *i. e.* substituted at the N atom and at both carbon atoms. The molecule consists of three planar moieties: the ethyl 3-amino-5-oxo-2,5-dihydroisoxazole-4-carboxylate unit (forming plane 1), the benzoxazol-2-yl group (plane 2) and the *p*-toluidino moiety (plane 3). All atoms of the benzoxazol and *p*-toluidino groups lie exactly in their planes (within 0.02 Å). However, atoms of the plane denoted as 1 slightly deviate from the mean plane with atom O(3) deviating by 0.27 Å and the remaining atoms being coplanar to within 0.16 Å. The dihedral angles between the planes of these three moieties are 66.6(1)° (between planes 1 and 2) and 60.4(1)° (between planes 1 and 3).

Atoms N(3) and C(14) are both in plane with the isoxazolonyl ring (see torsion angle C(14)–N(3)–C(3)–

Table 1. Crystal data and structure refinement details for **4**.

Crystal data	
Empirical formula	$C_{20}H_{17}N_3O_5$
Formula weight [g mol^{-1}]	379.37
Crystal size [mm^3]	$0.45 \times 0.25 \times 0.23$
Crystal color and form	colorless, needle
Crystal system, space group	monoclinic, $P2_1/n$
a [Å]	8.907(2)
b [Å]	13.136(3)
c [Å]	15.780(3)
β [deg]	103.08(3)
V [Å^3]	1798.4(7)
Z	4
D_{calc} [g cm^{-3}]	1.401
μ [mm^{-1}]	0.856
$F(000)$ [e]	792
Data collection	
Diffractometer	Xcalibur PX
Data collection method	ω scans and ϕ scans
Monochromator	graphite
Radiation type	CuK_α
T [K]	120(2)
θ range [°]	4.43 – 76.52
h, k, l range	$-5 \le h \le 11$, $-16 \le k \le 16$, $-17 \le l \le 19$
Absorption correction	analytical
T_{min}/T_{max}	0.715/0.846
Measured reflections	15656
Independent reflections	3541
Observed refl. [$I \ge 2\sigma(I)$]	3258
Completeness to $\theta = 70.00°$	0.976
Refinement	
Refinement on	F^2
Data/restraints/parameters	3541/0/322
R [$F_o^2 > 2\sigma(F_o^2)$]	$R1 = 0.0378$, $wR2 = 0.1062$
R (all data)	$R1 = 0.0400$, $wR2 = 0.1080$
GooF = S	1.058
Weighting parameter a/b	0.0661/0.5987
$\Delta\rho_{max}/\Delta\rho_{min}$ [e Å^{-3}]	0.27/−0.20

$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = \sqrt{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]}$; weighting scheme: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$.

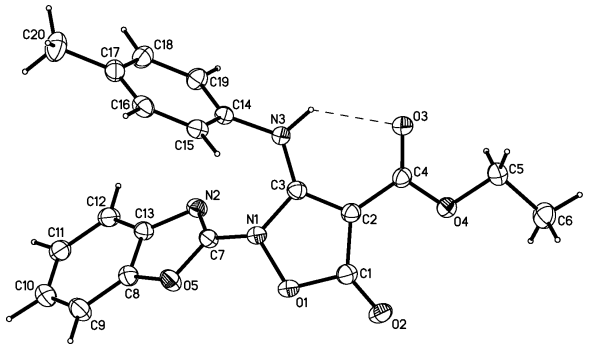


Fig. 1. Molecular structure of **4** in the crystal showing the atom numbering scheme and the intramolecular N(3)–H(3)···O(3) hydrogen bond forming an $S(6)$ motif (dashed line). Displacement ellipsoids are shown at the 50 % probability level.

C(2) in Table 2) because of the formal sp^2 hybridization of atom N(3). This results in a partial double bond character of the N(3)–C(3) linkage, which is reflected in the difference between its length and the length of the N(3)–C(14) bond, which is typical for a C–N single bond (see Table 2). Atom C(14) is only slightly displaced from the isoxazolonyl ring plane; the distance of C(14) from that plane is about 0.07 Å. However, the *p*-tolyl substituent is twisted relative to the isoxazolonyl ring by about 60°, which is also reflected by the C(3)–N(3)–C(14)–C(15) torsion angle value of 62.3(2)°. Such non-planar orientation of benzoxazyl and *p*-toluidinyl groups in relation to an isoxazolonyl ring prevents the steric hindrance between rather bulky substituents at atoms N(1) and N(3).

The conformation of the molecule is stabilized by the intramolecular N(3)–H(3)···O(3) hydrogen bond forming the usual six-membered $S(6)$ motif (see Fig. 1). It is possible that this intramolecular interaction is of the resonance-assisted hydrogen bond (RAHB) type, which often occurs when the hydrogen-bond donor and acceptor are connected by a short chain of conjugated single and double bonds [16] (compare with the geometry of the fragment involved in the $S(6)$ ring motif H(3)–N(3)–C(3)–C(2)–C(4)–O(3); Tables 2 and 3).

The same amine hydrogen atoms, H(3), along with the same donors, N(3), and carbonyl acceptors, O(3), are additionally involved in N(3)–H(3)···O(3)^i intermolecular contacts to form the centrosymmetric molecular dimers shown in Fig. 2. This gives rise to a planar three-centre N–H···$(O)_2$ system, with a sum of angles at H(4) of 354(2)° and additional $R_2^2(4)$ rings formed by the two adjacent molecules (see Table 3).

Table 2. Selected interatomic distances (Å), valence angles (deg) and torsion angles (deg) in **4**.

O(1)–C(1)	1.413(2)	N(2)–C(7)	1.283(2)
O(1)–N(1)	1.450(2)	N(2)–C(13)	1.413(2)
O(3)–C(4)	1.221(2)	N(3)–C(3)	1.328(2)
O(4)–C(4)	1.336(2)	N(3)–C(14)	1.435(2)
O(5)–C(7)	1.360(2)	C(1)–C(2)	1.430(2)
O(5)–C(8)	1.390(2)	C(2)–C(3)	1.380(2)
N(1)–C(7)	1.401(2)	C(2)–C(4)	1.454(2)
N(1)–C(3)	1.409(2)		
C(7)–N(1)–C(3)	119.93(10)	O(2)–C(1)–C(2)	135.14(13)
C(7)–N(1)–O(1)	107.12(9)	O(1)–C(1)–C(2)	107.27(11)
C(3)–N(1)–O(1)	106.48(9)	C(3)–C(2)–C(1)	108.58(11)
C(3)–N(3)–C(14)	126.15(11)	C(3)–C(2)–C(4)	123.43(11)
O(2)–C(1)–O(1)	117.56(12)	C(1)–C(2)–C(4)	127.98(11)
C(1)–O(1)–N(1)–C(7)	129.8(1)		
C(14)–N(3)–C(3)–C(2)	−176.8(2)		
C(7)–N(1)–C(3)–N(3)	59.6(2)		
C(7)–N(1)–C(3)–C(2)	−122.8(2)		
C(5)–O(4)–C(4)–O(3)	−2.4(2)		
C(5)–O(4)–C(4)–C(2)	175.0(1)		
C(3)–C(2)–C(4)–O(3)	11.0(2)		
C(1)–C(2)–C(4)–O(3)	−170.4(2)		
C(3)–C(2)–C(4)–O(4)	−166.5(1)		
C(4)–O(4)–C(5)–C(6)	174.1(2)		
C(3)–N(1)–C(7)–O(5)	−173.5(1)		
O(1)–N(1)–C(7)–O(5)	65.2(2)		
C(3)–N(3)–C(14)–C(15)	62.3(2)		

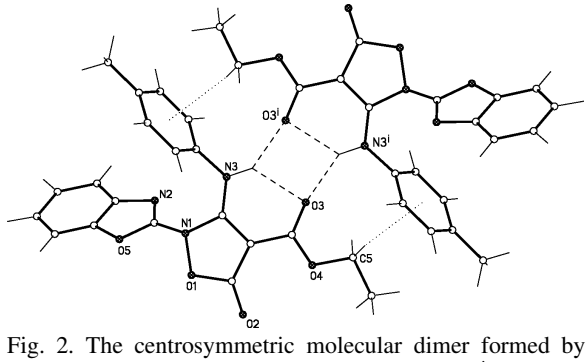


Fig. 2. The centrosymmetric molecular dimer formed by adjacent molecules joined by N(3)–H(3)···O(3)^i hydrogen bonds (dashed line) and C(5)–H(5A)···π[$Cg(4)^i$] (dotted line) to form $R_2^2(4)$ rings in addition to intramolecular $S(6)$ motifs. Symmetry codes are given in Table 3.

The structure of the dimer is additionally stabilized by C–H···π interactions, with atoms C(5) acting as donors and the *p*-toluidinyl phenyl rings as acceptors (Fig. 2 and Table 3).

Adjacent dimers are joined to each other by an extensive mode of interactions, *i. e.* by the hydrogen contacts of the C–H···O, C–H···N and C–H···π types on the one hand, and by the centrosymmetric C=O···C=O carbonyl interactions on the other. (For geometry

D–H···A	D−H (Å)	H···A (Å)	D···A (Å)	D−H···A (°)	Offset (Å)
N(3)–H(3)···O(3)	0.92(2)	2.18(2)	2.850(2)	129(2)	–
N(3)–H(3)···O(3)^{i}	0.92(2)	2.23(2)	2.952(2)	134(2)	–
C(6)–H(6A) ···O(1)^{ii}	1.03(2)	2.74(2)	3.528(2)	133(2)	–
C(6)–H(6A) ···N(1)^{ii}	1.03(2)	2.77(2)	3.763(2)	164(2)	–
C(11)–H(11) ···O(2)^{iii}	1.00(2)	2.38(2)	3.157(2)	135(2)	–
C(15)–H(15) ···N(2)^{iv}	0.98(2)	2.65(2)	3.324(2)	127(2)	–
C(20)–H(20C) ···O(2)^{iv}	0.94(3)	2.70(3)	3.622(2)	168(2)	–
C(5)–H(5A) ···Cg(4)^{i}	0.96(2)	2.58(2)	3.372(2)	140(2)	0.56
C(5)–H(5B) ···Cg(2)^{v}	0.98(2)	3.12(2)	4.084(2)	168(2)	0.89
C(5)–H(5B) ···Cg(3)^{v}	0.98(2)	3.27(2)	4.138(2)	150(2)	1.34
C(16)–H(16) ···Cg(1)^{iv}	1.01(2)	3.10(2)	3.994(2)	149(2)	0.85
C(20)–H(20B) ···Cg(3)^{vi}	1.00(3)	3.15(3)	3.845(2)	127(2)	0.96
Carbonyl interactions (see text)					
*A*1: C(1)=O(2) ···C(4)^{ii}	107.12(9)°				
*A*2: O2 ···C4^{ii}=O3^{ii}	93.68(8)°		*B*1: C1 ···O3^{ii}		4.087(2) Å
*A*3: C4^{ii}=O3^{ii}···C1	55.34(7)°		*B*2: O2 ···C4^{ii}		2.991(2) Å
*A*4: O3^{ii}···C1=O2	42.60(7)°		*T*: C1=O2 ···C4^{ii}=O3^{ii}		140.6(1)°

Table 3. Geometry of proposed hydrogen bonds, C–H···O/N/π close contacts and carbonyl interactions for **4** (Å, deg).

Symmetry codes: ^{i} $-x, -y+1, -z+1$; ^{ii} $-x+1, -y+1, -z+1$; ^{iii} $x-1/2, -y+1/2, z+1/2$; ^{iv} $-x+1/2, y+1/2, -z+3/2$; ^{v} $x-1/2, -y+1/2, z-1/2$; ^{vi} $-x, -y+1, -z+2$. Cg(1), Cg(2), Cg(3) and Cg(4) are the centroids of the isoxazyl, benzoxazyl O(5)–C(7)–N(2)–C(13)–C(8) and C(8)–C(9)–C(10)–C(11)–C(12)–C(13) rings, and toluidinyl rings, respectively.

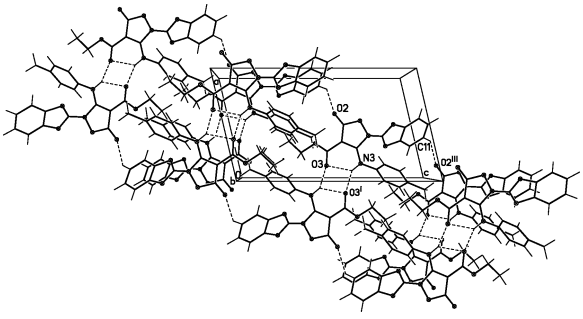


Fig. 3. The arrangement of the molecules within the layers parallel to the (101) plane. N(3)–H(3)···O(3), N(3)–H(3)···O(3)^{i} and C(11)–H(11)···O(2)^{iii} contacts are shown with dashed lines. Symmetry codes are given in Table 3.

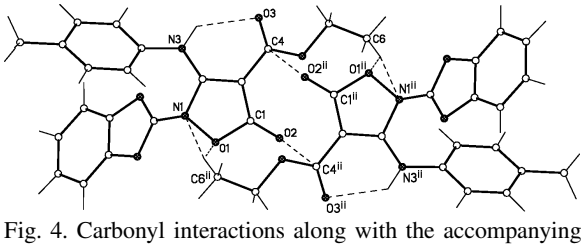


Fig. 4. Carbonyl interactions along with the accompanying C–H···O/N contacts formed between two molecules of two adjacent dimers. Symmetry codes are given in Table 3.

and symmetry codes see Table 3.) Symmetry-related dimers are linked by C(11)–H(11)···O(2)^{iii} bonds to form layers parallel to the (101) plane shown in Fig. 3. These interact with each other by means of rather weak C(15)–H(15)···N(2)^{iv}, C(20)–H(20C)···O(2)^{iv} and C–H···π contacts, as well as carbonyl interactions (Table 3).

The geometry of the carbonyl interactions, observed between C(1)=O(2) and C(4)^{ii}=O(3)^{ii} groups, especially the characteristic *A*1, *A*2, *A*3 and *A*4 angles, reveal the so-called motif III of such interactions (by Allen *et al.* [17]). The O(2) ···C(4)^{ii} distance (*B*2 in Table 3) is rather short at 2.991(2) Å even for this motif (see Fig. 4). It is probable that these interactions may be accompanied by weak, bifurcated C–H···O/N contacts formed by atom C(6) from one molecule and O(1)^{ii}, N(1)^{ii} from the other (also shown in Fig. 4).

The combination of all these N–H···O, C–H···O, C–H···N, C–H···π and C=O···C=O interactions observed in the crystal of compound **4** gives rise to a rather extensive three-dimensional network of hydrogen bonds and carbonyl interactions, which all stabilize the crystal packing of **4**.

Conclusions

In conclusion, we have developed a new and efficient solvent-less method for preparing ethyl 2-(1,3-benzoxazol-2-yl)-5-oxo-3-(4-toluidino)-2,5-dihydro-4-isoxazolecarboxylate (**4**). Other aspects of this process are under investigation. The X-ray structure of **4** revealed a variety of intra- and intermolecular interactions, from resonance-assisted N–H···O bonds to N–H···O, C–H···O/N/π and carbonyl interactions.

Experimental Section

General procedures

Freshly distilled solvents were used throughout, and anhydrous solvents were dried according to Perrin and Armarego [18]. Elemental analyses were performed using a Heraeus CHN-O-Rapid analyzer. ^{1}H (300 MHz) and ^{13}C (75.5 MHz) NMR measurements were carried out on a

Bruker 300 spectrometer in [D_6]DMSO or $CDCl_3$ with tetramethylsilane as internal standard. Infrared spectra were recorded on a Thermonicolet (Nexus 670) FT-infrared spectrometer, using sodium chloride cells, measured as Nujol mulls or films. Mass spectra were registered with an HP 5973 MSD instrument connected to an HP 6890 GC unit interfaced by a Pentium PC. Relative abundances of fragments are quoted in parentheses after the *m/z* values. Melting points were determined on a Philip Harris C4954718 apparatus and are uncorrected.

*Diethyl 2-(4-toluidinocarbothioyl)malonate (**2**)*

This thioamide was prepared by a literature method [19] as a pale-yellow solid. Yield: 90 %; m. p. 54 °C (lit. [16], 55 – 56 °C). – IR (KBr): ν = 3284, 1760, 1723, 1515, 1430, 1315, 1223, 1148, 1020, 831 cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 1.35 (t, 6 H, ^3J = 7.15 Hz, 2 CH_3 of 2 Et), 2.38 (s, 3H, CH_3), 4.32 (q, 2 H, ^3J = 7.15 Hz, CH_2 of Et), 4.33 (q, 2 H, ^3J = 7.15 Hz, CH_2 of Et), 5.11 (s, 1H, CH), 7.23 (d, 2 H, ^3J = 8.3 Hz, arom.), 7.66 (d, 2 H, ^3J = 8.3 Hz, arom.), 10.77 (bs, 1H, exchanged by D_2O addition, NH). – ^{13}C NMR ($CDCl_3$): δ = 14.35, 21.57, 63.47, 67.62, 123.64, 129.86, 136.41, 137.43, 166.16, 187.68.

*Ethyl 5-oxo-3-(4-toluidino)-2,5-dihydro-4-isoxazole-carboxylate (**3**)*

To a 50 mL flask containing a solution of hydroxylamine hydrochloride (4.71 g, 68 mmol) in water (20 mL), was added slowly potassium bicarbonate (6.78 g, 68 mmol). Ethanol (80 mL) was added and the resulting potassium chloride precipitate was filtered off. Compound **2** (10.50 g, 34 mmol) was added to the filtrate and the mixture was refluxed for 24 h. The reaction mixture was acidified with dilute hydrochloric acid and the white precipitate was collected by vacuum filtration. The white solid was recrystallized from ethanol to give colorless crystals. Yield: 7.85 g (85 %); m. p. 164 – 166 °C (lit. [20] 161 – 163 °C). – IR (KBr): ν = 3409, 2976, 1708, 1619, 1572, 1515, 1249, 1204, 1072, 787 cm^{-1}. – ^{1}H NMR ($CDCl_3$ + [D_6]DMSO): δ = 0.95 (t, 3 H, ^3J = 7.0 Hz, CH_3 of Et), 1.94 (s, 3H, CH_3), 3.91 (q, 2 H, ^3J = 7.0 Hz, CH_2 of Et), 6.78 (d, 2 H, ^3J = 9.2 Hz, arom.), 6.79 (bs, 1H, exchanged by D_2O addition, NH), 6.80 (d, 2 H, ^3J = 9.2 Hz, arom.), 8.85 (bs, 1 H, exchanged by D_2O addition, NH). – ^{13}C NMR ($CDCl_3$ + [D_6]DMSO): δ = 14.52, 20.85, 60.08, 74.69, 121.53, 130.13, 133.29, 135.64, 163.59, 165.51, 166.74.

*Ethyl 2-(1,3-benzoxazol-2-yl)-5-oxo-3-(4-toluidino)-2,5-dihydro-4-isoxazolecarboxylate (**4**)*

(a) Compound **3** (100 mg, 0.38 mmol) and 2-chlorobenzoxazole (58 mg, 0.38 mmol) were refluxed in chloroform (5 mL) for 24 h. The solvent was removed under reduced pressure to give a colorless oil. This residue was recrystallized from ethanol to give **4** as white needles. Yield: 61 mg (42 %); m. p. 129 – 131 °C. – IR (KBr): ν = 3267, 1790, 1667, 1630, 1561, 1514, 1491, 1450, 1356, 1294, 1234, 1201, 1030, 985, 931, 793, 763, 751 cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 1.45 (t, 3 H, ^3J = 7.1 Hz, CH_3 of Et), 2.12 (s, 3H, CH_3), 4.45 (q, 2 H, ^3J = 7.1 Hz, CH_2 of Et), 6.62 (d, 2 H, ^3J = 7.9 Hz, arom.), 7.08 (d, 2 H, ^3J = 8.3 Hz, arom.), 7.33 (t, 1 H, ^3J = 7.7 Hz, arom.), 7.40 (t, 1 H, ^3J = 8.2 Hz, arom.), 7.53 (d, 1 H, ^3J = 7.9 Hz, arom.), 9.90 (s, 1H, exchanged by D_2O addition, NH). – ^{13}C NMR ($CDCl_3$): δ = 14.81, 21.11, 61.50, 78.91, 111.27, 121.08, 122.94, 125.74, 127.13, 130.29, 132.99, 137.44, 139.91, 150.15, 151.76, 164.01, 164.85, 165.38. – GC-MS: *m/z* (%) = 379 (7 %) M^+, 335 (34) $[M–CO2]^+$, 290 (23), 289 (100), 251 (11), 250 (46), 230 (57), 158 (60), 117 (55), 91 (100), 77 (44), 65 (50), 44 (9), 29 (66). – $C_{20}H_{17}N_3O_5$ (379.37): calcd. C 63.32, H 4.52, N 11.08; found C 63.43, H 4.44, N 11.01.

(b) A mixture of 2-chlorobenzoxazole (58 mg, 0.38 mmol) and the corresponding isoxazolone (100 mg, 0.38 mmol) was heated neat to 130 °C in a sealed vial flushed with nitrogen in an oven for 1 h. The mixture was left to cool to r. t. and then extracted with dichloromethane. The solution was filtered and passed through a short plug of silica. Removal of the solvent gave a pale-yellow oil, which was crystallized from ethanol to give white needles. Yield: 59 mg (40 %); m. p. 129 – 131 °C. Its spectral data agreed with those given above.

*Preparation of single crystals of ethyl 2-(1,3-benzoxazol-2-yl)-5-oxo-3-(4-toluidino)-2,5-dihydro-4-isoxazole-carboxylate (**4**)*

Single crystals of **4** were prepared by using the branch tube method with a mixture of *n*-hexane/1,4-dioxane (10 : 1) kept at 45 °C for six weeks [21]. The colorless crystals were filtered off, washed with a cold mixture of *n*-hexane/1,4-dioxane (10 : 1 mL) and dried in vacuum over P_4O_{10} (m. p. 130 °C).

*Crystal structure determination of **4***

The crystallographic measurement was performed on a κ geometry Xcalibur PX automated four-circle diffractometer with graphite-monochromatized CuK_α radiation. The crystal data for the crystal were collected at 120(2) K using the Oxford Cryosystems cooler. A summary of the conditions for data collection and structure refinement parameters are given in Table 1. The data were corrected for Lorentz and polarization effects. Analytical absorption correction was applied. Data collection, cell refinement, and data reduction and analysis were carried out with the Xcalibur PX software (Oxford Diffraction Poland): CrysAlis CCD and CrysAlis RED, re-

spectively [22]. The structure was solved by Direct Methods using the SHELXS-97 program [23] and refined by a full-matrix least-squares technique using SHELXL-97 [24] with anisotropic thermal parameters for non-H atoms. All H atoms were found in difference Fourier maps and were refined isotropically. All figures were made using the XP program [25]. The extinction was also refined with the final extinction coefficient of 0.0173(9).

CCDC 619511 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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