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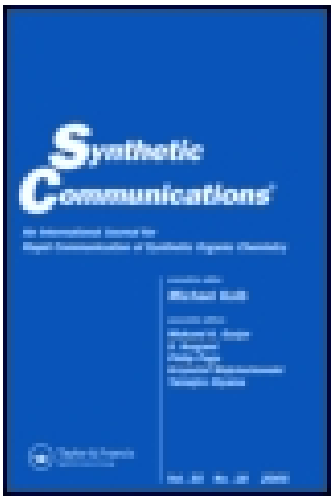

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Oxazolo[4,5-d]isoxazole Derivatives and 3,4-Disubstituted Isoxazoles from Isoxazol-5(4H)-ones

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SYNTHETIC COMMUNICATIONS, 23(5), 685-702 (1993)

OXAZOLO[4,5-d]ISOXAZOLE DERIVATIVES AND 3,4-DISUBSTITUTED ISOXAZOLES FROM ISOXAZOL-5(4H)-ONES

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Abstract: Synthesis for oxazolo[4,5-*d*]isoxazole derivatives and 3,4-disubstituted isoxazoles from isoxazol-5(4*H*)-ones is reported.

In continuation of our studies directed towards synthetic applications of isoxazol-5(4*H*)-ones[1], we wish to report here an efficient synthesis of derivatives of the hiterto unknown oxazolo[4,5-*d*]isoxazole ring system **3** and **4** starting from the isoxazol-5(4*H*)-ones **1** (Scheme), and on the following easy transformation of derivatives **4** to the 3,4-disubstituted isoxazoles **5.**

The reaction of isoxazol-5(4*H*)-ones **1** with di-*tert*-butyl azodicarboxylate in dichloromethane solution and in the presence of a catalytic amount of

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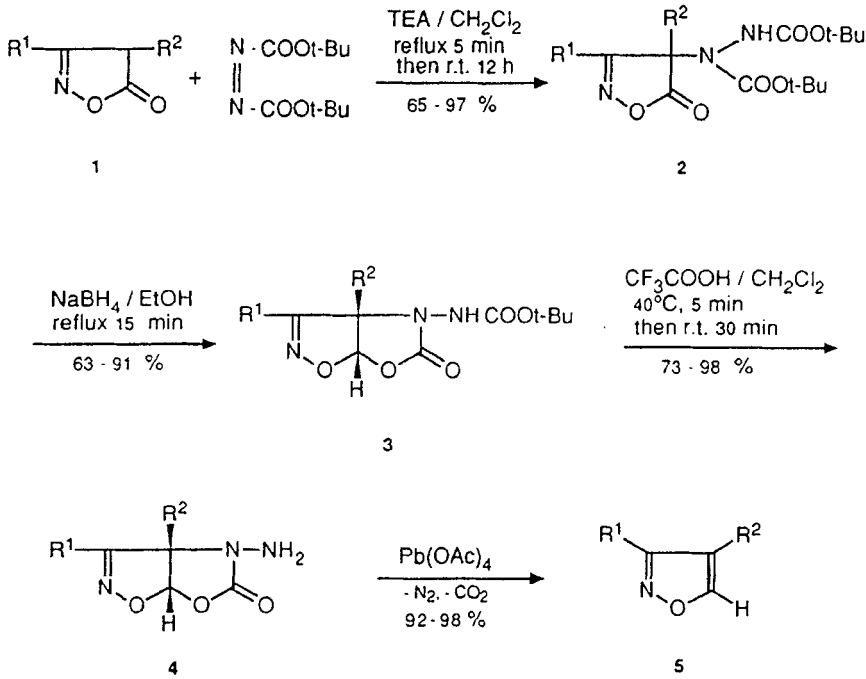
SCHEME



1-5	R^1	R^2	1-5	R^1	R^2
a	Me	CH_2Ph	**e**	Ph	CH_2Ph
b	Me	$(CH_2)_2Ph$	**f**	Ph	C_8H_{17}
c	Me	Ph	**g**	Ph	Et
d	Ph	Me			

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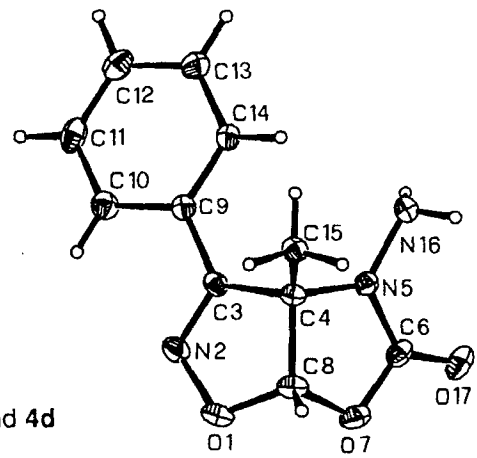
triethylamine gives in high yields the corresponding 4,4-disubstituted isoxazol-5(4*H*)-ones **2** (Table 1).

As known for the 4,4-disubstituted isoxazol-5(4*H*)-ones[2], $NaBH_4$ reduction in refluxing ethanol of compounds **2** so formed, results in reduction of the carbonyl group. The intermediate 5-hydroxyisoxazoline is not isolable and cyclizes to the oxazolo[4,5-*d*]isoxazole ring system **3**. The corresponding N-amino derivatives **4** are easily obtained from **3** by reaction with trifluoroacetic acid in dichloromethane.

The structure of new compounds follows from analytical and spectroscopic data (Table 5) as well as X-ray diffraction analysis on **4d** (Figure)[3].



ORTEP of Compound **4d**

The nmr spectra of derivatives **2** and **3** evidentiate that they are a mixture of rotamers. When compounds **4** are treated, at r.t. in dichloromethane solution, with $Pb(OAc)_4$, the corresponding isoxazole derivatives **5** are formed in quantitative yield in a very fast reaction. This reaction occurs

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very likely through the decomposition of an aminonitrene intermediate formed by oxidation[4].

The above reactions represent a useful method to convert the easily accessible isoxazol-5(4*H*)-ones **1** into the less available isoxazoles **5**. In this case the whole reaction sequence can be performed successfully without purification of the intermediates **2** - **4**. The present method is then a valid addition to the known processes for transformation of isoxazol-5(4*H*)-ones into the isoxazoles[5].

EXPERIMENTAL

Melting points were determined on a Buchi apparatus and were uncorrected. IR spectra were recorded on a Perkin-Elmer 298 instrument, in nujol mull for solids and CCl_4 solution or liquid film for oils. ^{1}H-NMR spectra were recorded on a Varian EM-390 spectrometer with TMS as an internal standard or on a Bruker AC 300 in $CDCl_3$ solution if not otherwise stated.

Column chromatography was performed on Merck Kieselgel 60, 0.063-0.2 mm. Na_2SO_4 was used as drying agent. Evaporation was carried out under vacuum in a rotary evaporation.

Compounds **1a**[6], **1b**[7], **1c**[8], **1d**[9], **1e**[10], **1f**[11], **1g**[12], were prepared according to literature procedure.

Reaction of 3,4-disubstituted isoxazol-5(4*H*)-ones 1 with di-*tert*-butyl azodicarboxylate; General Procedure:

To a solution of isoxazol-5(4*H*)-one **1** (10 mmol) in CH_2Cl_2 (50 mL), 2.5 mL (11 mmol) of di-*tert*-butyl azodicarboxylate and 0.05 mL TEA were added. The reaction was heated at 40 °C for 5 min then 12 h at room temperature.

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After evaporation of the solvent, the residue was purified by column chromatography to give pure compound **2** (Table 1).

Oxazolo[4,5-*d*]isoxazole derivatives 3; General Procedure:
The isoxazolone **2** (5mmol) was dissolved in EtOH (50 mL) and $NaBH_4$ (380 mg, 10 mmol) was added. The mixture was heated under reflux for 15 min, then the solvent evaporated, water added (20 mL) and the residue extracted with CH_2Cl_2 (2 x 30 mL). The organic layer was dried, filtered and evaporated. The residue was crystallized from the indicated solvent (Table 2).

Oxazolo[4,5-*d*]isoxazole derivatives 4; General Procedure:
The compound **3** (5 mmol) was dissolved in CH_2Cl_2 (40 mL) and then trifluoroacetic acid (7 mL) was added. The mixture was heated at 40 °C for 5 min and then 30 min at room temperature. After evaporation of the solvent, water (40 mL) was added and the solution neutralized with $NaHCO_3$. The mixture was extracted with CH_2Cl_2 (2 x 30 mL), the organic layer dried, filtered and evaporated. The crystallization of the residue gave pure product **4** (Table 3).

3,4-Disubstituted Isoxazoles 5; General Procedure:
To a solution of compound **4** (5 mmol) in CH_2Cl_2 (20 mL), $Pb(OAc)_4$ (10 mmol) was added in small portions. At the end of gas evolution, the solvent was evaporated, water added (20 mL) and the mixture extracted with CH_2Cl_2 (2 x 30 mL). The organic layer was dried, filtered and evaporated and the residue purified by distillation (Table 4).

X-ray Diffraction Analysis of Oxazolo[4,5-*d*]Isoxazole 4d:
($C_{11}H_{11}N_3O_3$) (233.2), see Figure, Table 6-8. Triclinic, space group *P1*,

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Table 1. 3,4-Disubstituted 4-Di-*tert*-butyl Azodicarboxylate Isoxazol -5(4*H*)-ones **2** Prepared

Prod.	Yield (%)	Eluent	mp (°C) (solvent)[a]	Molecular Formula[b]
2a	75	CH_2Cl_2	173-175 (Et_2O-Hx)	$C_{21}H_{29}N_3O_6$ (419.3)
2b	65	CH_2Cl_2-Et_2O (20:1)	96-98 (Hx)	$C_{22}H_{31}N_3O_6$ (433.5)
2c	67	CH_2Cl_2-Et_2O (20:1)	112-114 (Et_2O-Hx)	$C_{20}H_{27}N_3O_6$ (405.4)
2d	92	CH_2Cl_2	64-66 (Hx)	$C_{20}H_{27}N_3O_6$ (405.4)
2e	86	Hx-Et_2O (3:1)	156-157 (Et_2O-Hx)	$C_{26}H_{31}N_3O_6$ (481.5)
2f	97	CH_2Cl_2	oil	$C_{27}H_{41}N_3O_6$ (503.6)
2g	86	CH_2Cl_2	100-102 (Et_2O)	$C_{21}H_{29}N_3O_6$ (419.5)

[a] Hx: hexane.

[b] Satisfactory microanalyses obtained: C ± 0.11, H ± 0.11, N ± 0.13

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Table 2. Oxazolo[4,5-d]isoxazole Derivatives **3** Prepared

Product	Yield (%)	mp (°C) (solvent)[a]	Molecular Formula[b]
3a	80	176-177 dec (CH_2Cl_2-Et_2O)	$C_{17}H_{21}N_3O_5$ (347.4)
3b	68	163-164 (Et_2O)	$C_{18}H_{23}N_3O_5$ (361.4)
3c	65	187-188 (CH_2Cl_2-Et_2O)	$C_{16}H_{19}N_3O_5$ (333.3)
3d	67	175 dec (Et_2O-Hx)	$C_{16}H_{19}N_3O_5$ (333.3)
3e	63	193-194 dec (CH_2Cl_2-Hx)	$C_{22}H_{23}N_3O_5$ (409.4)
3f	91	103-105 (Hx)[c]	$C_{23}H_{33}N_3O_5$ (431.5)
3g	77	167-168 (Et_2O-Hx)	$C_{17}H_{21}N_3O_5$ (347.4)

[a] Hx: hexane

[b] Satisfactory microanalyses obtained: C ± 0.12, H ± 0.1, N ± 0.1

[c] After column chromatography on SiO_2, eluent Hx/Et_2O (1:1).

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Table 3. Oxazolo[4,5-d]isoxazole Derivatives **4** Prepared

Compd.	Yield (%)	mp (solvent)[a]	Molecular Formula[b]
4a	87	155-156 (CH_2Cl_2 - Et_2O)	$C_{12}H_{13}N_3O_3$ (247.2)
4b	85	142-144 (CH_2Cl_2-Et_2O)	$C_{13}H_{15}N_3O_3$ (261.3)
4c	80	178-179 (CH_2Cl_2-Et_2O)	$C_{11}H_{11}N_3O_3$ (233.2)
4d	83	123-125 (CH_2Cl_2-Et_2O)	$C_{11}H_{11}N_3O_3$ (233.2)
4e	98	161-162 (Et_2O)	$C_{17}H_{15}N_3O_3$ (309.3)
4f	93	74-75 (Et_2O-Hx)	$C_{18}H_{25}N_3O_3$ (331.4)
4g	73	148-150 (Et_2O)	$C_{12}H_{13}N_3O_3$ (247.2)

[a] Hx: hexane.

[b] Satisfactory microanalyses obtained: C ± 0.13, H ± 0.11, N ± 0.10.

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Table 4. 3,4-Disubstituted Isoxazoles **5** Prepared

Product	Yield (%)	bp (°C)/mm	Molecular Formula or Lit. bp (°C)/torr
5a	95	85-90/2	81-82/0.2[13]
5b	98	90-93/2	$C_{12}H_{13}NO$ (187.2)
5c	96	65-70/2	259/717[5]
5d	94	70-75/2	268/717[5]
5e	95	135-140/2	$C_{16}H_{13}NO$ (235.3)
5f	92	125-130/2	$C_{17}H_{23}NO$ (257.4)
5g	98	75-80/2	155/13[14]

a = 10.090(3), b = 10.743(1), c = 12.074(1) Å, α = 95.56(1), β = 113.54(2)°, Z = 4, d_{calc}= 1.433 g.cm^{-3}. *Nonius-CAD4* diffractometer, graphite-monochromated Mo-kα radiation (λ = 0.71073 Å); ω/2ϑ scan collection, 0 < ϑ < 27.5°, 4940 reflections collected, of which 3969 with I > σ(I) were considered as observed. Data were corrected for Lorentz and polarization effects. Solution by direct methods (MULTAN[15] routine), scattering factors from *International Tables for X-ray Crystallography*[16], Vol. IV; refinement by full-matrix least-squares; 395 variables, N, O, C anisotropic, H isotropic, a scale factor. Final refinement values: R = 0.052, R_w = 0.044, S = 1.91, $\Delta\rho_{max}$ = 0.20eÅ^{-3}, $(\Delta/\sigma)_{max}$ < 0.1 in the last cycle. The two independent molecules are very much alike: in fact, the greatest differences between chemically equivalent bond distances and bond angles involving heavy atoms are 0.009 Å and 0.4°, respectively. The

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Table 5. Spectroscopic Data of Compounds **2-5.**

Product	IR (Nujol or film) $\nu(cm^{-1})$	^{1}H-NMR ($CDCl_3$) δ, J (Hz)
2a	3263, 1805, 1752, 1720	1.50 (s, 9H), 1.60 (s, 9H), 2.37 (s, 3H), 3.12 and 3.32 (AB, 2H, J=12.5), 6.70 (br s, 1H)[a], 7.10 (m, 2H), 7.26 (m, 3H)
2b	3261, 1795, 1748, 1711	1.48 (s, 9H), 1.53 (s, 9H), 2.10 (m, 2H), 2.27 (s, 3H), 2.42 (m, 2H), 6.43 (br s, 1H)[a], 7.25 (m, 5H)
2c	3270, 1799, 1741, 1709	1.40 (s, 9H), 1.50 (s, 9H), 2.45 (s, 3H), 6.34 (br s, 1H)[a], 7.43 (m, 5H)
2d	3340, 1817, 1748, 1719	(two rotamers, population 67:33) 1.31, 1.38 (s, 9H), 1.51, 1.53 (s, 9H), 1.77, 1.82 (s, 3H), 6.61 (br s, 1H)[a], 7.49 (m, 3H), 7.61 (m, 1H), 8.31 (m, 1H)
2e	3310, 3255, 1809, 1769, 1730, 1712	(two rotamers, population 60:40) 1.35, 1.40 (s, 9H), 1.60, 1.65 (s, 9H), 3.43 and 3.66 (AB, 2H, J=12.9), 6.53 (br s, 1H)[a], 6.85 (m, 2H), 7.19 (m, 3H), 7.55 (m, 3H), 7.71 (m, 1H), 8.33, (m, 1H)
2f	(CCl_4) 3380, 3310, 1800, 1745, 1720sh	(two rotamers, population 67:33) 0.83 (m, 3H), 1.15 (m, 12H), 1.31, 1.37 (s, 9H), 1.50, 1.54 (s, 9H), 2.12 (m, 2H), 6.57 (br s, 1H)[a], 7.49 (m, 3H), 7.61 (m, 1H), 8.28 (m, 1H)

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2g	3310, 1810, 1791, 1738, 1710	(two rotamers, population 60:40) 0.83, 0.91 (m, 3H), 1.32, 1.39 (s, 9H), 1.50, 1.54 (s, 9H), 2.15, 2.30 (m, 2H), 6.59 (br s, 1H)[a], 7.51 (m, 3H), 7.60 (m, 1H), 8.28 (m, 1H)
3a	3280, 1776, 1747	1.57 (s, 9H), 2.20 (s, 3H), 3.33 (m, 2H), 6.10 (s, 1H), 7.30 (m, 6H, 5H after D_2O)
3b	3262, 1775, 1742	1.40 (s, 9H), 2.04 (s, 3H), 2.25 (m, 2H), 2.57 (m, 2H), 6.02 (s, 1H), 7.27 (m, 6H, 5H after D_2O)
3c	3287, 1783, 1745	1.55 (s, 9H), 2.12 (s, 3H), 5.95 (s, 1H), 7.03 (br s, 1H)[a], 7.25 (m, 2H), 7.47 (m, 3H)
3d	3248, 1785, 1728	(two rotamers, population 67:33) 1.03, 1.49 (br s, 9H), 1.91 (s, 3H), 6.16 (br s, 1H), 6.76, 7.05 (br s, 1H)[a], 7.49 (m, 3H), 7.80 (m, 2H)
3e	3240, 1780, 1729	(two rotamers, population 67:33) 1.06, 1.47 (br s, 9H), 3.34-3.66 (m, 2H), 6.15, 6.27 (s, 1H),6.67, (br s, 1H)[a], 7.08 (m, 2H), 7.25 (m, 3H), 7.49 (m, 3H), 7.91-8.07 (m, 2H)
3f	3248, 1778, 1738	(two rotamers, population 67:33) 0.86 (m, 3H), 1.03 (br s, 3H), 1.28 (m, 12H), 1.48 (br s, 6H), 2.25 (m, 2H), 6.16 (s, 1H), 6.43 (br s, 1H)[a], 7.45 (m, 3H), 7.81 (m, 2H)
3g	3245, 1793, 1738	(two rotamers, population 75:25) 0.94 (m, 3H), 0.99, 1.45 (br s, 9H), 2.24 (m, 1H), 2.38 (m, 1H), 6.09, 6.15 (s, 1H), 6.39, 6.61 (br s, 1H)[a], 7.44 (m, 3H), 7.78-7.96 (m, 2H)

(continued)

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Table 5 Continued

4a	3340, 3290, 1777	2.21 (s, 3H), 3.02 and 3.46 (AB, 2H, *J*=14.0), 4.08 (br s, 2H)[a], 5.95 (s, 1H), 7.09 (m, 2H), 7.25 (m, 3H)
4b	3362, 3300, 1773	2.10 (s, 3H), 2.27 (m, 2H), 2.62 (m, 2H), 3.78 (br s, 2H)[a], 5.98 (s, 1H), 7.25 (m, 5H)
4c	3352, 3240, 1776	2.15 (s, 3H), 4.12 (br s, 2H)[a], 5.87 (s, 1H), 7.18 (m, 2H), 7.49 (m, 3H)
4d	3361, 3305, 1776	1.90 (s, 3H), 3.97 (s, 2H)[a], 6.06 (s, 1H), 7.48 (m, 3H), 8.08 (m, 2H)
4e	3358, 3230, 1773	3.35 and 3.71 (AB, 2H, *J*=14.6), 4.06 (s, 2H)[a], 6.13 (s, 1H), 7.09 (m, 2H), 7.31 (m, 3H), 7.48 (m, 3H), 8.17 (m, 2H)
4f	3361, 3300, 1785	0.85 (m, 3H), 1.30 (m, 12H), 2.25 (m, 2H), 4.67 (s, 2H)[a], 6.10 (s, 1H), 7.48 (m, 3H), 8.06 (m, 2H)
4g	3370, 3230, 1788	0.94 (t, 3H, *J*=7.5), 2.20 (m, 1H), 2.23 (m, 1H), 3.93 (s, 2H)[a], 6.08 (s, 1H), 7.42 (m, 3H), 8.03 (m, 2H)
5b	1609, 1600	2.18 (s, 3H), 2.67 (t, 2H, *J*=7.1), 2.87 (t, 3H, *J*=7.1), 7.15 (m, 2H), 7.29 (m, 3H), 7.98 (s, 1H)
5e	1600, 1571	3.92 (s, 2H), 7.15 (m,2H), 7.23 (m, 3H), 7.45 (m, 3H), 7.61 (m, 2H), 8.08 (s, 1H)
5f	1600, 1572	0.86 (t, 3H, *J*=7.0), 1.20-1.35 (m, 10H), 1.55 (m, 2H), 2.53 (t, 2H, *J*=7.6), 7.45 (m, 3H), 7.62 (m, 3H), 8.22 (s, 1H)

[a] Exchange with D_2O.

Table 6. Final Coordinates and Equivalent Thermal Parameters for Compound **4d.**

	x	y	z	U_{eq}
O1B	0.61959	0.17229	0.19138	0.0591(5)
O1A	-0.0566(1)	0.3450(1)	-0.1244(1)	0.0567(5)
O7A	-0.0552(1)	0.1295(1)	-0.1298(1)	0.0552(5)
O7B	0.7607(1)	0.3821(1)	0.3456(1)	0.0558(4)
O17A	0.0832(1)	0.0005(1)	-0.1022(1)	0.0617(5)
O17B	0.8531(1)	0.5036(1)	0.5440(1)	0.0649(5)
N2B	0.5480(2)	0.0609(1)	0.2362(1)	0.0520(5)
N2A	0.0999(2)	0.4542(1)	-0.0833(1)	0.0510(5)
N5B	0.8563(1)	0.2927(1)	0.4993(1)	0.0393(4)
N5A	0.1795(1)	0.2087(1)	0.0383(1)	0.0386(4)
N16A	0.3073(2)	0.1997(1)	0.1362(1)	0.0487(5)
N16B	0.9529(2)	0.2948(1)	0.6216(1)	0.0512(5)
C3B	0.6535(2)	0.0671(1)	0.3430(1)	0.0373(5)
C3A	0.1997(2)	0.4410(1)	0.0160(1)	0.0380(5)
C4B	0.8155(2)	0.1896(1)	0.3893(1)	0.0369(5)
C4A	0.1254(2)	0.3148(1)	0.0559(1)	0.0364(5)
C6B	0.8266(2)	0.4014(2)	0.4722(2)	0.0468(6)
C6A	0.0738(2)	0.1037(2)	-0.0662(1)	0.0451(5)
C8A	-0.0435(2)	0.2486(2)	-0.0554(1)	0.0474(6)
C8B	0.7694(2)	0.2635(2)	0.2879(1)	0.0477(6)
C9B	0.6131(2)	-0.0406(1)	0.4056(1)	0.0361(5)
C9A	0.3672(2)	0.5455(1)	0.0808(1)	0.0389(5)
C10B	0.4654(2)	-0.1550(2)	0.3444(1)	0.0458(6)
C10A	0.4125(2)	0.6655(2)	0.0427(1)	0.0497(6)
C11B	0.4293(2)	-0.2587(2)	0.3999(2)	0.0536(6)
C11A	0.5671(2)	0.7644(2)	0.1036(2)	0.0575(6)
C12B	0.5382(2)	-0.2512(2)	0.5178(2)	0.0561(6)
C12A	0.6805(2)	0.7468(2)	0.2038(2)	0.0581(7)
C13B	0.6842(2)	-0.1385(2)	0.5791(1)	0.0527(6)
C13A	0.6378(2)	0.6303(2)	0.2432(2)	0.0582(7)

(continued)

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Table 6 Continued

C14A	0.4822(2)	0.5294(2)	0.1816(2)	0.0475(6)
C14B	0.7214(2)	-0.0341(2)	0.5241(1)	0.0436(6)
C15A	0.1301(2)	0.3481(2)	0.1824(1)	0.0422(5)
C15B	0.9491(2)	0.1498(2)	0.3990(1)	0.0453(5)
H8A	-0.136(2)	0.219(1)	-0.035(1)	0.045(4)*
H8B	0.843(2)	0.298(1)	0.254(1)	0.048(4)*
H10A	0.336(2)	0.674(2)	-0.023(1)	0.060(5)*
H11A	0.594(2)	0.846(2)	0.074(1)	0.062(5)*
H12A	0.789(2)	0.812(2)	0.247(2)	0.070(6)*
H13A	0.717(2)	0.620(2)	0.316(2)	0.076(6)*
H14A	0.455(2)	0.447(2)	0.207(1)	0.052(5)*
H10B	0.395(2)	-0.157(1)	0.265(1)	0.049(5)*
H11B	0.329(2)	-0.338(2)	0.354(1)	0.060(5)*
H12B	0.514(2)	-0.321(2)	0.557(1)	0.061(5)*
H13B	0.760(2)	-0.133(2)	0.660(1)	0.064(5)*
H14B	0.822(2)	0.044(1)	0.569(1)	0.044(4)*
H151A	0.070(2)	0.266(2)	0.198(1)	0.055(5)*
H152A	0.238(2)	0.388(1)	0.250(1)	0.052(5)*
H153A	0.084(2)	0.410(1)	0.183(1)	0.050(5)*
H151B	1.043(2)	0.231(1)	0.419(1)	0.050(5)*
H152B	0.970(2)	0.100(1)	0.462(1)	0.051(5)*
H153B	0.919(2)	0.090(2)	0.316(2)	0.070(6)*
H161A	0.386(2)	0.212(2)	0.112(2)	0.086(7)*
H162A	0.268(2)	0.116(2)	0.149(1)	0.062(5)*
H161B	0.895(2)	0.283(2)	0.660(2)	0.073(6)*
H162B	1.042(2)	0.381(2)	0.659(2)	0.073(6)*

$$U_{eq} = [a^{*2}\beta_{11} + \ldots 2b^{*}c^{*}\cos(\alpha^{*})\beta_{23}]/(6\pi^2)$$

Starred atoms were refined isotropically.

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Table 7. Selected Bond Distances (Å) and Bond Angles for Compound **4d.**

Bond distances (Å)

		molecule **A**	molecule **B**
O1	N2	1.442(1)	1.441(1)
O1	C8	1.400(2)	1.393(1)
O7	C6	1.363(2)	1.362(2)
O7	C8	1.430(2)	1.439(2)
O17	C6	1.200(2)	1.206(2)
N2	C3	1.282(1)	1.281(1)
N5	N16	1.402(1)	1.402(1)
N5	C4	1.457(2)	1.456(1)
N5	C6	1.345(1)	1.342(2)
C3	C4	1.528(1)	1.529(2)
C3	C9	1.475(2)	1.470(1)
C4	C8	1.535(1)	1.530(2)
C4	C15	1.513(2)	1.517(3)
C9	C10	1.397(2)	1.393(2)
C9	C14	1.384(2)	1.389(1)
C10	C11	1.369(2)	1.370(3)
C11	C12	1.379(2)	1.382(2)
C12	C13	1.371(3)	1.375(2)
C13	C14	1.383(2)	1.374(2)

Bond angles (°)

N2	O1	C8	109.3(1)	109.1(1)
C6	O7	C8	109.7(1)	109.3(2)
O1	N2	C3	109.0(1)	109.0(1)
C4	N5	C6	113.5(1)	113.5(1)
N16	N5	C6	122.6(2)	122.4(1)
N16	N5	C4	121.8(1)	122.2(1)
N2	C3	C9	119.4(1)	119.7(1)
N2	C3	C4	113.7(1)	113.3(1)
C4	C3	C9	126.9(1)	126.9(1)
N5	C4	C3	112.5(2)	112.8(1)
C3	C4	C15	114.6(1)	114.5(1)
C3	C4	C8	99.3(1)	99.2(1)
N5	C4	C15	114.3(1)	114.5(1)
N5	C4	C8	100.2(1)	100.3(1)
C8	C4	C15	114.1(2)	113.8(1)
O17	C6	N5	128.3(2)	128.1(2)
O7	C6	N5	109.2(2)	109.3(2)
O7	C6	O17	122.5(1)	122.5(2)
O7	C8	C4	106.5(2)	106.2(1)
O1	C8	C4	107.2(2)	107.3(1)
O1	C8	O7	109.8(1)	110.2(2)
C3	C9	C14	121.5(2)	121.5(1)
C3	C9	C10	120.2(1)	120.1(1)
C10	C9	C14	118.4(2)	118.3(1)
C9	C10	C11	120.7(2)	120.5(2)
C10	C11	C12	120.3(2)	120.7(2)
C11	C12	C13	119.8(2)	119.3(2)
C12	C13	C14	120.3(2)	120.4(2)
C9	C14	C13	120.6(2)	120.8(1)

Table 8. Anisotropic Thermal Parameters in the form:

$$T = \exp(-2\pi^2(U_{11}a^{*2}h^2 + \ldots\ldots 2U_{23}b^{*}c^{*}hk))$$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1B)	0.0648(6)	0.0699(6)	0.0430(5)	0.0330(4)	0.0182(4)	0.0309(4)
O(1A)	0.0436(5)	0.0715(6)	0.0402(5)	0.0256(4)	0.0051(4)	0.0144(5)
O(7A)	0.0464(5)	0.0530(6)	0.0383(5)	0.0072(5)	0.0091(4)	-0.0007(5)
O(7B)	0.0673(5)	0.0526(5)	0.0679(5)	0.0370(3)	0.0361(4)	0.0348(4)
O(17A)	0.0807(6)	0.0369(5)	0.0603(5)	0.0133(5)	0.0386(4)	0.0025(5)
O(17B)	0.0700(5)	0.0371(5)	0.0933(7)	0.0209(4)	0.0462(4)	0.0110(5)
N(2B)	0.0523(6)	0.0568(7)	0.0430(6)	0.0266(5)	0.0145(5)	0.0189(5)
N(2A)	0.0529(6)	0.0575(7)	0.0397(6)	0.0267(5)	0.0152(5)	0.0169(5)
N(5B)	0.0434(5)	0.0375(5)	0.0401(5)	0.0187(4)	0.0204(4)	0.0129(4)
N(5A)	0.0378(5)	0.0366(5)	0.0349(5)	0.0131(4)	0.0142(4)	0.0057(5)
N(16A)	0.0500(5)	0.0445(6)	0.0502(6)	0.0236(4)	0.0179(5)	0.0171(5)
N(16B)	0.0479(6)	0.0505(7)	0.0389(6)	0.0149(5)	0.0116(5)	0.0072(5)
C(3B)	0.0366(5)	0.0429(6)	0.0333(6)	0.0209(4)	0.0133(4)	0.0110(5)
C(3A)	0.0456(5)	0.0443(6)	0.0297(5)	0.0244(5)	0.0175(4)	0.0126(5)
C(4B)	0.0382(5)	0.0431(6)	0.0358(6)	0.0202(5)	0.0193(4)	0.0165(5)
C(4A)	0.0326(5)	0.0422(7)	0.0307(6)	0.0150(5)	0.0126(4)	0.0082(5)
C(6B)	0.0432(6)	0.0408(7)	0.0661(7)	0.0178(5)	0.0328(5)	0.0215(6)
C(6A)	0.0501(6)	0.0380(7)	0.0404(6)	0.0072(6)	0.0255(5)	0.0077(6)
C(8A)	0.0359(6)	0.0603(9)	0.0353(6)	0.0152(6)	0.0124(5)	0.0081(7)
C(8B)	0.0528(6)	0.0577(7)	0.0470(6)	0.0298(5)	0.0280(5)	0.0278(6)
C(9B)	0.0347(5)	0.0388(6)	0.0358(6)	0.0168(4)	0.0167(4)	0.0089(5)
C(9A)	0.0458(6)	0.0388(6)	0.0378(6)	0.0201(5)	0.0227(4)	0.0114(5)
C(10B)	0.0361(6)	0.0511(8)	0.0407(7)	0.0146(5)	0.0142(5)	0.0055(6)
C(10A)	0.0632(7)	0.0498(8)	0.0442(6)	0.0251(6)	0.0297(5)	0.0206(6)
C(11B)	0.0442(6)	0.0437(8)	0.0651(8)	0.0077(6)	0.0296(5)	0.0066(7)
C(11A)	0.0770(8)	0.0405(8)	0.0645(7)	0.0169(6)	0.0476(5)	0.0186(6)
C(12B)	0.0612(7)	0.0479(8)	0.0726(8)	0.0224(6)	0.0414(5)	0.0283(7)
C(12A)	0.0507(7)	0.0462(9)	0.0698(9)	0.0097(6)	0.0326(6)	0.0065(8)
C(13B)	0.0539(7)	0.0575(8)	0.0488(7)	0.0241(6)	0.0230(6)	0.0251(6)
C(13A)	0.0431(7)	0.0477(8)	0.070(1)	0.0156(6)	0.0173(7)	0.0120(8)
C(14A)	0.0427(6)	0.0376(7)	0.0553(7)	0.0157(5)	0.0168(6)	0.0167(6)
C(14B)	0.0385(6)	0.0422(7)	0.0406(6)	0.0124(5)	0.0136(5)	0.0122(6)
C(15A)	0.0479(6)	0.0469(7)	0.0339(6)	0.0220(5)	0.0195(5)	0.0109(5)
C(15B)	0.0462(6)	0.0484(7)	0.0527(7)	0.0262(5)	0.0272(5)	0.0183(6)

group O1, N2, C3, C4 and C4, N5, C6, C7 are both planar within 0.01 Å and both the five-membered ring have envelope conformation. The double bond between N2 and C3 is conjugated with the phenyl ring. The molecule A and B are linked together by strong hydrogen bonds between the amino nitrogen N16 and the ring oxygen O1: they form an infinite chain ...A...B...A'...B'... (were ' means 1+x, y, 1+z). This chain interact

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troughout inversion centers by mean of weaker hydrogen bonds between O17 and the methyl group and by coupling phenyl group.

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