Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

5-Methoxy-2-methyl-4-nitro-1-phenyl-1*H*-imidazole

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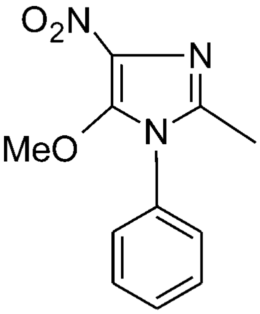
Received 11 May 2007; accepted 18 July 2007

Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.003 Å; R factor = 0.034; wR factor = 0.058; data-to-parameter ratio = 9.0.

The title compound, $C_{11}H_{11}N_3O_3$, contains two planar fragments, *viz*. the imidazole and phenyl rings. These rings are significantly twisted with respect one to another, with a dihedral angle of 63.99 (8)°. The nitro group is almost coplanar with the imidazole plane, while the methoxy group is almost perpendicular to it [the C—C—O—C torsion angle is 65.1 (4)°]. In spite of this, there is a short C(methoxy)—H⋯O(nitro) contact that might be regarded as an intramolecular hydrogen bond. Weak intermolecular C—H⋯N(imidazole) and C—H⋯O(nitro) hydrogen bonds create quite a complicated network that consists of stacks of imidazole rings strengthened by these hydrogen bonds. The significant twist between the planar fragments is a necessary condition for creating such a packing, which has also been observed in some other 1-aryl-4-nitroimidazole derivatives.

Related literature

The present work is a part of our study of intermolecular interactions in 4-nitroimidazole derivatives, which started with 1-phenyl-4-nitroimidazole (Kubicki *et al.*, 2001, 2002). A similar packing of 1-aryl-4-nitroimidazoles was described in detail by Kubicki (2004). For related literature, see: Smithen & Hardy (1982).



Experimental

Crystal data

$C_{11}H_{11}N_3O_3$
M_r = 233.23
Orthorhombic, $P2_12_12_1$
a = 6.6179 (4) Å
b = 7.4711 (5) Å
c = 23.1087 (15) Å
V = 1142.56 (13) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 100 (1) K
0.2 × 0.2 × 0.05 mm

Data collection

Kuma KM4 CCD four-circle diffractometer
Absorption correction: multi-scan (*SORTAV*; Blessing, 1989) T_{min} = 0.989, T_{max} = 0.989
7520 measured reflections
1739 independent reflections
1210 reflections with $I > 2\sigma(I)$
R_{int} = 0.045

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.058
S = 1.00
1739 reflections
194 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C51—H51A⋯O42	1.01 (2)	2.36 (2)	3.081 (3)	127.2 (18)
C12—H12⋯O41^{i}	0.93 (2)	2.567 (19)	3.343 (3)	141.6 (15)
C16—H16⋯O41^{ii}	0.93 (2)	2.69 (2)	3.363 (3)	129.5 (15)
C21—H21A⋯O5^{iii}	0.94 (2)	2.84 (2)	3.626 (3)	141.2 (18)
C51—H51B⋯N3^{iv}	0.98 (2)	2.54 (2)	3.510 (3)	168.8 (19)

Symmetry codes: (i) $x-\frac{1}{2}, -y+\frac{1}{2}, -z$; (ii) $x+\frac{1}{2}, -y+\frac{1}{2}, -z$; (iii) $x, y-1, z$; (iv) $x, y+1, z$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2002); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Stereochemical Workstation Operation Manual* (Siemens, 1989); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: KJ2062).

References

Blessing, R. H. (1989). *J. Appl. Cryst.* **22**, 396–397.
Kubicki, M. (2004). *J. Mol. Struct.* **696**, 67–73.
Kubicki, M., Borowiak, T., Dutkiewicz, G., Souhassou, M., Jelsch, C. & Lecomte, C. (2002). *J. Phys. Chem. B*, **106**, 3706–3714.
Kubicki, M., Borowiak, T., Suwiński, J. & Wagner, P. (2001). *Acta Cryst.* C**57**, 106–108.
Oxford Diffraction (2002). *CrysAlis CCD* (Version 1.69) and *CrysAlis RED* (Version 1.69). Oxford Diffraction, Wrocław, Poland.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Siemens (1989). *Stereochemical Workstation Operation Manual.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Smithen, C. E. & Hardy, C. R. (1982). *Advanced Topics on Radiosensitizers of Hypoxic Cells*, edited by A. Breccia, C. Rimondi & G. E. Adams, pp. 1–47. New York: Plenum Press.

doi:10.1107/S1600536807035301

supplementary materials

Acta Cryst. (2007). E**63**, o3587 [**doi:10.1107/S1600536807035301**]

5-Methoxy-2-methyl-4-nitro-1-phenyl-1*H*-imidazole

P. Wagner and **M. Kubicki**

Comment

Nitroimidazoles have been intensively investigated as radiosensitizers of hypoxic tumor cells and as veterinary drugs (Smithen & Hardy, 1982). For some time we have studied weak intermolecular interactions in 4-nitroimidazole derivatives (*e.g.* Kubicki *et al.*, 2001, 2002).

Similar packing by means of weak C—H···N and C—H···O hydrogen bonds was observed in the crystal structures of (1–4'-methylphenyl)- and (1–4'-methoxyphenyl)-4-nitro-5-methylimidazole (Kubicki, 2004). Interestingly, both these compounds have similar packing modes in spite of crystallizing in different space groups, the former one in the non-centrosymmetric Pna2_1, and the latter in centrosymmetric $P2_1/c$. The title compound is a third example, in still another space group ($P2_12_12_1$). All three compounds have also similar unit-cell parameters a, b and c. A comparison of the unit-cell parameters of the title compound determined at 100 K with those determined at room temperature [6.800 (1), 7.527 (1), 23.103 (2)] shows that the compression perpendicular to the imidazole ring planes (*i.e.* along stack axis, a) is the strongest. That might be related to the lack of π-π interactions in this case, the imidazole planes are parallel but shifted.

Experimental

1.2 g of Sodium was dissolved in 50 ml of dry methanol. To the resulting warm solution, 0.52 g (2 mmol) of 5-bromo-2-methyl-4-nitro-1-phenylimidazole was added and the reaction mixture was stirred at room temperature for 24 h. Afterwards the mixture was neutralized by concentrated HCl to pH 7 and the excess of methanol was removed under vacuum. The residue was treated by 20 ml of water and the organic solid was filtered off, dried then recrystallized from hot methanol to give 0.25 g (54%) of the product.

Refinement

Friedel pairs were merged by *SORTAV* (Blessing, 1989). Hydrogen atoms were freely refined, for hydrogen atoms of each methyl group one common isotropic displacement parameter was used.

Figures

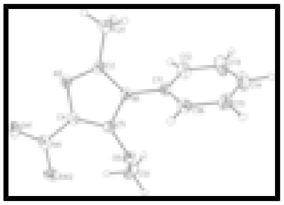


Fig. 1. Anisotropic displacement ellipsoid representation (at the 50% probability level) of the title compound (Siemens, 1989), together with numbering scheme. The hydrogen atoms are drawn as spheres with arbitrary radii.

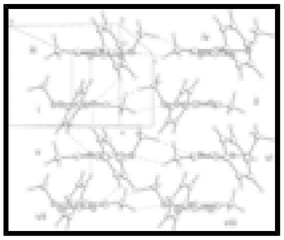


Fig. 2. View of the stacking of molecules with weak hydrogen bonds depicted as dashed lines. The view is approximately along direction [103] and the stacking is parallel to (100). The symmetry codes: (i) x,y,z, (ii): $x,-1+y,z$, (iii) $-1/2+x,1/2-y,-z$, (iv) $-1/2+x,-1/2-y,-z$, (v) $1/2+x,1/2-y,-z$, (vi) $1/2+x,-1/2-y,-z$, (vii) $1+x,y,z$, (viii) $1+x,-1+y,z$.

5-Methoxy-2-methyl-4-nitro-1-phenyl-1*H*-imidazole

Crystal data

$C_{11}H_{11}N_3O_3$
$M_r = 233.23$
Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab
$a = 6.6179$ (4) Å
$b = 7.4711$ (5) Å
$c = 23.1087$ (15) Å
$V = 1142.56$ (13) Å^3
$Z = 4$

$F_{000} = 488$
$D_x = 1.356$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 4053 reflections
$\theta = 3\text{–}20°$
$\mu = 0.10$ mm^{-1}
$T = 100$ (1) K
Block, colourless
0.2 × 0.2 × 0.05 mm

Data collection

Kuma KM4 CCD four-circle diffractometer
Radiation source: fine-focus sealed tube
Monochromator: graphite
$T = 100(1)$ K
ω scans
Absorption correction: multi-scan (SORTAV; Blessing, 1989)
$T_{\min} = 0.989$, $T_{\max} = 0.989$
7520 measured reflections

1739 independent reflections
1210 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.045$
$\theta_{\max} = 29.3°$
$\theta_{\min} = 3.2°$
$h = -8 \rightarrow 8$
$k = -9 \rightarrow 9$
$l = -26 \rightarrow 30$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.058$
$S = 1.00$
1739 reflections
194 parameters

Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.019P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.15$ e Å^{-3}
$\Delta\rho_{\min} = -0.24$ e Å^{-3}

Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.7905 (3)	0.35064 (19)	0.09665 (6)	0.0177 (3)
C11	0.7920 (3)	0.4361 (2)	0.15235 (8)	0.0204 (4)
C12	0.6282 (4)	0.4126 (3)	0.18903 (9)	0.0305 (6)
H12	0.522 (3)	0.343 (2)	0.1755 (8)	0.025 (6)*
C13	0.6299 (4)	0.4964 (4)	0.24273 (10)	0.0394 (6)
H13	0.509 (4)	0.471 (3)	0.2681 (9)	0.056 (8)*
C14	0.7895 (4)	0.6040 (3)	0.25869 (9)	0.0347 (6)
H14	0.788 (3)	0.660 (3)	0.2980 (9)	0.039 (6)*
C15	0.9515 (4)	0.6282 (3)	0.22155 (9)	0.0298 (5)
H15	1.071 (3)	0.715 (3)	0.2320 (8)	0.039 (6)*
C16	0.9536 (4)	0.5429 (3)	0.16797 (9)	0.0242 (5)
H16	1.063 (3)	0.558 (2)	0.1431 (9)	0.031 (6)*
C2	0.7919 (3)	0.1686 (2)	0.08417 (7)	0.0193 (4)
C21	0.7984 (4)	0.0271 (3)	0.12882 (9)	0.0279 (5)
H21A	0.859 (4)	−0.080 (3)	0.1163 (10)	0.053 (5)*
H21B	0.662 (3)	0.001 (3)	0.1402 (10)	0.053 (5)*
H21C	0.862 (3)	0.059 (3)	0.1615 (10)	0.053 (5)*
N3	0.7887 (3)	0.14035 (18)	0.02801 (6)	0.0190 (4)
C4	0.7847 (3)	0.3083 (2)	0.00357 (8)	0.0179 (4)
N4	0.7881 (3)	0.3282 (2)	−0.05751 (6)	0.0230 (4)
O41	0.7858 (2)	0.19203 (18)	−0.08821 (5)	0.0314 (4)
O42	0.7943 (2)	0.48142 (18)	−0.07788 (5)	0.0288 (4)
C5	0.7861 (3)	0.4404 (2)	0.04442 (8)	0.0184 (4)
O5	0.7854 (2)	0.61860 (15)	0.04423 (5)	0.0209 (3)
C51	0.6031 (4)	0.7009 (3)	0.02080 (12)	0.0300 (6)
H51A	0.572 (4)	0.647 (3)	−0.0184 (10)	0.054 (4)*
H51B	0.635 (3)	0.829 (3)	0.0222 (9)	0.054 (4)*
H51C	0.502 (4)	0.678 (3)	0.0476 (10)	0.054 (4)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0194 (8)	0.0163 (8)	0.0173 (8)	−0.0006 (8)	0.0005 (8)	−0.0010 (7)
C11	0.0250 (11)	0.0194 (10)	0.0169 (9)	0.0053 (9)	−0.0023 (11)	−0.0022 (8)
C12	0.0266 (13)	0.0399 (15)	0.0250 (13)	−0.0019 (11)	0.0009 (11)	−0.0061 (11)
C13	0.0331 (14)	0.0573 (17)	0.0277 (13)	0.0048 (14)	0.0067 (11)	−0.0091 (13)
C14	0.0422 (14)	0.0404 (14)	0.0215 (11)	0.0139 (13)	−0.0065 (13)	−0.0107 (10)
C15	0.0379 (14)	0.0237 (12)	0.0277 (12)	0.0033 (12)	−0.0102 (11)	−0.0056 (10)
C16	0.0267 (13)	0.0232 (12)	0.0227 (11)	−0.0018 (10)	−0.0012 (10)	0.0002 (10)
C2	0.0179 (10)	0.0177 (10)	0.0224 (10)	−0.0003 (9)	0.0001 (10)	−0.0015 (8)
C21	0.0374 (14)	0.0232 (12)	0.0231 (11)	−0.0020 (13)	−0.0004 (12)	0.0022 (9)
N3	0.0177 (8)	0.0186 (8)	0.0205 (8)	0.0025 (8)	0.0005 (8)	−0.0007 (7)
C4	0.0156 (10)	0.0221 (10)	0.0162 (9)	−0.0001 (10)	−0.0002 (9)	0.0003 (8)
N4	0.0183 (9)	0.0307 (11)	0.0199 (9)	−0.0010 (9)	−0.0008 (8)	−0.0015 (8)
O41	0.0408 (9)	0.0326 (8)	0.0208 (7)	−0.0001 (8)	0.0004 (8)	−0.0093 (6)
O42	0.0333 (9)	0.0294 (8)	0.0237 (7)	−0.0015 (9)	−0.0024 (7)	0.0078 (6)
C5	0.0156 (10)	0.0187 (10)	0.0210 (10)	−0.0019 (9)	0.0004 (10)	0.0017 (8)
O5	0.0240 (7)	0.0145 (7)	0.0244 (7)	−0.0006 (7)	−0.0045 (7)	0.0013 (5)
C51	0.0241 (13)	0.0229 (12)	0.0430 (15)	0.0035 (10)	−0.0059 (11)	−0.0010 (12)

Geometric parameters (Å, °)

N1—C5	1.381 (2)	C2—C21	1.478 (3)
N1—C2	1.390 (2)	C21—H21A	0.94 (2)
N1—C11	1.437 (2)	C21—H21B	0.96 (2)
C11—C16	1.382 (3)	C21—H21C	0.90 (2)
C11—C12	1.388 (3)	N3—C4	1.376 (2)
C12—C13	1.390 (3)	C4—C5	1.366 (2)
C12—H12	0.93 (2)	C4—N4	1.419 (2)
C13—C14	1.378 (4)	N4—O42	1.2384 (18)
C13—H13	1.01 (2)	N4—O41	1.2404 (18)
C14—C15	1.385 (3)	C5—O5	1.332 (2)
C14—H14	1.00 (2)	O5—C51	1.458 (2)
C15—C16	1.392 (3)	C51—H51A	1.01 (2)
C15—H15	1.05 (2)	C51—H51B	0.98 (2)
C16—H16	0.93 (2)	C51—H51C	0.93 (2)
C2—N3	1.315 (2)		
C5—N1—C2	107.08 (14)	C2—C21—H21A	113.9 (14)
C5—N1—C11	124.57 (13)	C2—C21—H21B	107.9 (14)
C2—N1—C11	128.35 (14)	H21A—C21—H21B	108 (2)
C16—C11—C12	121.21 (18)	C2—C21—H21C	114.3 (15)
C16—C11—N1	119.74 (19)	H21A—C21—H21C	106 (2)
C12—C11—N1	119.04 (19)	H21B—C21—H21C	105 (2)
C11—C12—C13	118.8 (2)	C2—N3—C4	105.01 (15)
C11—C12—H12	117.1 (12)	C5—C4—N3	112.03 (15)
C13—C12—H12	124.1 (12)	C5—C4—N4	127.70 (16)

C14—C13—C12	120.5 (2)	N3—C4—N4	120.21 (16)
C14—C13—H13	124.2 (13)	O42—N4—O41	122.75 (14)
C12—C13—H13	115.2 (13)	O42—N4—C4	118.39 (15)
C13—C14—C15	120.2 (2)	O41—N4—C4	118.86 (16)
C13—C14—H14	118.7 (13)	O5—C5—C4	136.08 (17)
C15—C14—H14	121.1 (13)	O5—C5—N1	119.24 (15)
C14—C15—C16	119.9 (2)	C4—C5—N1	104.68 (14)
C14—C15—H15	121.3 (11)	C5—O5—C51	115.18 (17)
C16—C15—H15	118.7 (11)	O5—C51—H51A	109.3 (14)
C11—C16—C15	119.2 (2)	O5—C51—H51B	102.7 (14)
C11—C16—H16	120.5 (12)	H51A—C51—H51B	117.3 (19)
C15—C16—H16	120.2 (13)	O5—C51—H51C	105.8 (15)
N3—C2—N1	111.20 (15)	H51A—C51—H51C	112.2 (19)
N3—C2—C21	125.09 (16)	H51B—C51—H51C	108.4 (19)
N1—C2—C21	123.71 (16)		

C5—N1—C11—C16	−63.6 (3)	C21—C2—N3—C4	−179.5 (2)
C2—N1—C11—C16	116.7 (2)	C2—N3—C4—C5	0.2 (3)
C5—N1—C11—C12	114.9 (2)	C2—N3—C4—N4	177.62 (19)
C2—N1—C11—C12	−64.7 (3)	C5—C4—N4—O42	0.4 (4)
C16—C11—C12—C13	−1.1 (3)	N3—C4—N4—O42	−176.55 (18)
N1—C11—C12—C13	−179.62 (19)	C5—C4—N4—O41	−179.9 (2)
C11—C12—C13—C14	1.4 (4)	N3—C4—N4—O41	3.1 (3)
C12—C13—C14—C15	−0.7 (4)	N3—C4—C5—O5	179.4 (2)
C13—C14—C15—C16	−0.3 (3)	N4—C4—C5—O5	2.2 (5)
C12—C11—C16—C15	0.1 (3)	N3—C4—C5—N1	−0.2 (3)
N1—C11—C16—C15	178.63 (17)	N4—C4—C5—N1	−177.4 (2)
C14—C15—C16—C11	0.6 (3)	C2—N1—C5—O5	−179.5 (2)
C5—N1—C2—N3	0.0 (2)	C11—N1—C5—O5	0.8 (3)
C11—N1—C2—N3	179.7 (2)	C2—N1—C5—C4	0.1 (2)
C5—N1—C2—C21	179.4 (2)	C11—N1—C5—C4	−179.6 (2)
C11—N1—C2—C21	−0.9 (4)	C4—C5—O5—C51	65.1 (4)
N1—C2—N3—C4	−0.1 (2)	N1—C5—O5—C51	−115.4 (2)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C51—H51A···O42	1.01 (2)	2.36 (2)	3.081 (3)	127.2 (18)
C12—H12···O41$^{\rm i}$	0.93 (2)	2.567 (19)	3.343 (3)	141.6 (15)
C16—H16···O41$^{\rm ii}$	0.93 (2)	2.69 (2)	3.363 (3)	129.5 (15)
C21—H21A···O5$^{\rm iii}$	0.94 (2)	2.84 (2)	3.626 (3)	141.2 (18)
C51—H51B···N3$^{\rm iv}$	0.98 (2)	2.54 (2)	3.510 (3)	168.8 (19)

Symmetry codes: (i) $x-1/2, -y+1/2, -z$; (ii) $x+1/2, -y+1/2, -z$; (iii) $x, y-1, z$; (iv) $x, y+1, z$.

Fig. 1

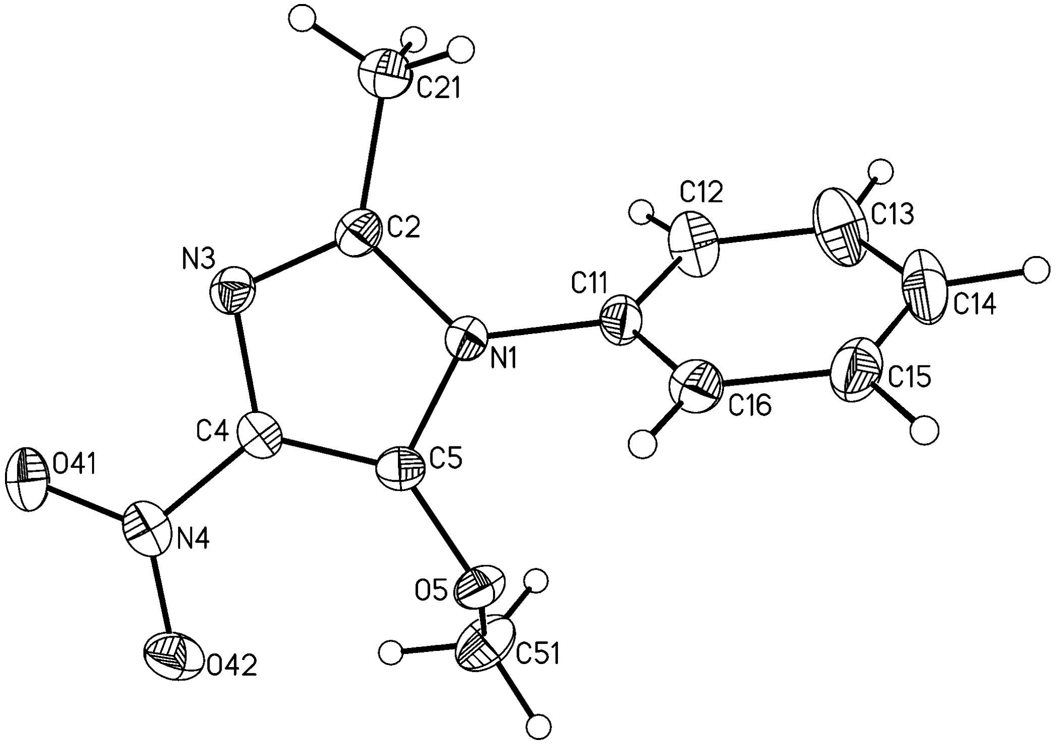


Fig. 2