

# Bis(1-methyl-1*H*-tetrazol-5-yl)diazene and two its copper(I) chloride complexes poly[[ $\mu$ -1,2-bis(1-methyl-1*H*-tetrazol-5-yl)diazene- $\kappa^4 N', N^4: N, N^4'$ ]-dicopper(I)]-di- $\mu$ -chloro] and *catena*-poly[[chlorocopper(I)]- $\mu$ -1,2-bis(1-methyl-1*H*-tetrazol-5-yl)diazene- $\kappa^4 N', N^4: N, N^4'$ ]

Alexander S. Lyakhov, Tatiyana V. Serebryanskaya,  
Pavel N. Gaponik, Sergei V. Voitekhovich and Ludmila S. Ivashkevich\*

Physico-Chemical Research Institute, Belarusian State University, Leningradskaya  
Str. 14, Minsk 220050, Belarus  
Correspondence e-mail: lyakhov@bsu.by

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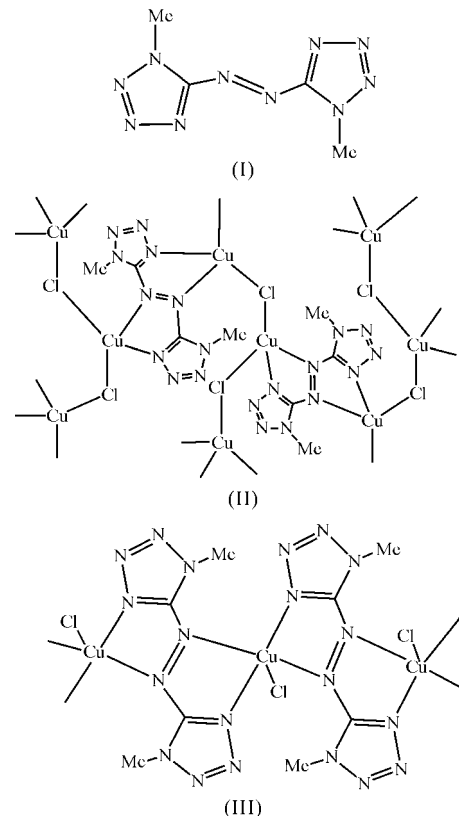
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While bis(1-methyl-1*H*-tetrazol-5-yl)diazene, C<sub>4</sub>H<sub>6</sub>N<sub>10</sub>, (I), has no crystallographically imposed symmetry, in the two title chlorocopper(I) complexes, [Cu<sub>2</sub>Cl<sub>2</sub>(C<sub>4</sub>H<sub>6</sub>N<sub>10</sub>)]<sub>n</sub>, (II), and [CuCl(C<sub>4</sub>H<sub>6</sub>N<sub>10</sub>)]<sub>n</sub>, (III), the organic ligands lie across centres of inversion; in (III), the Cu and Cl atoms additionally lie about a twofold rotation axis in the space group *P2*/*c*. Complex (II) forms a two-dimensional coordination polymer containing tetrahedrally coordinated Cu<sup>I</sup> atoms, and complex (III) forms a one-dimensional coordination polymer containing five-coordinate square-pyramidal Cu<sup>I</sup> atoms.

## Comment

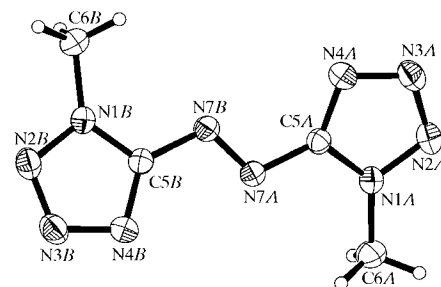
*N*-Substituted bis-tetrazoles are of considerable interest for coordination and supramolecular chemistry owing to their attractiveness as chelating agents and as initial compounds for synthesis of one-, two- and three-dimensional coordination polymers (Voitekhovich *et al.*, 2002; Ivashkevich *et al.*, 2003; Grunert *et al.*, 2004; Bronisz, 2004; Lyakhov *et al.*, 2004). Recently, we investigated the molecular and crystal structures of the coordination compounds of bis-tetrazoles in which two *N*-substituted tetrazole rings are connected *via* their C atoms by –CH<sub>2</sub>–CH<sub>2</sub>– (Ivashkevich *et al.*, 2003), –CH<sub>2</sub>–CH<sub>2</sub>–O–CH<sub>2</sub>–CH<sub>2</sub>– (Voitekhovich *et al.*, 2002) and –N=N–NH– (Lyakhov *et al.*, 2004) bridges. Compounds with a –CH(CN)– bridge were also investigated (Saalfrank *et al.*, 1995). Complexes of *N*-substituted bis-tetrazoles with a diazene bridge, –N=N–, have not been described, although these ligands are attractive because of the possible participation of

bridging N atoms in metal coordination. To date, only one bistetrazole, *viz.* bis(2-methyl-1*H*-tetrazol-5-yl)diazene, and a series of salts of the anionic form of bis(tetrazol-5-yl)diazene with alkali, alkaline earth and several trivalent metal cations have been synthesized and structurally characterized (Hammerl *et al.*, 2002).



We report here both a new synthesis and the structure of a bis-tetrazole containing a diazene bridge, namely bis(1-methyl-1*H*-tetrazol-5-yl)diazene, (I), and two related copper(I)–chloro complexes, Cu<sub>2</sub>Cl<sub>2</sub>L, namely poly[[ $\mu$ -1,2-bis(1-methyl-1*H*-tetrazol-5-yl)diazene]dicopper(I)]-di- $\mu$ -chloro], (II), and CuClL, namely *catena*-poly[[chlorocopper(I)]- $\mu$ -1,2-bis(1-methyl-1*H*-tetrazol-5-yl)diazene]], (III).

The present investigation showed that compound (I) did not form any complexes with copper(II) chloride under the usual conditions for the preparation of *N*-substituted bis-tetrazoles (Voitekhovich *et al.*, 2002; Ivashkevich *et al.*, 2003; Grunert *et*

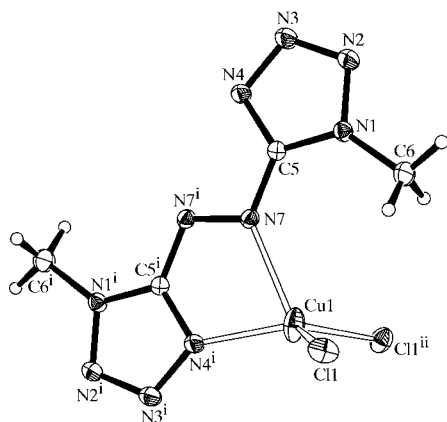


**Figure 1**  
An ORTEP-3 plot (Farrugia, 1997) of the asymmetric unit of (I). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as spheres of arbitrary radii.

*al.*, 2004; Bronisz, 2004; Lyakhov *et al.*, 2004). Rather unusual conditions were needed to prepare complexes (II) and (III), which were obtained under reflux followed by slow evaporation of a solution containing compound (I) and an excess of copper(II) chloride dihydrate in ethanol–triethyl orthoformate at room temperature. Because (II) and (III) are Cu<sup>I</sup> complexes, reduction of Cu<sup>II</sup> by ethanol has occurred under the reaction conditions. Attempts to prepare any chloride complexes of Co and Ni with (I) have failed. Thus, compound (I) shows low coordination ability in spite of the presence of N atoms of different types as potential donor atoms.

The molecules of (I) (Fig. 1) exhibit no symmetry, exhibiting the *trans* orientation of the tetrazole rings relative to the diazene bridge. Tetrazole rings *A* and *B* are planar to within 0.0009 (10) and 0.0035 (10) Å, respectively. The dihedral angle between the least-squares planes of the rings is 22.87 (7)°. In the fragment C5A–N7A=N7B–C5B, the mean deviation of the atoms from the least-squares plane is 0.0113 (6) Å. The bond length of the N=N bridge is 1.2530 (17) Å and the N4A=C5A–N7A=N7B and N4B=C5B–N7B=N7A torsion angles are 10.7 (2) and 14.4 (2)°, respectively. The non-planarity of the molecule does not permit significant conjugation. The tetrazole ring geometry in (I) (Table 1) is typical of that of 1,5-disubstituted tetrazoles. Only van der Waals interactions exist in the crystal structure of (I).

In complex (II), the organic ligands lie across centres of inversion in the space group *Pbca*. The coordination geometry around the Cu<sup>I</sup> atom is best described as distorted tetrahedral (Fig. 2). The Cu–N and Cu–Cl bond lengths lie in the narrow range 2.025 (3)–2.2696 (10) Å (Table 2). The distortion of the tetrahedron is related to the rather small value of the bite angle [N4–Cu1–N7 = 75.90 (10)°]. The remaining bond angles of atom Cu1 lie in the range 107.24 (7)–119.01 (9)°. The tetrazole rings are essentially planar, with an r.m.s. deviation from the least-squares plane of 0.0001 (19) Å. Atom C6 of the methyl group and atom N7 of the diazene group lie 0.052 (6) and 0.055 (5) Å, respectively, out of the tetrazole ring plane. The organic ligand is planar to within 0.013 (3) Å (without taking into account the methyl group atoms).



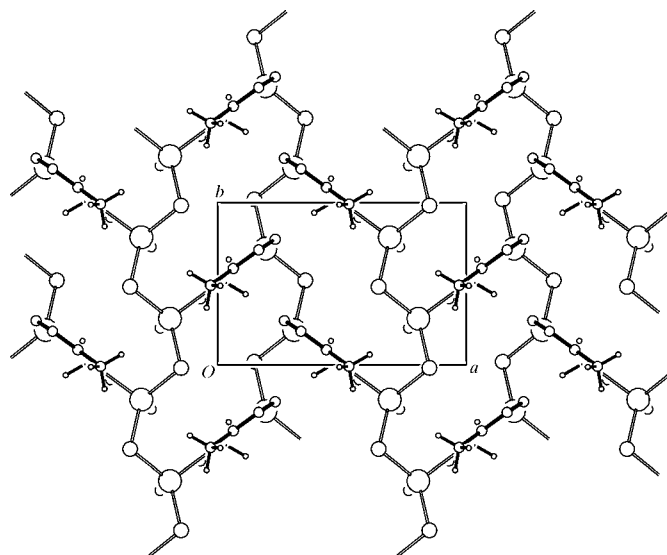
**Figure 2**  
The environment of the Cu<sup>I</sup> atom in the structure of (II). Displacement ellipsoids are drawn at the 30% probability level. Symmetry codes (i) and (ii) correspond to those in Table 2.

Complex (II) forms a two-dimensional coordination polymer with layers parallel to the *ab* plane (Fig. 3). The nearest Cu atoms, separated by *ca* 3.440 Å, are linked by Cl atoms to form polymeric chains running along the *b* axis. These chains are connected through the tetrazole ligands *via* atoms N4 and N7 to give a polymeric sheet. No hydrogen bonds exist in complex (II).

In complex (III), the Cu<sup>I</sup> atom, lying on a twofold axis, is surrounded by five atoms forming a distorted square pyramid, with a  $\tau$  value of 0.22 (the extreme values are 1 for a trigonal bipyramid and 0 for a square pyramid; Addison *et al.*, 1984). The Cl atom, also on the twofold axis, lies in the apical position of the pyramid, while the basal sites are occupied by two N4 and two N7 atoms from two organic ligands. Atom Cu1 is displaced 1.0325 (16) Å above the least-squares basal plane of the four N atoms [their r.m.s. deviation from the least-squares plane is 0.0835 (15) Å]. Two significantly different sets of Cu–N bond lengths characterize the equatorial asymmetry, *viz.* two Cu1–N4 bonds [2.004 (2) Å] and two Cu1–N7 bonds [2.594 (2) Å]. A similar geometry of the atomic environment of five-coordinate Cu<sup>I</sup> atoms has been observed in complexes with rigid macrocyclic ligands (Cambridge Structural Database; Version 5.27 of November 2005; Allen, 2002).

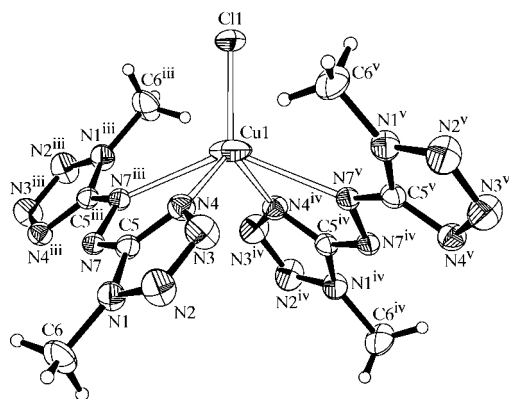
The tetrazole ligand in (III) lies across an inversion centre at the mid-point of the N=N bond (Fig. 4). The tetrazole rings are planar to within 0.002 (2) Å. Atom C6 of the methyl group and atom N7 of the diazene group are displaced from the tetrazole ring plane by 0.130 (6) and 0.038 (4) Å, respectively. Excluding the methyl group atoms, the organic ligand is planar to within 0.009 (2) Å. In complex (III), the Cu ions are linked together by organic ligands, giving polymeric chains running along the *c* axis, with van der Waals interactions between the chains (Fig. 5).

In both investigated complexes, the organic ligands are linked in a bidentate fashion with two Cu atoms and show

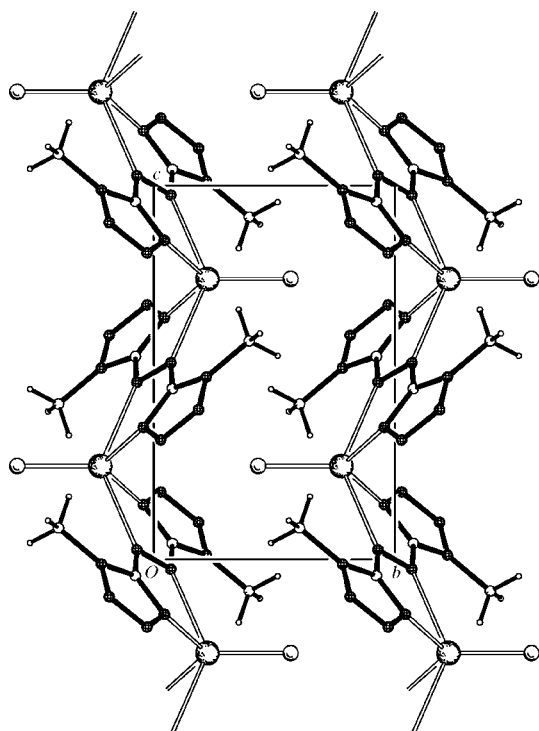


**Figure 3**  
The atomic arrangement of a layer in (II), viewed along the *c* axis.

chelating and bridging properties. Comparison of the bond lengths of the ligands in (I), (II) and (III) shows that the corresponding values are rather close, although some elongation of the N=N bond and shortening of the C5—N7 bond in the complexes relative to (I) is observed. The participation of the ligand in complexation gives rise to essential deformation of the molecule. In both complexes, an increase of the N1—C5—N7 angle and a decrease of the N4=C5—N7 and C5—N7=N7 angles in comparison with those of (I) are observed (Tables 1–3). Moreover, torsion angles in the bridge of molecules correspond to a more flattened molecular geometry in (II) and (III) than in (I). Probably, the coordi-



**Figure 4**  
The environment of the Cu<sup>I</sup> atom in the structure of (III). Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (iii)  $-x + 2, -y, -z + 1$ ; (iv)  $-x + 2, y, -z + \frac{3}{2}$ ; (v)  $x, -y, z + \frac{1}{2}$ .]



**Figure 5**  
Polymeric chains in the structure of (III), viewed along the *a* axis.

nation of diazene N atoms by Cu atoms is responsible for the change in ligand molecule conformation. Complexation and chelation in (II) and (III) make it possible to stabilize the flattened ligand conformation and to form an extended conjugation system. N=N bond elongation, as well as C5—N7 bond shortening, may be considered as a confirmation of the conjugation.

## Experimental

For the synthesis of (I), a mixture of 5-amino-1-methyltetrazole (0.99 g, 10 mmol), *N*-bromosuccinimide (3.56 g, 20 mmol) and 2,2'-azobis(isobutyronitrile) (17 mg, 0.1 mmol) in acetonitrile (25 ml) was stirred for 5 h under reflux. The solvent was removed *in vacuo*. Recrystallization of the residue from water and then from ethyl acetate gave an orange solid of (I) [0.61 g, yield 63%; m.p. 455–457 K, in agreement with data published by Williams *et al.* (1957)]. Single crystals of (I) were prepared by slow evaporation of an ethyl acetate solution. For the synthesis of (II) and (III), a solution of bis(1-methyl-1H-tetrazol-5-yl)diazene (0.097 g, 0.5 mmol) and copper(II) chloride dihydrate (0.51 g, 3 mmol) in ethanol and triethyl orthoformate (75 ml, 3:1 *v/v*) was heated for 1 h at 343–353 K. The solution was kept at room temperature for several (10–15) days, whereupon black crystals of complexes (II) and (III) suitable for X-ray analysis formed.

## Compound (I)

### Crystal data

$C_4H_6N_{10}$	$Z = 4$
$M_r = 194.19$	$D_x = 1.520 \text{ Mg m}^{-3}$
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 6.889 (2) \text{ \AA}$	$\mu = 0.12 \text{ mm}^{-1}$
$b = 9.684 (3) \text{ \AA}$	$T = 294 (2) \text{ K}$
$c = 12.719 (4) \text{ \AA}$	Prism, orange
$V = 848.5 (4) \text{ \AA}^3$	$0.4 \times 0.3 \times 0.2 \text{ mm}$

### Data collection

Nicolet R3m four-circle diffractometer	$R_{\text{int}} = 0.023$
$\omega/2\theta$ scans	$\theta_{\text{max}} = 30.1^\circ$
1569 measured reflections	3 standard reflections
1455 independent reflections	every 100 reflections
1297 reflections with $I > 2\sigma(I)$	intensity decay: none

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.060P)^2 + 0.0346P]$
$R[F^2 > 2\sigma(F^2)] = 0.031$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.092$ ; $S = 1.04$	$(\Delta/\sigma)_{\text{max}} < 0.001$
1455 reflections	$\Delta\rho_{\text{max}} = 0.15 \text{ e \AA}^{-3}$
130 parameters	$\Delta\rho_{\text{min}} = -0.15 \text{ e \AA}^{-3}$
H-atom parameters constrained	Extinction correction: <i>SHELXL97</i>
	Extinction coefficient: 0.107 (9)

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (I).

N1A—N2A	1.3340 (17)	N1B—N2B	1.3309 (17)
N1A—C5A	1.3392 (18)	N1B—C5B	1.3359 (18)
N2A—N3A	1.306 (2)	N2B—N3B	1.305 (2)
N3A—N4A	1.346 (2)	N3B—N4B	1.343 (2)
N4A—C5A	1.3195 (19)	N4B—C5B	1.320 (2)
C5A—N7A	1.3978 (18)	C5B—N7B	1.4009 (19)
N7A—N7B	1.2530 (17)		
N4A—C5A—N7A	130.72 (14)	N4B—C5B—N7B	130.73 (14)
N1A—C5A—N7A	119.57 (13)	N1B—C5B—N7B	119.62 (13)
N7B—N7A—C5A	112.26 (12)	N7A—N7B—C5B	112.47 (12)

## Compound (II)

### Crystal data

[Cu <sub>2</sub> Cl <sub>2</sub> (C <sub>4</sub> H <sub>6</sub> N <sub>10</sub> )]	Z = 4
<i>M<sub>r</sub></i> = 392.16	<i>D<sub>x</sub></i> = 2.202 Mg m <sup>-3</sup>
Orthorhombic, <i>Pbca</i>	Mo <i>K</i> α radiation
<i>a</i> = 9.943 (2) Å	<i>μ</i> = 4.05 mm <sup>-1</sup>
<i>b</i> = 6.4899 (18) Å	<i>T</i> = 292 (2) K
<i>c</i> = 18.330 (4) Å	Plate, black
<i>V</i> = 1182.8 (5) Å <sup>3</sup>	0.28 × 0.28 × 0.08 mm

### Data collection

Nicolet <i>R3m</i> four-circle diffractometer	1370 independent reflections
<i>ω/2θ</i> scans	1199 reflections with <i>I</i> > 2σ( <i>I</i> )
Absorption correction: Gaussian (Coppens <i>et al.</i> , 1965)	<i>R<sub>int</sub></i> = 0.012
<i>T<sub>min</sub></i> = 0.331, <i>T<sub>max</sub></i> = 0.760	<i>θ<sub>max</sub></i> = 27.6°
1517 measured reflections	3 standard reflections every 100 reflections
	intensity decay: none

### Refinement

Refinement on <i>F</i> <sup>2</sup>	$w = 1/[\sigma^2(F_o^2) + (0.0349P)^2 + 3.5322P]$
$R[F^2 > 2\sigma(F^2)] = 0.037$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.093$	( $\Delta/\sigma$ ) <sub>max</sub> = 0.001
<i>S</i> = 1.06	$\Delta\rho_{max} = 0.94 \text{ e } \text{Å}^{-3}$
1370 reflections	$\Delta\rho_{min} = -1.48 \text{ e } \text{Å}^{-3}$
83 parameters	
H-atom parameters constrained	

**Table 2**

Selected geometric parameters (Å, °) for (II).

Cu1—N4 <sup>i</sup>	2.025 (3)	N2—N3	1.304 (4)
Cu1—N7	2.206 (2)	N3—N4	1.348 (4)
Cu1—Cl1	2.2617 (11)	N4—C5	1.325 (4)
Cu1—Cl1 <sup>ii</sup>	2.2696 (10)	C5—N7	1.378 (4)
N1—C5	1.335 (4)	N7—N7 <sup>i</sup>	1.296 (5)
N1—N2	1.337 (4)		
N4—C5—N7	125.5 (3)	N7 <sup>i</sup> —N7—C5	110.5 (3)
N1—C5—N7	125.4 (3)		

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

## Compound (III)

### Crystal data

[CuCl(C <sub>4</sub> H <sub>6</sub> N <sub>10</sub> )]	Z = 2
<i>M<sub>r</sub></i> = 293.18	<i>D<sub>x</sub></i> = 1.886 Mg m <sup>-3</sup>
Monoclinic, <i>P2<sub>1</sub>/c</i>	Mo <i>K</i> α radiation
<i>a</i> = 8.528 (2) Å	<i>μ</i> = 2.36 mm <sup>-1</sup>
<i>b</i> = 6.2456 (13) Å	<i>T</i> = 292 (2) K
<i>c</i> = 10.059 (2) Å	Prism, black
<i>β</i> = 105.462 (19)°	0.34 × 0.24 × 0.18 mm
<i>V</i> = 516.38 (19) Å <sup>3</sup>	

**Table 3**

Selected geometric parameters (Å, °) for (III).

Cu1—N4	2.004 (2)	N2—N3	1.299 (4)
Cu1—Cl1	2.1550 (12)	N3—N4	1.356 (3)
Cu1—N7 <sup>iii</sup>	2.594 (2)	N4—C5	1.318 (3)
N1—C5	1.331 (3)	C5—N7	1.387 (3)
N1—N2	1.339 (4)	N7—N7 <sup>iii</sup>	1.270 (4)
N4—C5—N7	128.2 (2)	N7 <sup>iii</sup> —N7—C5	111.0 (2)
N1—C5—N7	122.5 (2)		

Symmetry code: (iii)  $-x + 2, -y, -z + 1$ .

### Data collection

Nicolet <i>R3m</i> four-circle diffractometer	1517 independent reflections
<i>ω/2θ</i> scans	1191 reflections with <i>I</i> > 2σ( <i>I</i> )
Absorption correction: <i>ψ</i> scan (North <i>et al.</i> , 1968)	<i>R<sub>int</sub></i> = 0.013
<i>T<sub>min</sub></i> = 0.485, <i>T<sub>max</sub></i> = 0.655	<i>θ<sub>max</sub></i> = 30.1°
1607 measured reflections	3 standard reflections every 100 reflections
	intensity decay: none

### Refinement

Refinement on <i>F</i> <sup>2</sup>	$w = 1/[\sigma^2(F_o^2) + (0.0532P)^2 + 0.4842P]$
$R[F^2 > 2\sigma(F^2)] = 0.046$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.127$	( $\Delta/\sigma$ ) <sub>max</sub> = 0.001
<i>S</i> = 1.07	$\Delta\rho_{max} = 0.85 \text{ e } \text{Å}^{-3}$
1517 reflections	$\Delta\rho_{min} = -0.75 \text{ e } \text{Å}^{-3}$
76 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	Extinction coefficient: 0.014 (3)

For all compounds, methyl H atoms were included in geometrically calculated positions, with C—H distances of 0.96 Å, and refined using a riding model, with *U*<sub>iso</sub>(H) equal to 1.5*U*<sub>eq</sub>(C).

For all compounds, data collection: *R3m Software* (Nicolet, 1980); cell refinement: *R3m Software*; data reduction: *R3m Software*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PLATON*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3013). Services for accessing these data are described at the back of the journal.

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