

Four 3-cyanodifurazanyl ethers: potential propellants

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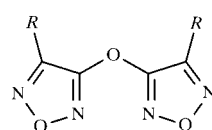
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In earlier papers, we described the synthesis and structures of bis(3-nitrofurazan-4-yl) ether, C₄N₆O₇, (I), bis[3-(nitro-*N,N,O*-azoxy)furazan-4-yl] ether, C₄N₁₀O₉, (II), and bis[3-(5*H*-[1,2,3]triazolo[4,5-*c*]furazan-5-yl)furazan-4-yl] ether, C₈N₁₄O₅, (III). Here we compare the structures of (I)–(III) with those of four 3-cyanodifurazanyl ethers, namely bis(3-cyanofurazan-4-yl) ether, C₆N₆O₃, (IV), 3-cyanofurazanyl 3-nitrofurazanyl ether, C₅N₆O₅, (V), 3,4-bis(3-cyanofurazan-4-yloxy)furazan, C₈N₈O₅, (VI), and bis[3-(3-cyanofurazan-4-yloxy)furazan-4-yl]diazene, C₁₀N₁₂O₆, (VII). It was found that the geometric parameters of the difurazanyl ether fragments are similar in these structures and therefore not influenced by substituent effects; however, the conformation of this fragment is different, *viz.* structures (I), (III), (V) and (VI) have approximate C₂ symmetry, and structures (II), (IV) and (VII) have C_s symmetry. Dense crystal packing (1.626–1.898 Mg m⁻³) is characteristic for all these hydrogen-free compounds. A linear correlation is also determined between crystal density and ‘molecular density’ (*M/V*), where *M* is the mass of a molecule and *V* is the molecular volume.

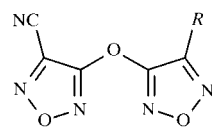
Comment

Symmetrical difurazanyl ether derivatives, such as bis(3-nitrofurazan-4-yl) ether, (I) (Sheremetev, 1998; Sheremetev *et al.*, 1996), bis[3-(nitro-*N,N,O*-azoxy)furazan-4-yl] ether, (II) (Sheremetev, Semenov *et al.*, 1998), and bis[3-(5*H*-[1,2,3]triazolo[4,5-*c*]furazan-5-yl)furazan-4-yl] ether, (III) (Sheremetev *et al.*, 1999), have been developed as highly energetic materials having good explosive performance in a variety of industrial, military, and space applications. The impact and friction sensitivities of these compounds are similar to those of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX). In addition to continuing efforts in the preparation of highly energetic

materials, recent research in our group has focused on hydrogen-free propellant ingredients. Our approach to the synthesis of energetic compounds is to employ the inherent stability and flexibility of the difurazanyl ether skeleton, and to enhance the enthalpy of formation by the inclusion of cyano groups. We have prepared a large number of known and novel cyano derivatives of furazan and studied their properties (Sheremetev *et al.*, 1995; Sheremetev & Pivina, 1996; Sheremetev, Mantseva *et al.*, 2000; Sinditskii *et al.*, 1998). The different functional groups were chosen in order to modify the physical properties of the target ethers (*e.g.* melting point, oxygen balance, plasticity and solubility) and to probe the effects of the substituents on the overall lattice architecture and crystal density. 3-Cyanofurazanyl 3-nitrofurazanyl ether, (IV) (Sheremetev, Aleksandrova *et al.*, 2000; Sheremetev *et al.*, 2002), and bis(3-cyanofurazonyl) ether, (V) (Sheremetev *et al.*, 1996), incorporating two furazan rings, and 3,4-bis(3-cyanofurazan-4-yloxy)furazan, (VI) (Sheremetev, Kulagina *et al.*, 1998), having three rings were prepared as previously described. We report here their structures, along with that of the new compound bis[3-(3-cyanofurazan-4-yloxy)furazan-4-yl]diazene, (VII).



(I)–(III)



(IV)–(VII)

(I) $R = \text{NO}_2$

(II) $R = -\text{N}(\text{O})=\text{NNO}_2$

(III) $R =$

(IV) $R = \text{CN}$

(V) $R = \text{NO}_2$

(VI) $R =$

(VII) $R =$

We have explored the influence on the difurazanyl ether fragment of different functional groups, such as nitro [$R = \text{NO}_2$, (IV)], less electron-withdrawing substituents [$R = -\text{N}=\text{N}$ -furazan, (VII), and $R = \text{CN}$, (V)] and an electron-donating moiety [$R = \text{O}$ -furazan, (VI)]. The bond lengths within the difurazanyl ether fragments in molecules (II)–(V) and (VII) are very similar and close to the average values published for each type of bond (Allen *et al.*, 1987; Table 1). There are two topologically equivalent N–O bonds in each furazan ring. According to experimental data, these N–O bonds have different lengths in (II)–(V) and (VII); those adjacent to an electron-withdrawing substituent are in the range 1.360 (2)–1.375 (5) Å (mean 1.369 Å), while the N–O bonds adjacent to the electron-donating oxygen bridge are in the range 1.385 (3)–1.390 (2) Å (mean 1.388 Å) (see Table 1). This is in agreement with a report by Batsanov & Struchkov (1985), where the shortening of furazan N–O bonds adjacent

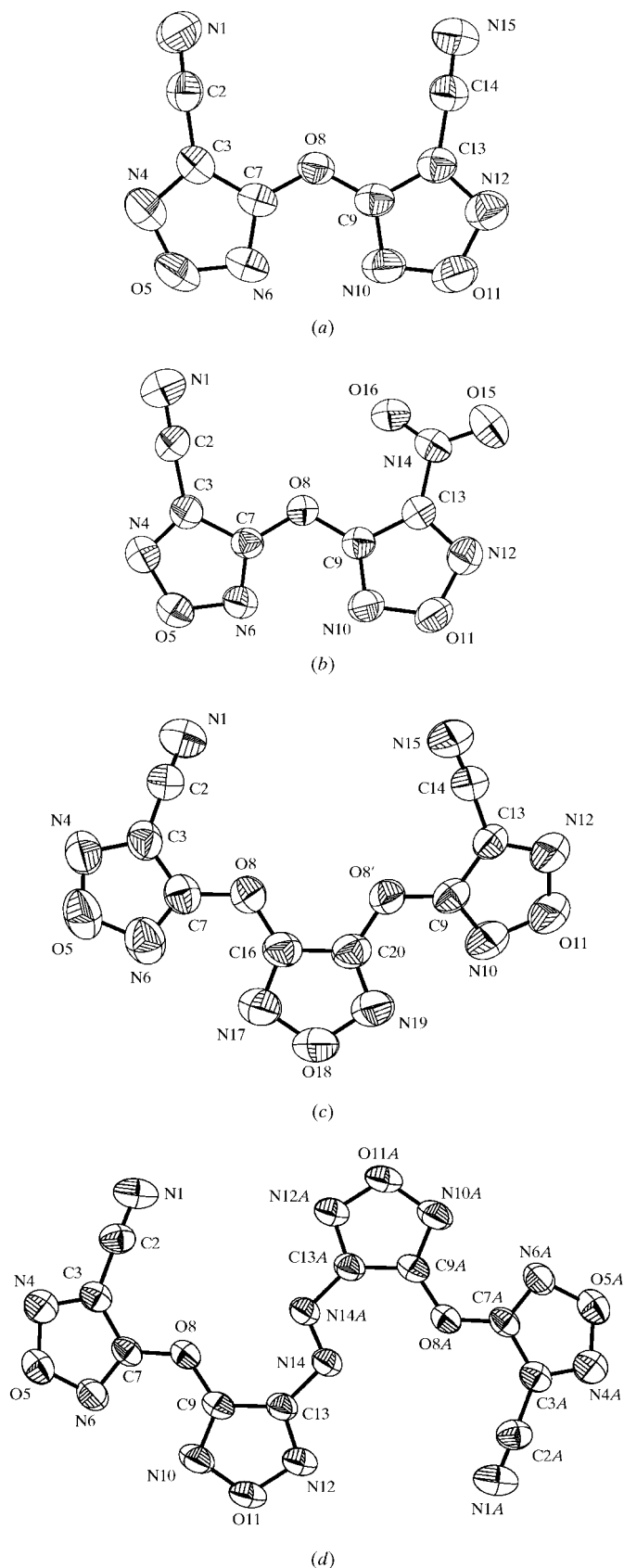


Figure 1
General views of (a) compound (IV), (b) compound (V), (c) compound (VI) and (d) compound (VII). Displacement ellipsoids are drawn at the 50% probability level. In (d), suffix A represents symmetry code $(-x, 1-y, 1-z)$.

to electron-withdrawing substituents, relative to those adjacent to electron-releasing substituents, was first pointed out. Molecule (VI) is similar to molecule (IV), but contains an additional furazan ring between the two terminal cyano-bearing furazan rings. It was found that these terminal rings in molecule (VI) have the same geometry as in molecules (II)–(V) and (VII), while its symmetrically substituted central furazan ring has very similar N–O bond lengths of N17–O18 = 1.387 (4) and N19–O18 = 1.389 (4) Å.

The bond lengths in the two independent molecules of (I) differ significantly from those in molecules (II)–(VII). However, as there are also large discrepancies of up to 0.06–0.07 Å in the lengths of chemically equivalent bonds in the two independent molecules of (I), we cannot consider the structure of (I) to be reliable at a level sufficient to allow discussion of its bond lengths. For structures (II)–(VII), the ether C–O bond distances are in the range 1.336 (3)–1.358 (4) Å (mean 1.350 Å), intermediate between single C–O (1.42 Å) and double C=O (1.21 Å) bonds, indicating resonance between the furazan π -system and the lone pairs of bridging atom O8. This is also confirmed by the increase in the bond angle at O8 to an average value of 121°. The bond lengths of the cyano groups in (IV)–(VII) are in the range 1.116 (5)–1.134 (3) Å (mean 1.127 Å). Due to conjugation between the furazan rings and the cyano groups, the cyano NC–C(furazan) bonds are shortened and have bond lengths in the range 1.428 (3)–1.4359 (19) Å (mean 1.432 Å). In (V), the dihedral angle between the furazan ring and the plane of the nitro group is 18.1°, and the length of the N(nitro)–C(furazan) bond is 1.452 (3) Å. Analysis of data from the Cambridge Structural Database (CSD; Allen, 2002) shows that the latter value is close to the standard value of 1.46 Å for a Csp^2 –NO₂ bond. In (VII), the azo group conjugates neighbouring furazan rings, as evidenced by the N=N bond length of 1.247 (3) Å and the N(azo)–C(furazan) bond length of 1.410 (3) Å.

Molecules (I)–(III) and (V)–(VII) are non-planar. In contrast, (IV) can be considered as approximately planar, as the r.m.s. deviation from the molecular least-squares mean plane is only 0.18 Å. The only difference between the difurazanyl ether fragments in all seven structures is the twist between the two component rings. The conformation of the difurazanyl ether fragment can be described by the torsion angles N6–C7–O8–C9 and N10–C9–O8–C7 (Table 2). If these torsion angles have the same sign, the approximate symmetry of the difurazanyl ether is C_2 (Fig. 2a), but with opposing signs it is C_s (Fig. 2b). It is clear from Table 2 and Figs. 2(a) and 2(b) that the dihedral angle between the furazan rings does not uniquely describe the conformation of the difurazanyl ether fragment. Structures (I), (III), (V) and (VI) have a C_2 conformation for the difurazanyl ether fragment, while structures (II), (IV) and (VII) adopt C_s conformation.

To determine the optimal conformation of the difurazanyl ether fragment, we optimized the geometry of (IV) using the GAUSSIAN94 program (Frisch *et al.*, 1994) at the MP2/cc-pvdz level of theory. This showed that the conformations of the calculated and experimental molecules are different. The calculated N6–C7–O8–C9 and N10–C9–O8–C7 torsion



Figure 2
Two types of difurazanyl ether fragment distortion.

angles have the same sign and value (7.1°). Hence, in contrast to experimental molecule (IV), which has approximate C_s symmetry, the calculated molecule has C_2 symmetry. The observed dihedral angle between the furazan rings is $24.3 (1)^\circ$, whereas the calculated value is 11.8° . To compare the energies of these two conformations, we carried out another calculation with the torsion angles fixed at the experimentally observed values of -28.6 and 20.3° , respectively. This calculation revealed that the energy difference between the two conformations is rather small ($1.313 \text{ kJ mol}^{-1}$), so the difference between experimentally determined and calculated conformations could be due to crystal-packing effects which were not included in the calculations.

In the crystal packing of (IV), essentially planar molecules are arranged to form flat ribbons normal to the (201) crystallographic plane, with the ribbons adopting a parquet motif. The packing arrangements for (V), (VI) and (VII) do not assume a readily identifiable motif, a common situation with space groups $P2_12_12_1$ and $Pbca$. In (V) and (VI), two intermolecular contacts involving cyano groups were found; in (V), the cyano group approaches nitro atom O15 [$C2 \cdots O15(\frac{1}{2} - x, 1 - y, z - \frac{1}{2}) = 2.957 (3) \text{ \AA}$], while in (VI), there is a contact between the cyano group and a furazan ring [$N21 \cdots C15(\frac{1}{2} + x, -\frac{1}{2} - y, -z) = 2.969 (3) \text{ \AA}$]. These interactions can be ascribed to the coulombic interactions of atoms bearing partial opposite charges. No other intermolecular contacts in (IV)–(VII) lie within the sum of the relevant van der Waals radii (Bondi, 1964).

It is well known that high density is a factor favouring good explosive performance (Lee & Block-Bolten, 1993). Although we do not have enough data for a representative statistical analysis, we decided to investigate the relationship between the molecular structure and the density of crystal packing for the seven difurazanyl ethers (I)–(VII). For this purpose, molecular volume (V) or molecular surface (S), and molecular mass (M) were used. All calculations were carried out using the *NONVLOT* program (Shil'nikov, 1994) and the radii of Bondi (1964). Comparison of the calculated ratio M/S with X-ray density, $d_{X\text{-ray}}$, shows a moderate dependence of M/S on $d_{X\text{-ray}}$, with a correlation coefficient of 0.884. Better agreement was found by considering 'molecular density', d_{mol} , which is the ratio of molecular mass M to molecular volume V . Fig. 3 shows the dependence of crystal density on molecular density, the correlation coefficient in this case being 0.916. Fig. 3 also shows that while the crystal density of (III) is higher than

expected, the values for (II) and (V) are lower. According to Kitaigorodsky (1961), crystal density can be presented as a product of packing coefficient k and molecular density, *viz.* $d_{X\text{-ray}} = k \times d_{\text{mol}}$. Calculated packing coefficients, molecular densities and crystal densities for compounds (I)–(VII) are presented in Table 3. Since the packing coefficient influences crystal density, the search for crystals with high density should consider ways of increasing both d_{mol} and k . According to Kuzmina *et al.* (1990), there is a tendency for k to decrease with increasing d_{mol} . This relationship restricts the possibilities of obtaining extremely dense structures, but because of its

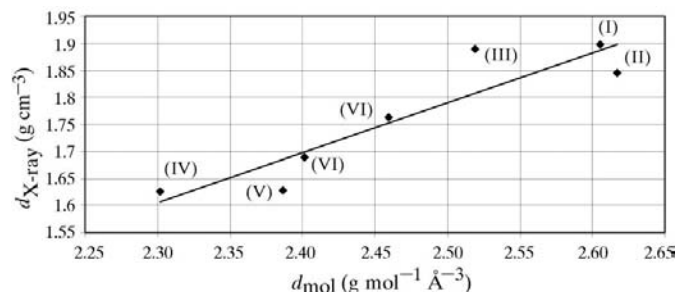


Figure 3
The correlation between molecular density, d_{mol} , and crystal density, $d_{X\text{-ray}}$.

statistical nature exceptions do occur. Compound (III), which has a rather large value of d_{mol} , is a good example of such an exception; while the mean k value for (I)–(VII) is 0.71, for (III) it is higher, at 0.749. Analysis of the factors responsible for the high packing coefficients for this and other compounds will help us to predict compounds likely to exhibit high density.

Experimental

The syntheses of compounds (IV)–(VI) have been published previously; *cf.* Sheremetev, Aleksandrova *et al.* (2000) and Sheremetev *et al.* (2002) for the preparation of (IV), Sheremetev *et al.* (1996) for the preparation of (V), and Sheremetev, Kulagina *et al.* (1998) for the preparation of (VI). Crystals of (IV)–(VI) suitable for X-ray analysis were grown from CHCl_3 solutions. Compound (VII) was prepared by the dropwise addition of 4,4'-dinitroazofurazan (2.56 g, 10 mmol) in diglyme (10 ml) to a stirred solution of 3-cyano-4-hydroxyfurazan sodium salt (2.66 g, 20 mmol) in diglyme (40 ml) under dry conditions. The resulting mixture was stirred for 1.5–2.0 h at 323–333 K. Thin-layer chromatography indicated complete reaction. The mixture was cooled, poured into water, and extracted with CH_2Cl_2 ($3 \times 60 \text{ ml}$). The combined extracts were washed with water, dried (MgSO_4), filtered and concentrated to give 2.73 g (72%) of (VII) as yellow–orange crystals. An analytically pure sample and a sample for X-ray analysis were prepared by recrystallization from hexane (m.p. 420–421 K). ^{13}C NMR (acetone- d_6 , δ): 106.5 (C \equiv N), 128.9 (C–C \equiv N), 155.4 (C–NN), 158.8 (C–C–NN), 182.6 (C–O). MS (EI), m/z : 384 (M^+), 354 ($M^+ - \text{NO}$), 324 ($M^+ - 2\text{NO}$). IR: 2270 (CN), 1565, 1480, 1415, 1395, 1255, 1220, 1025 cm^{-1} . $\text{C}_{10}\text{N}_{12}\text{O}_6$ ($M_r = 384.19$): calculated: C 31.26, N 43.75%; found: C 31.18, N 43.82%.

Table 1
Selected bond lengths (Å) for structures (I)–(VII).

	(Ia)	(Ib)	(II)	(III)	(IV)	(V)	(VI)	(VII)	CSD
C3–C7	1.464 (6)	1.406 (6)	1.397	1.411 (6)	1.411 (2)	1.422 (3)	1.408 (4)	1.410 (3)	1.428 (7)
C9–C13	1.393 (6)	1.444 (5)	1.403	1.408 (6)	1.414 (2)	1.408 (3)	1.406 (4)	1.413 (3)	1.428 (7)
C3–N4	1.266 (8)	1.289 (6)	1.304	1.289 (5)	1.297 (2)	1.293 (3)	1.295 (4)	1.302 (2)	1.298 (6)
C13–N12	1.242 (5)	1.309 (7)	1.281	1.295 (6)	1.295 (2)	1.289 (3)	1.286 (4)	1.295 (3)	1.298 (6)
C7–N6	1.302 (8)	1.270 (6)	1.293	1.287 (6)	1.293 (2)	1.283 (2)	1.295 (4)	1.291 (2)	1.298 (6)
C9–N10	1.254 (5)	1.313 (7)	1.290	1.287 (5)	1.291 (2)	1.284 (3)	1.297 (3)	1.292 (2)	1.298 (6)
N4–O5	1.355 (9)	1.317 (7)	1.375	1.375 (5)	1.370 (2)	1.370 (3)	1.364 (4)	1.366 (2)	1.385 (13)
N12–O11	1.409 (8)	1.312 (8)	1.372	1.373 (5)	1.360 (2)	1.360 (3)	1.358 (4)	1.370 (2)	1.385 (13)
N6–O5	1.340 (8)	1.409 (6)	1.390	1.386 (5)	1.386 (2)	1.385 (3)	1.389 (4)	1.389 (2)	1.385 (13)
N10–O11	1.404 (7)	1.379 (8)	1.390	1.386 (6)	1.389 (2)	1.387 (3)	1.379 (4)	1.390 (2)	1.385 (13)
C7–O8	1.344 (8)	1.348 (5)	1.348	1.358 (6)	1.349 (2)	1.349 (3)	1.347 (3)	1.347 (2)	1.354 (16)
O8–C9	1.385 (6)	1.324 (5)	1.347	1.358 (5)	1.352 (2)	1.355 (2)	1.336 (3) ^a	1.354 (2)	1.354 (16)

Note: (a) for structure (VI), the value for O8'–C9 is given.

Compound (IV)

Crystal data

C₆N₆O₃
M_r = 204.12
 Monoclinic, *P*₂₁/*c*
a = 13.639 (3) Å
b = 8.899 (2) Å
c = 6.9254 (17) Å
 β = 97.13 (2)°
V = 834.1 (4) Å³
Z = 4
D_x = 1.626 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 24 reflections
 θ = 12–13°
 μ = 0.14 mm⁻¹
T = 293 (2) K
 Rectangular prism, colourless
 0.5 × 0.4 × 0.4 mm

Data collection

Siemens *P3/PC* diffractometer
 θ/2θ scans
 1534 measured reflections
 1471 independent reflections
 1276 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.008
 θ_{max} = 25.1°
h = 0 → 16
k = 0 → 10
l = -8 → 8
 2 standard reflections every 98 reflections
 intensity decay: 12%

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.034
wR(*F*²) = 0.101
S = 1.09
 1471 reflections
 136 parameters
 $w = 1/[\sigma^2(F_o^2) + (0.072P)^2 + 0.022P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 0.13 e Å⁻³
 Δρ_{min} = -0.19 e Å⁻³

Compound (V)

Crystal data

C₅N₆O₅
M_r = 224.11
 Orthorhombic, *P*₂₁2₁2₁
a = 7.853 (2) Å
b = 8.791 (2) Å
c = 12.229 (3) Å
V = 844.2 (4) Å³
Z = 4
D_x = 1.763 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 24 reflections
 θ = 11–12°
 μ = 0.16 mm⁻¹
T = 293 (2) K
 Rectangular prism, yellow
 0.6 × 0.5 × 0.4 mm

Data collection

Siemens *P3/PC* diffractometer
 θ/2θ scans
 1433 measured reflections
 1433 independent reflections
 1164 reflections with *I* > 2σ(*I*)
 θ_{max} = 30.1°
h = 0 → 11
k = 0 → 12
l = 0 → 17
 2 standard reflections every 98 reflections
 intensity decay: 3%

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.045
wR(*F*²) = 0.121
S = 1.02
 1433 reflections
 145 parameters
 $w = 1/[\sigma^2(F_o^2) + (0.0882P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} = 0.001
 Δρ_{max} = 0.27 e Å⁻³
 Δρ_{min} = -0.23 e Å⁻³

Compound (VI)

Crystal data

C₈N₈O₅
M_r = 288.16
 Orthorhombic, *P*₂₁2₁2₁
a = 7.8295 (15) Å
b = 8.6273 (18) Å
c = 17.409 (3) Å
V = 1175.9 (4) Å³
Z = 4
D_x = 1.628 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 24 reflections
 θ = 13–14°
 μ = 0.14 mm⁻¹
T = 293 (2) K
 Rectangular prism, colourless
 0.4 × 0.3 × 0.3 mm

Data collection

Siemens *P3/PC* diffractometer
 θ/2θ scans
 1469 measured reflections
 1469 independent reflections
 1267 reflections with *I* > 2σ(*I*)
 θ_{max} = 27.1°
h = 0 → 10
k = 0 → 11
l = 0 → 22
 2 standard reflections every 98 reflections
 intensity decay: 2%

Table 2

Conformational parameters (°) for the difurazanyl ether fragment of compounds (I)–(VII).

	N6–C7–O8–C9	N10–C9–O8–C7	τ ^a	Symmetry
(Ia)	15.9	49.1	53	C ₂
(Ib)	14.4	20.1	29	C ₂
(II)	-13.2	12.1	11	C _s
(III)	10.8	42.0	48	C ₂
(IV)	-28.6 (2)	20.3 (2)	24.3 (1)	C _s
(V)	17.3 (3)	8.6 (3)	22.5 (1)	C ₂
(VI) ^b	20.2 (4)	4.7 (4)	24.0 (2)	C ₂
(VI) ^c	13.6 (4)	10.4 (4)	20.9 (2)	C ₂
(VII)	-9.6 (3)	32.0 (3)	27.8 (1)	C _s

Notes: (a) τ is the dihedral angle between the furazanyl rings; (b) torsion angles N6–C7–O8–C16 and N17–C16–O8–C7 are given; (c) torsion angles N19–C20–O8'–C9 and N10–C9–O8'–C20 are given.

Table 3
Molecular ($\text{g mol}^{-1}\text{\AA}^{-3}$) and crystal densities (Mg m^{-3}), and packing coefficients for structures (I)–(VII).

	d_{mol}	$d_{\text{X-ray}}$	k
(I)	2.605	1.898	0.728
(II)	2.617	1.845	0.704
(III)	2.519	1.888	0.749
(IV)	2.302	1.626	0.706
(V)	2.459	1.763	0.717
(VI)	2.386	1.628	0.682
(VII)	2.401	1.690	0.704

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.045$	$\Delta\rho_{\text{max}} = 0.16 \text{ e \AA}^{-3}$
$wR(F^2) = 0.128$	$\Delta\rho_{\text{min}} = -0.18 \text{ e \AA}^{-3}$
$S = 1.05$	Extinction correction: <i>SHELXL97</i>
1469 reflections	Extinction coefficient: 0.230 (18)
191 parameters	
$w = 1/[\sigma^2(F_o^2) + (0.092P)^2 + 0.0462P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Compound (VII)

Crystal data

$\text{C}_{10}\text{N}_{12}\text{O}_6$	Mo $K\alpha$ radiation
$M_r = 384.22$	Cell parameters from 24 reflections
Orthorhombic, <i>Pbca</i>	$\theta = 10\text{--}11^\circ$
$a = 6.4300$ (13) \AA	$\mu = 0.14 \text{ mm}^{-1}$
$b = 13.709$ (3) \AA	$T = 293$ (2) K
$c = 17.134$ (3) \AA	Rectangular prism, yellow–orange
$V = 1510.4$ (5) \AA^3	$0.4 \times 0.2 \times 0.2 \text{ mm}$
$Z = 4$	
$D_x = 1.690 \text{ Mg m}^{-3}$	

Data collection

Enraf–Nonius CAD-4 diffractometer	$h = 0 \rightarrow 7$
θ/ω scans	$k = 0 \rightarrow 16$
1326 measured reflections	$l = 0 \rightarrow 20$
1326 independent reflections	2 standard reflections every 98 reflections
1044 reflections with $I > 2\sigma(I)$	intensity decay: 3%
$\theta_{\text{max}} = 25.0^\circ$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.063P)^2 + 0.290P]$
$R[F^2 > 2\sigma(F^2)] = 0.040$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.111$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.13 \text{ e \AA}^{-3}$
1326 reflections	$\Delta\rho_{\text{min}} = -0.19 \text{ e \AA}^{-3}$
127 parameters	

For compounds (IV), (V) and (VI), data collection: *P3/PC* (Siemens, 1989); cell refinement: *P3/PC*; data reduction: *P3/PC*. For compound (VII), data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms, 1996). For all four compounds, program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1529). Services for accessing these data are described at the back of the journal.

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