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Geometry and bond-length alternation in nonlinear optical materials. I. Standard parameters in two precursors

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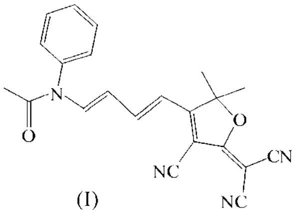
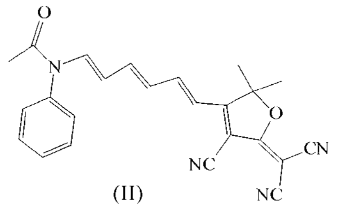
2-{3-Cyano-4-[4-(*N*-formylanilino)-*trans*-1,3-butadienyl]-5,5-dimethyl-2,5-dihydrofuran-2-ylidene}propanedinitrile, $C_{22}H_{18}N_4O_2$, (I), and 2-{3-cyano-4-[6-(*N*-formylanilino)-*trans*,*trans*-1,3,5-hexatrienyl]-5,5-dimethyl-2,5-dihydrofuran-2-ylidene}propanedinitrile, $C_{24}H_{20}N_4O_2$, (II), show the alternating single/double-bond behaviour of push–pull chromophores. In the two structures, the planar polyene chains are twisted with respect to the furanylidene ring by 18.2 (2) and 12.4 (2)°, respectively. Comparison with structures of related and parent molecules shows subtle but consistent bond-length variations consistent with charge-delocalized structures. Crystal cohesion is provided by various sets of hydrogen bonds, *viz.* $\text{C}-\text{H}_{\text{methyl}}\cdots\text{N}_{\text{cyano}}$ and bifurcated $(\text{C}{=}\text{C}-\text{H})_2\cdots\text{O}{=}\text{C}$ in (I), and $\text{C}-\text{H}_{\text{methyl/phenyl}}\cdots\text{O}$ and $\text{C}{=}\text{C}-\text{H}\cdots\text{N}_{\text{cyano}}$ in (II).

Comment

The development of organic nonlinear optical (NLO) polymers continues to attract considerable interest because of their potential application in a number of photonic and optoelectronic devices (Dalton, 2002). Polymeric organic materials offer a number of advantages over conventional inorganic electro-optical materials such as lithium niobate. These include better performance, the ability to be processed in a range of solvents, lower cost and lower drive voltages (Ma *et al.*, 2002). Crucial to the creation of such materials is the preparation of high figure of merit ($\mu.\beta$) chromophores which can be incorporated into the polymer system and which act as the active component. Recently, we reported the synthesis of a suite of such compounds using a range of acetanilide-based precursors (Kay *et al.*, 2004). The methodology permits a flexible route to 'right-hand side' (RHS) chromophore systems, with chromophores derived from the two title compounds affording the highest figures of merit ($\mu.\beta_0$ = 6400–9400 × 10^{-48} e.s.u.). RHS NLO materials are readily differentiated from their left-hand side counterparts as they have an aromatizable donor system, which leads to zwitterionic charge-separated ground states and high figure of merit molecules (Marder *et al.*, 1993). Owing to this charge delocalization, RHS molecules are expected to exhibit large changes in bond order across the conjugated π system. As part of our ongoing interest, we intend to study a range of NLO compounds containing a variety of donor systems, to examine the effect of the donor on bond order within these molecules. In order to establish some standard parameters, we have characterized the two title precursor compounds, (I) and (II). These contain a weak donor system, which permits us to establish standard geometrical parameters for analogues derived from the powerful electron acceptor [3-cyano-5,5-dimethyl-2,5-dihydrofuran-2-ylidene]propanedinitrile (hereafter CDFP).

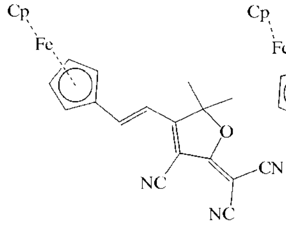


(I)

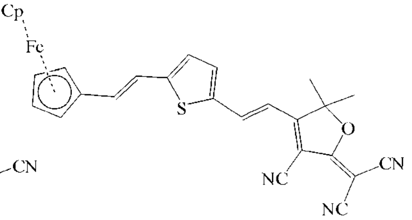


(II)

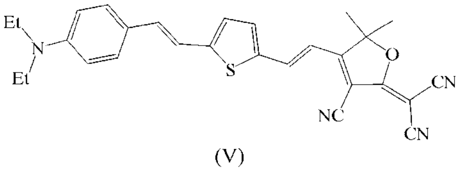
The asymmetric units of (I) and (II), each consisting of one molecule, are shown in Figs. 1 and 2, with selected dimensions in Tables 1 and 3. A comparison of some key bond lengths with those of related structures (see scheme below) containing the CDFP group with bound alkene units at the C4 position is given in Table 5 [sourced from the Cambridge Structural Database (CSD), Version 5.38, May 2007 updates (Allen, 2002); refcodes KAJBUT, (III), and KAJCAA, (IV) (Liao *et al.*, 2005), HESKIA, (V) (Kinnibrugh *et al.*, 2006), JETGEV, (VI) (Wang *et al.*, 2007), and PANLUM, (VII) (Li *et al.*, 2005)]. The consistency of the CDFP dimensions for (I) and (II) is remarkable, with only insignificant changes also noted in



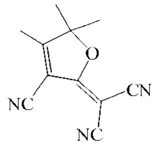
(III)



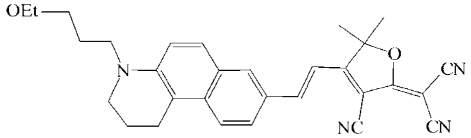
(IV)



(V)



(VI)



(VII)

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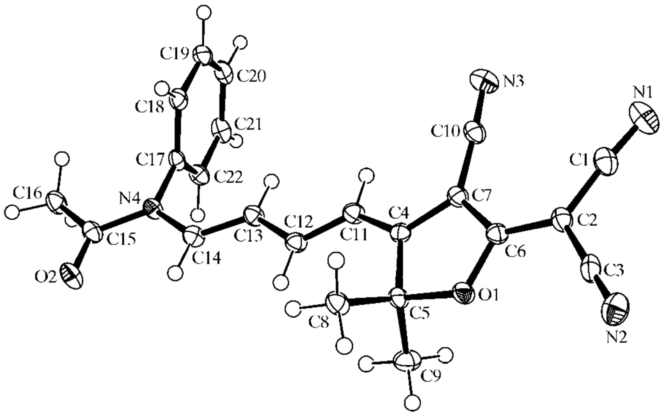

Figure 1
The molecular structure of (I) (*ORTEP-3*; Farrugia, 1997); displacement ellipsoids are shown at the 50% probability level.

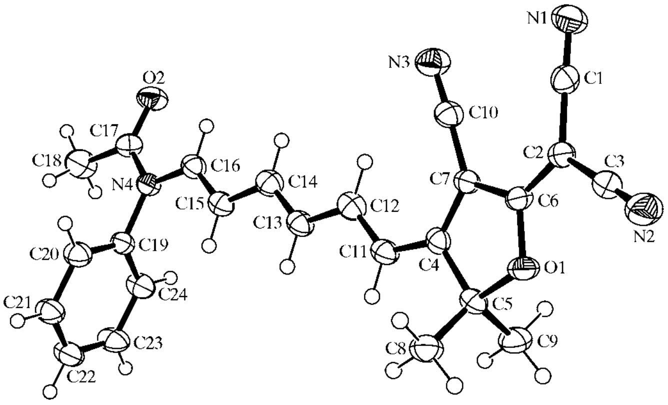

Figure 2
The molecular structure (II) (*ORTEP-3*; Farrugia, 1997); displacement ellipsoids are shown at the 50% probability level.

comparison with compounds (III)–(VI). The first double-bond lengths in the donor–acceptor chains (C11═C12) are similar, except for that in structure (II), which is marginally longer by 0.012 (4)° [the mean of (I) and (III)–(VI) is 1.354 (1) Å]. The 'extra' alkene bond length in (II) (C13═C14) appears normal.

Both structures contain three major planar groups, *viz.* the CDFP five-membered ring [with average out-of-plane deviations, hereafter ADs, for (I) and (II), respectively, of 0.005 (2) and 0.016 (2) Å], the alternating alkene/alkane (polyene) chain, hereafter AC [C12–C14 for (I) and C12–C16 for (II); ADs 0 (three atoms) and 0.005 (2) Å] and the planar phenyl rings [C17–C22 for (I) and C19–C24 for (II)]. The CDFP five-membered ring and the AC planes are twisted at atom C11, with interplanar angles of 18.17 (19) and 12.4 (2)° in (I) and (II), respectively. Similar twisting has been noted before [*e.g.* 14.15 (3)° in HESKIA; Kinnibrugh *et al.*, 2006]. Atom C11 is almost coplanar with the CDFP five-membered ring in (I), with a deviation of 0.018 (2) Å, but definitely out of this plane in (II) [the deviation is 0.142 (6) Å]. The phenyl ring plane is approximately normal to the AC plane; the dihedral angles are 79.49 (18) and 83.4 (2)°, respectively, in (I) and (II). The capping acetanilide atoms (N4 and O2 with C15 for (I) and C17 for (II)] are tilted slightly with respect to the AC plane by 2.2 (2) and 10.6 (4)°, respectively. The minor distortions of the cyano groups bound to C2 probably reflect packing considerations [*e.g.* the methyl hydrogen bond H8$\cdots$N2^{i} in (I) (Table 2)].

There are also two major geometrical differences between (I) and (II). The phenyl rings are oriented differently with respect to the CDFP five-membered ring, at interplanar angles of 80.23 (16) and 68.31 (9)°, respectively. However, an even more noteworthy feature is the different configuration of the alkene/alkane (polyene) chain binding to the CDFP group, (I)

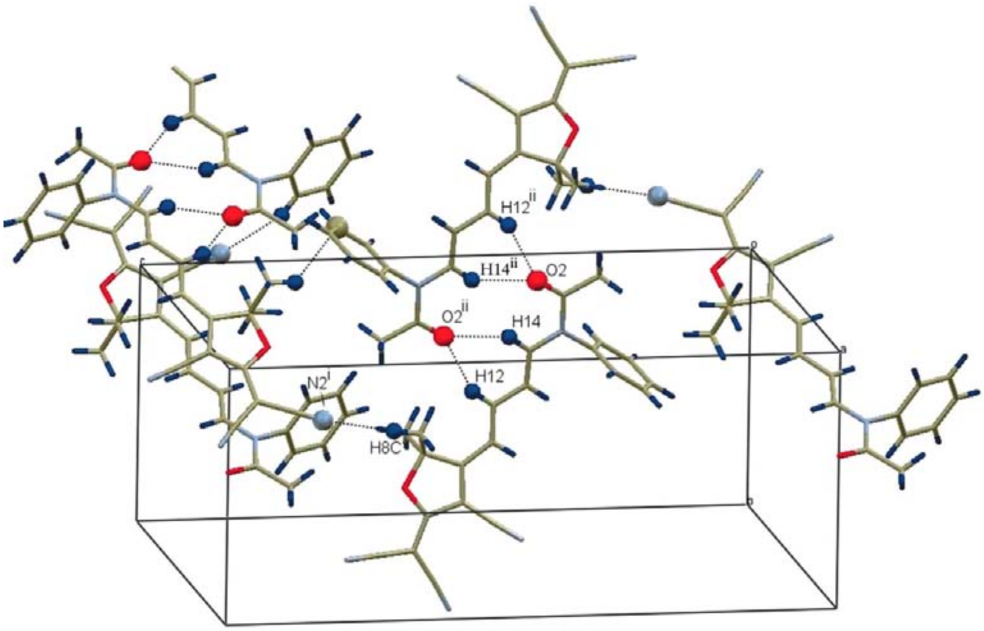

Figure 3
A partial packing diagram of (I) (*Mercury*; Bruno *et al.*, 2002), normal to the hydrogen-bonded layers, showing key intermolecular contacts (dotted lines between ball-shaped atoms). For symmetry designations, see Table 2.

being synperiplanar while (II) is antiperiplanar with respect to the atom sequence C7—C4—C11—C12 (see torsion angles in Tables 1 and 3, and Figs. 1 and 2). The two possible orientations of the precursor molecule are very similar in energy (within 2 kcal mol^{-1}; Kay *et al.*, 2004) and so crystal packing forces can determine which isomer (rotamer) crystallizes out. Tables 2 and 4 list the important intermolecular interactions shown in Figs. 3 and 4 and confirm that different hydrogen-bonding regimes exist in (I) and (II) (see below).

Both compounds are derived from 2-dicyanomethylene-4,5,5-trimethyl-2,5-dihydrofuran-3-carbonitrile, (VII). Comparison of the bond lengths in (VII) with the corresponding bonds in (I) and (II) reveals some subtle variations. The endocyclic double-bond lengths in (I) and (II) (C4═C7, entry 1 in Table 5), averaging 1.370 (3) Å, indicate more single-bond character in comparison with the parent (VII) molecule [1.343 (4) Å], with a significant bond difference [0.027 (5) Å]. Conversely, the adjacent endocyclic single-bond lengths (C6—C7, entry 2), averaging 1.437 (3) Å, are marginally shorter than the corresponding bond in (VII) [1.445 (4) Å]. Finally, the dicyanomethylene bonds (C2—C6, entry 3), averaging 1.370 (3) Å, are also marginally longer than that observed in (VII) [1.359 (4) Å]. The bond lengths in (VII) observed at 298 K would be expected to be longer than the low-temperature values presented here. Taking all these observations together it appears to us that charge from the acetanilide N atoms of both compounds is delocalized throughout the molecules from N4 to the dicyanomethylene C atom (C2), resulting in a consistent change in bond lengths across the conjugated π systems. The scale of this change is small, which is not surprising given the weak donating power of atom N4 as a result of the presence of the adjacent electron-withdrawing carbonyl group.

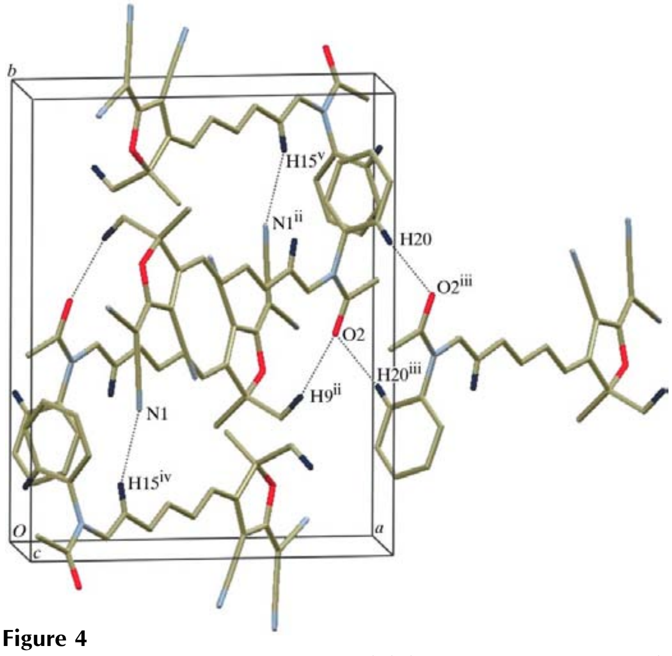

Figure 4
A partial packing diagram of the cell of (II) (*Mercury*; Bruno *et al.*, 2002), showing the layer structure with key intermolecular contacts (dotted lines). H atoms not involved in hydrogen bonding have been omitted for clarity. [Symmetry codes: (ii) $-x+1, -y+1, -z+1$; (iii) $-x+2, -y+1, -z+1$; (iv) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$; (v) $x, -y+\frac{3}{2}, z-\frac{1}{2}$.]

For (I), the crystal packing is dominated by strong C═C—H···O═C interactions of molecules related by inversion symmetry, involving a bifurcated carbonyl O atom (O2), and a C—H$_{\rm methyl}$···N$_{\rm cyano}$ hydrogen bond (Table 2 and Fig. 3). These three interactions result in layers lying approximately parallel to the *bc* plane. C—H···N$_{\rm cyano}$ bonding has been noted before in the related structure HESKIA (Kinnibrugh *et al.*, 2006), with H···N distances of 2.42 and 2.50 Å and C—H···N angles of 147 and 160°. Similar (C═C—H)$_2$···O bifurcated interactions are found in the CSD [*e.g.* GAMFOP (Krasnaya *et al.*, 1987), with H···O = 2.60 and 2.39 Å and H···O···H = 50°, compared with 59° here].

In (II), the molecules pack in layers parallel to the (101) plane (Fig. 4), the layers being joined by bifurcated C—H···O hydrogen bonds with phenyl and methyl atoms as donors and carbonyl atom O2 as acceptor (entries 2 and 3 in Table 4). A survey of C—H$_{\rm methyl}$···O interactions in the CSD indicates that these interactions are stronger than those commonly found, with typical H···O distances greater than 2.43 Å [*e.g.* DEFYOD (Bream *et al.*, 2006), with H···O = 2.45 Å and C—H···O = 155°]. C—H$_{\rm phenyl}$···O intermolecular interactions are more common, with H···O distances ranging upwards from 2.33 Å [*e.g.* YABFIR (Carella *et al.*, 2004), with H···O = 2.49 Å and C—H···O = 177°]. One C═C—H···N$_{\rm cyano}$ hydrogen bond provides the linkage between molecules within the layer (Fig. 4); such interactions occur with H···N distances ranging from 2.51 to 2.61 Å [*e.g.* CISDEN, with H···N = 2.56 Å and C—H···N = 150° (Murata *et al.*, 1984)].

These two structures are representative of our nonlinear optical chromophore precursors (Kay *et al.*, 2004), where the donor effect is observable but not large. Our future work will include examples where the acetanilide group is replaced with a more powerful donor, such as piperidine, and the magnitude of bond-length alternation in comparison with (I), (II) and (VII) is examined.

Experimental

The title compounds were prepared as described by Kay *et al.* (2004; compounds 11*b* and 11*c*, p. 1328). The crystals were recrystallized from dichloromethane/hexane [for (I)] and dichloromethane/ethyl acetate [for (II)].

Compound (I)

Crystal data

$C_{22}H_{18}N_4O_2$
M_r = 370.40
Orthorhombic, *Pbca*
a = 17.5731 (14) Å
b = 9.6510 (8) Å
c = 22.7965 (19) Å
V = 3866.2 (5) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 105 (2) K
0.75 × 0.20 × 0.04 mm

Data collection

Bruker–Nonius APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (Blessing, 1995)
$T_{\rm min}$ = 0.744, $T_{\rm max}$ = 0.997
23770 measured reflections
5714 independent reflections
3318 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.062

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.113$
$S = 1.00$
5714 reflections
325 parameters
All H-atom parameters refined
$\Delta\rho_{\max} = 0.36$ e Å^{-3}
$\Delta\rho_{\min} = -0.27$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

N4—C14	1.391 (2)	C13—C14	1.341 (2)
C11—C12	1.352 (2)	C15—C16	1.496 (2)
C12—C13	1.427 (2)		
C6—O1—C5	110.18 (11)	C12—C11—C4	126.40 (16)
C14—N4—C15	120.12 (13)	C11—C12—C13	121.59 (16)
N1—C1—C2	175.63 (19)	C14—C13—C12	121.96 (16)
N2—C3—C2	179.38 (19)	C13—C14—N4	123.39 (15)
C7—C4—C11—C12	−171.59 (17)	C15—N4—C14—C13	−179.47 (15)
C4—C11—C12—C13	174.27 (16)	C17—N4—C14—C13	4.0 (2)
C11—C12—C13—C14	−167.40 (16)	C17—N4—C15—C16	−0.4 (2)
C12—C13—C14—N4	174.85 (15)		

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
C8—H8C···N2$^{\rm i}$	1.005 (18)	2.627 (18)	3.603 (2)	163.8 (14)
C12—H12···O2$^{\rm ii}$	0.967 (16)	2.467 (16)	3.352 (2)	152.0 (13)
C14—H14···O2$^{\rm ii}$	0.990 (19)	2.476 (18)	3.358 (2)	148.2 (14)

Symmetry codes: (i) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x+1, -y, -z+1$.

Compound (II)

Crystal data

$C_{24}H_{20}N_4O_2$
$M_r = 396.44$
Monoclinic, $P2_1/c$
$a = 12.7040$ (15) Å
$b = 15.154$ (2) Å
$c = 11.7651$ (14) Å
$\beta = 107.440$ (7)°
$V = 2160.8$ (5) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.08$ mm^{-1}
$T = 95$ (2) K
0.40 × 0.10 × 0.04 mm

Data collection

Bruker–Nonius APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (Blessing, 1995)
$T_{\min} = 0.743$, $T_{\max} = 0.997$
22431 measured reflections
6628 independent reflections
1966 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.155$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.067$
$wR(F^2) = 0.169$
$S = 0.92$
6628 reflections
275 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.29$ e Å^{-3}
$\Delta\rho_{\min} = -0.25$ e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (II).

C11—C12	1.367 (4)	C14—C15	1.428 (4)
C12—C13	1.422 (4)	C15—C16	1.344 (4)
C13—C14	1.357 (4)		
C6—O1—C5	110.2 (2)	C11—C12—C13	122.2 (3)
C6—C2—C1	122.5 (3)	C14—C13—C12	125.4 (3)
N2—C3—C2	177.6 (3)	C13—C14—C15	121.8 (3)
O1—C5—C4	102.6 (2)	C16—C15—C14	122.6 (3)
C4—C7—C10	126.6 (3)	C15—C16—N4	124.2 (3)
C12—C11—C4	127.6 (3)		
C6—O1—C5—C4	−3.0 (3)	C11—C12—C13—C14	−177.6 (3)
C7—C4—C5—O1	4.3 (3)	C12—C13—C14—C15	−179.5 (3)
C7—C4—C11—C12	5.2 (5)	C13—C14—C15—C16	−178.8 (3)
C4—C11—C12—C13	−175.7 (3)	C14—C15—C16—N4	−178.8 (2)

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
C15—H15···N1$^{\rm i}$	0.95	2.57	3.466 (4)	156
C9—H9A···O2$^{\rm ii}$	0.98	2.37	3.277 (4)	153
C20—H20···O2$^{\rm iii}$	0.95	2.42	3.355 (4)	167

Symmetry codes: (i) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x+1, -y+1, -z+1$; (iii) $-x+2, -y+1, -z+1$.

All H atoms in (I) were freely refined with isotropic displacement parameters. All H atoms in (II) were positioned geometrically and allowed to ride on their respective parent atoms [C—H = 0.95 and 0.98 Å, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(phenyl C) or 1.5$U_{\rm eq}$(methyl C)], in response to a weaker data set with fewer observed data.

For both compounds, data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT* and *SADABS* (Sheldrick, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *Mercury* (Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

We thank Professor Ward T. Robinson and Dr J. Wikaira of the University of Canterbury, New Zealand, for their assistance.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ3086). Services for accessing these data are described at the back of the journal.

Table 5
Selected bond lengths (Å) in (I)–(VII) at temperature T (K) (see *Comment*).

	(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)
T	105	95	130	130	100	100	298
C4—C7	1.374 (2)	1.366 (4)	1.348 (5)	1.375 (4)	1.373 (3)	1.374 (3)	1.343 (4)
C6—C7	1.431 (2)	1.443 (4)	1.451 (5)	1.439 (4)	1.433 (3)	1.438 (3)	1.445 (4)
C2—C6	1.371 (2)	1.368 (4)	1.362 (7)	1.370 (4)	1.368 (3)	1.381 (3)	1.359 (4)
C6—O1	1.3320 (19)	1.332 (3)	1.331 (6)	1.328 (3)	1.331 (2)	1.333 (3)	1.333 (3)
C5—O1	1.4846 (18)	1.480 (3)	1.494 (4)	1.482 (3)	1.482 (2)	1.475 (3)	1.481 (4)
C10—N3	1.144 (2)	1.142 (4)	1.141 (6)	1.146 (4)	1.141 (3)	1.150 (3)	1.131 (4)
C4—C11	1.419 (2)	1.419 (4)	1.426 (6)	1.423 (4)	1.416 (3)	1.425 (3)	1.472 (4)
C11—C12	1.352 (2)	1.367 (4)	1.344 (8)	1.352 (4)	1.359 (3)	1.355 (3)	–

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