

Geometry and bond-length alternation in nonlinear optical materials. III. Structural parameters of two chromophores containing aromatizable donors¹

Graeme J. Gainsford,* M. Delower H. Bhuiyan and Andrew J. Kay

Industrial Research Limited, PO Box 31-310, Lower Hutt, New Zealand
Correspondence e-mail: g.gainsford@irl.cri.nz

Received 24 September 2008

Accepted 14 October 2008

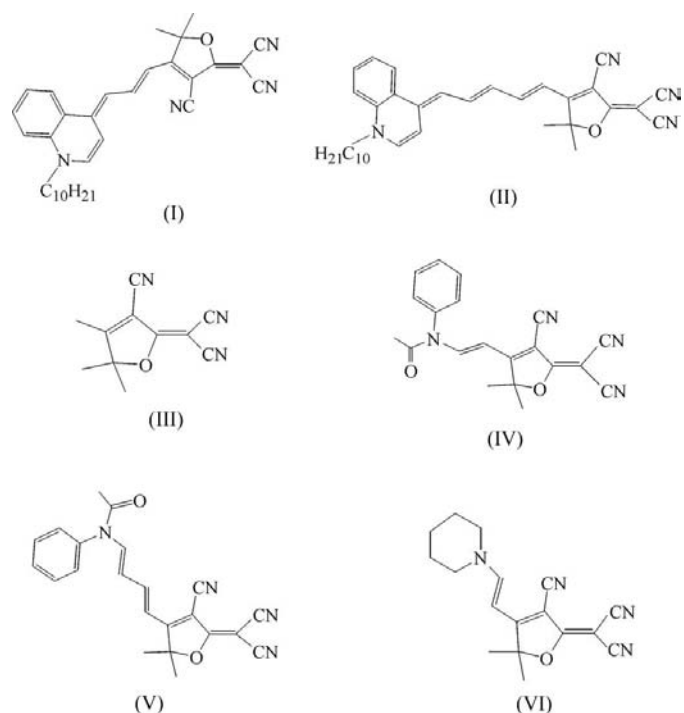
Online 25 October 2008

The planar component of 2-[3-cyano-4-[3-(1-decyl-1,4-dihydroquinolin-4-ylidene)prop-1-enyl]-5,5-dimethyl-2,5-dihydrofuran-2-ylidene]malononitrile, $C_{32}H_{46}N_4O$, (I), forms into layers parallel to the $(\bar{1}01)$ plane. The larger of the two spaces between layers is filled by the alkyl chains, giving a 'sandwich stack' appearance. The packing of 2-[3-cyano-4-[5-(1-decyl-1,4-dihydroquinolin-4-ylidene)penta-1,3-dienyl]-5,5-dimethyl-2,5-dihydrofuran-2-ylidene]malononitrile, $C_{34}H_{38}N_4O$, (II), which has partial disorder in the 1-decyl group, utilizes weak $C-H \cdots N$, $C-H \cdots O$ and $C-N \cdots \pi$ interactions in a three-dimensional 'herring-bone' array with molecular segments parallel to the (111) and $(\bar{1}\bar{1}\bar{1})$ planes. Different rotational isomers with respect to the polyene chain and the 5,5-dimethyl-2,5-dihydrofuran-2-ylidene link are observed in the two structures. The significance of the study lies in the delocalization of charge along the polyene chain and the supramolecular aggregation present, which highlight the difficulty in obtaining the noncentrosymmetric alignment required for high nonlinear optical (NLO) responses in zwitterionic chromophores.

Comment

The X-ray crystallographic and structural properties of zwitterionic dyes and their precursors have been a subject of some interest to us (Gainsford *et al.*, 2007; Gainsford, Bhuiyan & Kay, 2008*a,b*; Gainsford, Bhuiyan, Kay & Spek, 2008) due to their potential application in a number of photonic and optoelectronic devices (Dalton, 2002; Kay *et al.*, 2004). Basic structural parameters for a series of zwitterionic chromophores and their precursors were presented at a recent conference (Kay *et al.*, 2008) and we report here the complete

crystallographic data for two of these compounds, namely 2-[3-cyano-4-[3-(1-decyl-1,4-dihydroquinolin-4-ylidene)prop-1-enyl]-5,5-dimethyl-2,5-dihydrofuran-2-ylidene]malononitrile, (I), and 2-[3-cyano-4-[5-(1-decyl-1,4-dihydroquinolin-4-ylidene)penta-1,3-dienyl]-5,5-dimethyl-2,5-dihydrofuran-2-ylidene]malononitrile, (II), as part of our ongoing studies into how changes in bond order brought about by charge delocalization impact on the magnitude of the nonlinear optical (NLO) response. Given that such molecules are prone to aggregation, we were also very interested to know through structural study whether modifications to the polyene chain length or the substituent on the donor N atom could mitigate this potentially deleterious effect.



The asymmetric unit contents of compound (I) are shown in Fig. 1. Excluding the alkyl (1-decyl) chain atoms (C23–C32), the terminal cyano atoms N1 and C1, and the methyl groups C8 and C9 and their associated H atoms, the molecule is close to planar, with an r.m.s. deviation of 0.023 (2) Å for the 23 atoms. In the quinoline part, rings C17–C22 and C14–C16/N4/C17/C22 are each rigorously planar [r.m.s. deviations = 0.003 (2) and 0.006 (2) Å, respectively], with a dihedral angle between them of 1.69 (12)° and a puckering amplitude of 0.045 (3) Å (PLATON; Spek, 2003). The five-membered ring plane of atoms C4/C5/O1/C6/C7 [the (3-cyano-5,5-dimethyl-2,5-dihydrofuran-2-ylidene)propanedinitrile part, hereinafter CDFP] can also be regarded as planar in this case [r.m.s. deviation = 0.009 (2) Å]. The dicyanomethylene group (N1/C1–C3/N2) is planar but twisted by 5.69 (17)° with respect to the CDFP group.

The almost-planar components of the molecules in (I) (excluding the alkyl chain atoms C23–C32) are arranged into nearly planar layers parallel to the $(\bar{1}01)$ plane, with only weak and possibly adventitious $C-H \cdots N(\text{cyano})$ contacts between them (Table 1). The larger of the unequal spaces between the

¹ Part II: Gainsford, Bhuiyan & Kay (2008*a*).

layers (~ 10.3 Å, compared with ~ 3.4 Å for the smaller) are filled by the alkyl chains, resulting in a 'sandwich stack' appearance, with the alkyl chains providing the filling (Fig. 2).

Compound (II) crystallizes as the alternative (*transoid*) rotamer (by rotation about the C4–C11 bond), as shown in Figs. 1 and 3 and quantified by the C7–C4–C11–C12 torsion angles (Table 3). Gas-phase density functional theory calculations using the *Amsterdam Density Functional* program system, *ADF* (SCM, 2007), indicate that the *cisoid* rotamer of (II) is very similar in energy to the *transoid* isomer (differing

by less than 0.6 kcal mol $^{-1}$; 1 kcal mol $^{-1} = 4.184$ kJ mol $^{-1}$). By contrast, the *transoid* rotamer for (I) is calculated to be some 4 kcal mol $^{-1}$ more stable than the *cisoid* counterpart. This implies that the observed structure in (I) is possibly determined by crystal packing forces. Also unlike (I), the non-alkyl chain atoms in (II) are twisted from planarity; this is shown by the dihedral angles between the CDFP ring and the polyene and quinoline planes (Table 3, entries 1 and 2). The CDFP ring is planar [r.m.s. deviation = 0.017 (2) Å], but has some bond-distance deviations from those in (I), notably in the atoms bound to C7 (Table 3). The dicyanomethylene group (N1/C1–

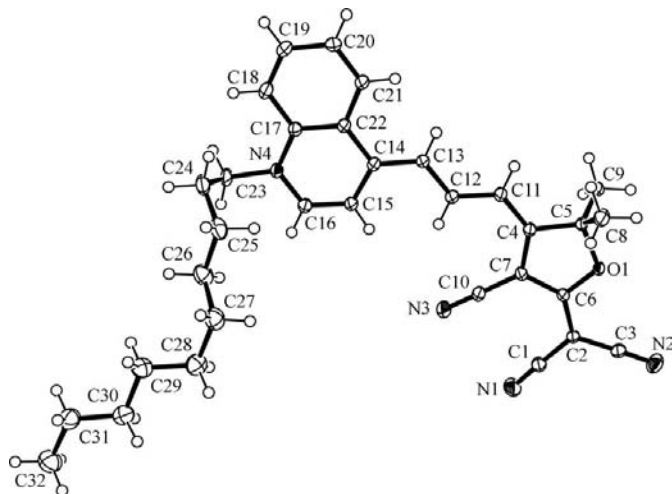


Figure 1
The molecular structure of the asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

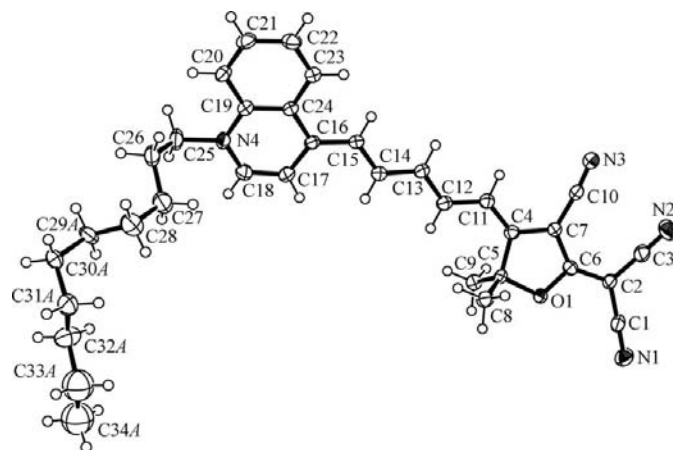


Figure 3
The molecular structure of the asymmetric unit of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Only the major conformer atoms (set A) are shown.

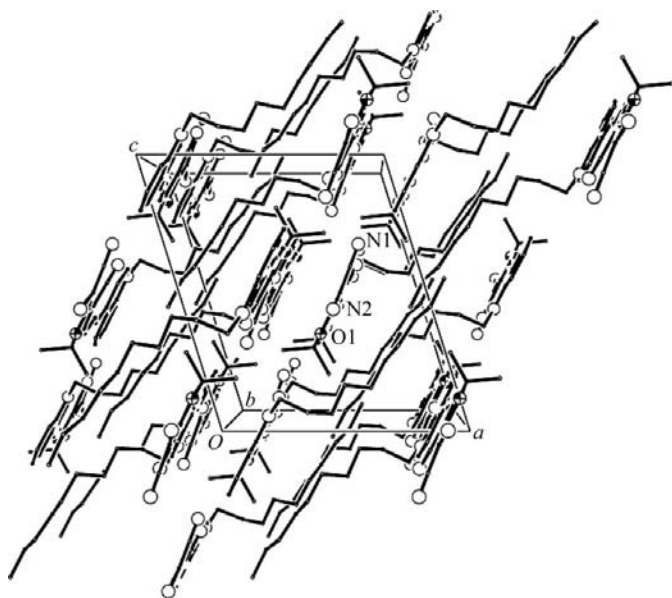


Figure 2
A 'sandwich' packing diagram (see *Comment*) of the cell of (I), viewed approximately down the *b* axis. For clarity, stick bonding is used, with all H atoms excluded. N and O atoms are depicted as open and filled circles, respectively. Three asymmetric unit atom labels are given.

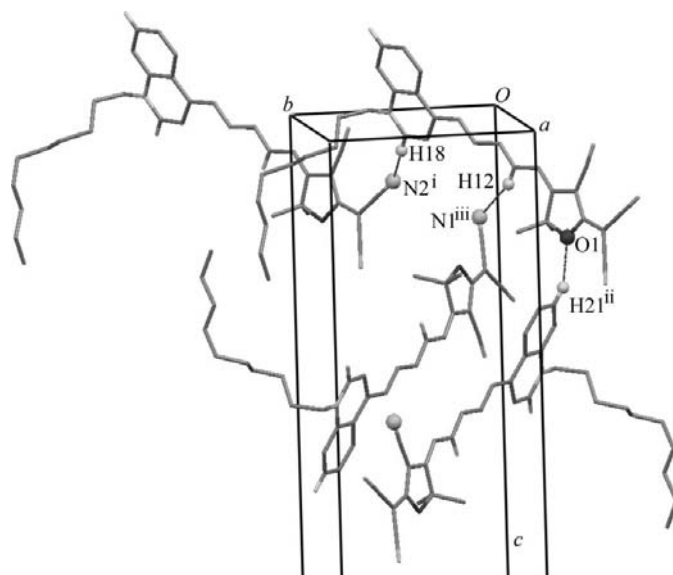


Figure 4
A partial packing diagram of the cell of (II), viewed approximately down the *a* axis, showing key intermolecular interactions. For clarity, only H atoms involved in hydrogen bonds (dashed lines) and disordered atom set A are pictured. All labelled contact atoms and other atoms are shown in ball and stick forms, respectively (see Table 2). [Symmetry codes: (i) $x - 1, y + 1, z$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (iii) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.]

C3/N2) has a twist from the CDFP plane of $6.74 (16)^\circ$, similar to (I). Data for the parent CDFP structure, (III), 2-dicyanomethylene-4,5,5-trimethylene-4,5,5-trimethyl-2,5-dihydrofuran-3-carbonitrile [Cambridge Structural Database (Allen, 2002) refcode PANLUM (Li *et al.*, 2005)] are also given in Table 3.

In (II), there are hydrogen-bond interactions (Fig. 4) between CDFP atom O1 and quinoline atom H21, between polyene atom H12 and cyano atom N1, and between quinoline atom H18 and cyano atom N2, as well as a weak interaction between the π orbitals of the adjacent quinoline ring and one set of CDFP cyano atoms (Table 2, last entry). The packing has elements of the well known 'herring-bone' structure, with the π and $N2 \cdots H18$ links (Table 2) binding adjacent molecules parallel to the $(\bar{1}11)$ plane, and the $H21 \cdots O1$ and $N1 \cdots H12$ interactions providing crosslinks to the other herring-bone set which are parallel to the (111) plane.

Both (I) and (II) show considerable delocalization of charge along the polyene/CDFP chain, with bond-length alternation (BLA) values (Marder *et al.*, 1993) of -0.015 and -0.042 \AA , respectively, compared with the free CDFP value of 0.108 \AA in (III) (Li *et al.*, 2005). It should be noted that the BLA values were calculated by considering the bonds C2–C6 to C12–C13 in (I) and C2–C6 to C14–C15 in (II), inclusive. The degrees of BLA in (I) and (II) are considerably different from the values found for analogous compounds with far weaker donors, such as those derived from acetanilide and piperidine (see scheme): 0.073 \AA in (IV) (Gainsford, Bhuiyan & Kay, 2008*a*), 0.060 \AA in (V) (Gainsford *et al.*, 2007) and 0.000 \AA in (VI) (Gainsford, Bhuiyan & Kay, 2008*a*). This is to be expected because compounds (I) and (II) here, with their dihydroquinolinylidene aromatic donor systems, will allow additional charge delocalization to occur in concert with their aromaticity. We note that the first hyperpolarizabilities of two analogues of (I) and (II) (*N*-methyl rather than *N*-decyl) have been reported (Kay *et al.*, 2004) as 440 and $560 \times 10^{-30} \text{ e.s.u.}$, respectively. Thus, our findings for (I) and (II) are in line with the theory that the closer variances in BLA are to approximately -0.05 \AA , the greater the NLO response (Marder *et al.*, 1993).

Our final comment concerns the intramolecular parameters affected by the alternative *cisoid/transoid* conformations. In the crystal structures of 12 compounds containing the CDFP/polyene moiety which we have studied, the *transoid* conformation is found in seven. The average of the close methyl-H \cdots polyene-H intramolecular interactions [*e.g.* $H12 \cdots H9B$ in (II)] for well characterized models is $2.27 (5) \text{ \AA}$ for the *transoid* and $2.51 (4) \text{ \AA}$ for the *cisoid* [*e.g.* $H11 \cdots H8B$ in (I)]. The interaction distances of the C11 polyene H atom with cyano atom C10 average to $2.68 (4)$ and $2.54 (6) \text{ \AA}$, respectively. We conclude that the shorter contact distances observed in the *transoid* molecules are not close enough to encourage the molecules into favouring the *cisoid* conformation.

Experimental

Compounds (I) and (II) were prepared *via* condensation of 1-decyl-4-methylquinolinium bromide (Ashwell *et al.*, 1990) with either [4-(2-

acetanilidoethenyl)-3-cyano-5,5-dimethyl-2(5*H*)-furanlydene]-propanedinitrile (compound 11*a*) or [4-(2-acetanilido-*trans*-1,3-butadienyl)-3-cyano-5,5-dimethyl-2(5*H*)-furanlydene]propanedinitrile (compound 11*b*) using the procedure previously described by Kay *et al.* (2004), method B, with methanol as solvent. The resultant powders were washed with copious quantities of hot water, followed by small portions of cold methanol to afford the target molecules as coloured powders. Recrystallization for (I) was from methanol–dichloromethane (1:1 *v/v*) and for (II) was from acetone.

Compound (I)

Crystal data

$C_{32}H_{36}N_4O$	$V = 2816.5 (2) \text{ \AA}^3$
$M_r = 492.65$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 11.9830 (6) \text{ \AA}$	$\mu = 0.07 \text{ mm}^{-1}$
$b = 17.5374 (8) \text{ \AA}$	$T = 106 (2) \text{ K}$
$c = 14.0363 (7) \text{ \AA}$	$0.90 \times 0.70 \times 0.03 \text{ mm}$
$\beta = 107.289 (3)^\circ$	

Data collection

Bruker–Nonius APEXII CCD area-detector diffractometer	8166 independent reflections
53106 measured reflections	3764 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.128$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.055$	337 parameters
$wR(F^2) = 0.203$	H-atom parameters constrained
$S = 1.08$	$\Delta\rho_{\text{max}} = 0.48 \text{ e \AA}^{-3}$
8166 reflections	$\Delta\rho_{\text{min}} = -0.31 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bond and short-contact geometry (\AA , $^\circ$) for (I).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$C9-H9B \cdots N3^i$	0.98	2.45	$3.367 (3)$	156
$C21-H21 \cdots N1^i$	0.95	2.53	$3.424 (3)$	158

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

Compound (II)

Crystal data

$C_{34}H_{38}N_4O$	$V = 3015.4 (3) \text{ \AA}^3$
$M_r = 518.68$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 12.5261 (7) \text{ \AA}$	$\mu = 0.07 \text{ mm}^{-1}$
$b = 9.8849 (5) \text{ \AA}$	$T = 97 (2) \text{ K}$
$c = 24.3711 (13) \text{ \AA}$	$0.26 \times 0.24 \times 0.10 \text{ mm}$
$\beta = 92.211 (3)^\circ$	

Data collection

Bruker–Nonius APEXII CCD area-detector diffractometer	5267 independent reflections
18727 measured reflections	2887 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.083$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.054$	24 restraints
$wR(F^2) = 0.148$	H-atom parameters constrained
$S = 0.95$	$\Delta\rho_{\text{max}} = 0.39 \text{ e \AA}^{-3}$
5267 reflections	$\Delta\rho_{\text{min}} = -0.34 \text{ e \AA}^{-3}$
370 parameters	

Table 2

Hydrogen-bond and short-contact geometry (Å, °) for (II).

Cg2 is the centroid of atoms C16–C18/N4/C19/C24

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C18–H18 \cdots N2 ⁱ	0.95	2.43	3.371 (4)	169
C21–H21 \cdots O1 ⁱⁱ	0.95	2.49	3.328 (3)	146
C12–H12 \cdots N1 ⁱⁱⁱ	0.95	2.63	3.527 (4)	158
C10–N3 \cdots Cg2 ^{iv}	1.15 (1)	3.13 (1)	3.481 (3)	98 (2)

Symmetry codes: (i) $x-1, y+1, z$; (ii) $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (iii) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (iv) $-x+1, -y, -z$.**Table 3**Selected bond lengths and angles (Å, °) in (I), (II) and (III) (Li *et al.*, 2005).Dihedral angles: Dih¹ = polyene chain [e.g. C11–C15 in (II)] and CDFP ring; Dih² = quinoline [e.g. C16–C24 in (II)] and CDFP ring (see *Comment*).

Bonds/angles	(I)	(II)	(III) (relabelled)
Dih ¹	0.7 (3)	12.3 (3)	–
Dih ²	0.9 (2)	24.44 (12)	–
C2–C6	1.391 (3)	1.396 (4)	1.359 (4)
C6–C7	1.413 (3)	1.394 (3)	1.445 (4)
C4–C7	1.406 (3)	1.423 (4)	1.343 (4)
C4–C11	1.381 (3)	1.361 (4)	1.472 (4)
C11–C12	1.412 (3)	1.411 (4)	–
C12–C13	1.375 (3)	1.361 (4)	–
C13–C14	1.423 (3)	1.409 (4)	–
C14–C15	1.401 (3)	1.356 (3)	–
C15–C16	1.361 (3)	1.428 (4)	–
C6–O1	1.341 (3)	1.352 (3)	1.333 (3)
C5–O1	1.477 (3)	1.488 (3)	1.481 (3)
C4–C7–C6	109.1 (2)	109.8 (2)	109.4 (3)
C7–C6–C2	131.3 (2)	132.4 (2)	131.0 (3)
C11–C4–C7	132.8 (2)	125.8 (2)	128.6 (3)
C4–C11–C12–C13	179.0 (3)	172.9 (2)	–
C7–C4–C11–C12	1.0 (5)	–176.6 (2)	–

On the basis of average $I/\sigma(I)$ analysis, data were excluded for $\theta > 30^\circ$ for (I) and excluded for $\theta > 25^\circ$ for (II). For (I) and (II), respectively, 8 and 17 reflections affected by the backstop or clearly outlier data were omitted from the refinements using OMIT (*SHELXL97*; Sheldrick, 2008), and a further 5 and 7 reflections within $\theta \leq 25^\circ$ were either not measured or failed to meet processing requirements. All methyl and tertiary H atoms were treated as riding, with C–H = 0.95–0.99 Å and $U_{\text{iso}}(\text{H}) = 1.5$ or 1.2, respectively, times U_{eq} of their parent atom. All non-H atoms were refined with anisotropic displacement parameters in (I). In compound (II), the alkyl atom chain was disordered into two ‘strands’, starting at C29 and ending at C34. Each strand, *A* or *B*, was refined with a common complementary occupancy to 0.683 (4):0.317 (4), with all *B* strand atoms and C33*A* and C34*A* refined with isotropic displacement parameters. Atom C31*B* was given a fixed U value of 0.14 Å² (the

average U value of adjacent *B* strand atoms). Finally, the bond distances between identical atoms in the two strands (e.g. C33*A*–C34*A* and C33*B*–C34*B*) and the C–C–C angles (e.g. C31*A*–C32*A*–C33*A* and C31*B*–C32*B*–C33*B*) were restrained to the same common values with an s.u. of 0.02 using the *SHELXL97* SADI command. In total, 24 restraints were used in (II).

For both compounds, data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008). Molecular graphics: *ORTEP-3* in *WinGX* (Farrugia, 1997) for (I); *ORTEP-3* in *WinGX* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006) for (II). For both compounds, software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

The authors thank Drs J. Wikaira and C. Fitchett of the University of Canterbury for their assistance in the data collection.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3060). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Ashwell, G. J., Dawnay, E. J. C., Kuczynski, A. P., Szablewski, M., Sandy, I. M., Bryce, M. R., Grainger, A. M. & Hasan, M. (1990). *J. Chem. Soc. Faraday Trans.* **86**, 1117–1121.
- Bruker (2005). *APEX2* (Version 2.0-2), *SAINT* (Version 7.12A) and *SADABS* (Version 2004/1). Bruker AXS Inc., Madison, Wisconsin, USA.
- Dalton, L. (2002). *Polymers for Photonics Applications 1, Advances in Polymer Science*, edited by K. S. Lee, pp. 1–86. Heidelberg: Springer-Verlag.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Gainsford, G. J., Bhuiyan, M. D. H. & Kay, A. J. (2007). *Acta Cryst.* **C63**, o633–o637.
- Gainsford, G. J., Bhuiyan, M. D. H. & Kay, A. J. (2008a). *Acta Cryst.* **C64**, o195–o198.
- Gainsford, G. J., Bhuiyan, M. D. H. & Kay, A. J. (2008b). *Acta Cryst.* **E64**, o2036–o2037.
- Gainsford, G. J., Bhuiyan, M. D. H., Kay, A. J. & Spek, A. L. (2008). *Acta Cryst.* **E64**, o503.
- Kay, A. J., Gainsford, G. J. & Bhuiyan, M. D. H. (2008). *ICONO10*, Santa Fe, New Mexico, USA, 18–23 May 2008. Abstract booklet p. 141.
- Kay, A. J., Woolhouse, A. D., Zhao, Y. & Clays, K. (2004). *J. Mater. Chem.* **14**, 1321–1330.
- Li, S.-Y., Song, Y.-Y., You, Z.-L., Wen, Y.-W. & Qin, J.-G. (2005). *Acta Cryst.* **E61**, o2093–o2095.
- Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
- Marder, S. R., Perry, J. W., Tiemann, B. G., Gorman, C. B., Gilmour, S., Biddle, S. L. & Bourhill, G. (1993). *J. Am. Chem. Soc.* **115**, 2524–2526.
- SCM (2007). *ADF* Version 2007.01. SCM NV, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands. <http://www.scm.com>
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.