

Geometry and bond-length alternation in nonlinear optical materials. II. Effects of donor strength in two push–pull molecules

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

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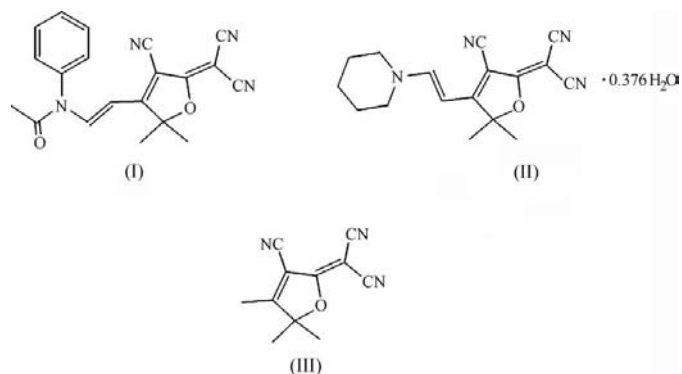
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The compounds *N*-[2-(4-cyano-5-dicyanomethylene-2,2-dimethyl-2,5-dihydrofuran-3-yl)vinyl]-*N*-phenylacetamide, C₂₀H₁₆N₄O₂, (I), and 2-[3-cyano-5,5-dimethyl-4-[2-(piperidin-1-yl)vinyl]-2,5-dihydrofuran-2-ylidene]malononitrile 0.376-hydrate, C₁₇H₁₈N₄O·0.376H₂O, (II), are novel push–pull molecules. The significant bonding changes in the polyene chain compared with the parent molecule 2-dicyanomethylene-4,5,5-trimethyl-2,5-dihydrofuran-3-carbonitrile are consistent with the relative electron-donating properties of the acetanilido and piperidine groups. The packing of (I) utilizes one phenyl–cyano C–H···N and two phenyl–carbonyl C–H···O hydrogen bonds. Compound (II) crystallizes with a partial water molecule (0.376H₂O), consistent with cell packing that is dominated by attractive C–H···N(cyano) interactions. These compounds are precursors to novel nonlinear optical chromophores, studied to assess the impact of donor strength and the extent of conjugation on bond-length alternation, crystal packing and aggregation.

Comment

Organic nonlinear optical materials continue to gain attention owing to their potential use in next generation photonic and optoelectronic devices. These devices will find applications in areas such as telecommunications and computing, and will be cheaper and easier to fabricate, have faster operating speeds and lower drive voltages than current devices based on inorganic materials such as lithium niobate (Dalton, 2002). We have reported the synthesis of a number of high figure-of-merit chromophores for nonlinear optics (Kay *et al.*, 2004), as well as the X-ray crystallographic and structural properties of two of the crucial dye precursors used (Gainsford *et al.*, 2007). We now report the structural properties of two related derivatives, one involving the acetanilido donor unit, (I), and the other involving the more powerful electron-donating nucleus

piperidine, (II), in which the conjugated π -system between donor and acceptor has been shortened to just two C atoms.



The asymmetric unit contents of the title compounds (I) and (II) are shown in Figs. 1 and 2, respectively, with selected dimensions in Tables 1, 3 and 5. The structures have different configurations with regard to the C11=C12 bond (so atoms C7 and C12 are *cis* and *trans* with respect to the C4–C11 bond, as indicated by the C7–C4–C11=C12 torsion angles. This alternative configurational arrangement has been

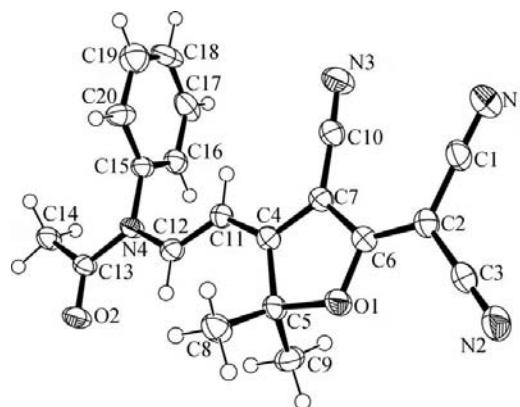


Figure 1
The molecular structure of the independent molecule of (I) (Farrugia, 1997); displacement ellipsoids are shown at the 50% probability level.

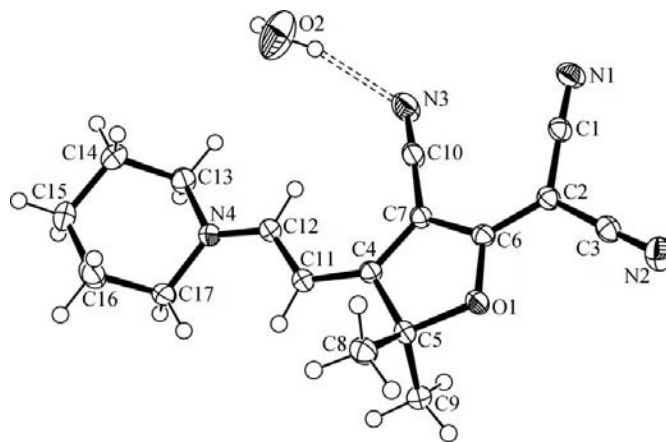


Figure 2
The molecular structure of the independent molecule of (II) (Farrugia, 1997); displacement ellipsoids are shown at the 50% probability level. One hydrogen bond is shown by dashed lines (see Table 4 for details).

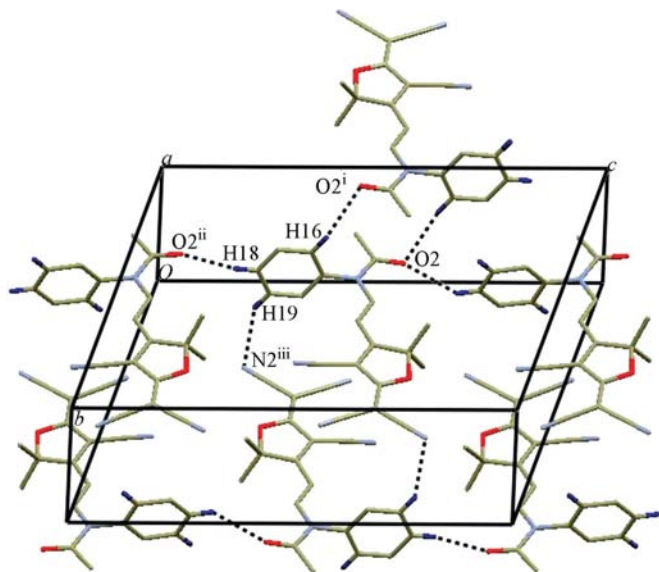


Figure 3
A partial packing diagram of (I) (Mercury; Bruno *et al.*, 2002). Only H atoms involved in selected hydrogen bonds (dashed lines) are shown. See Table 2 for symmetry codes.

observed before for closely related precursors (Gainsford *et al.*, 2007). In this case, the C4–C7–C11 angle has increased [by 9.7 (2)°], possibly in response to packing interactions involving atoms H11 and N3 (see below).

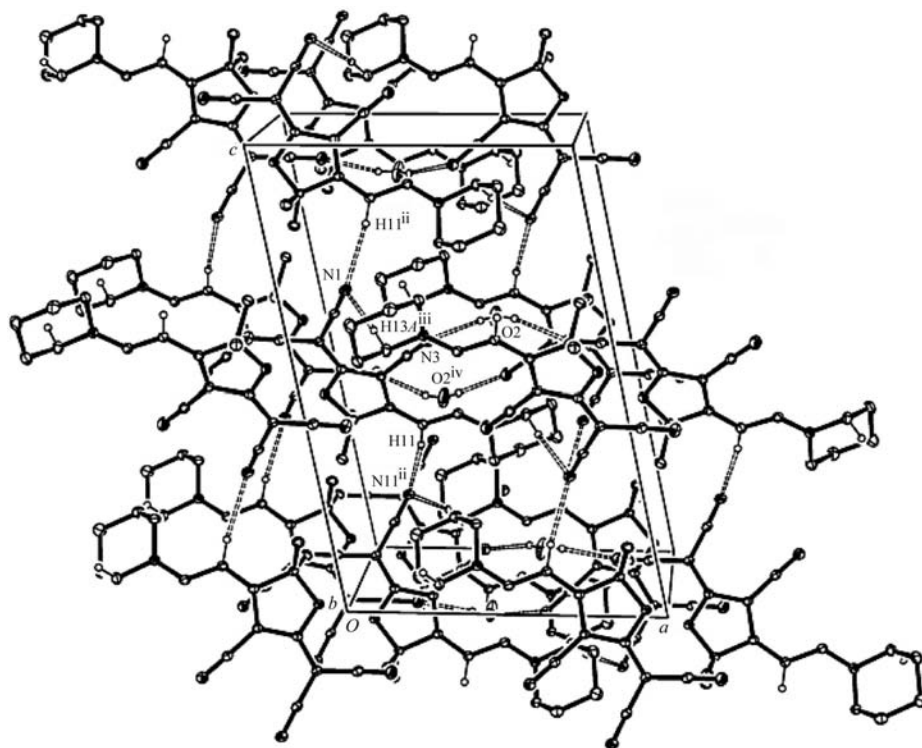


Figure 4
The packing of (II) (Farrugia, 1997), viewed down the *b* axis. Only H atoms involved in selected hydrogen bonds (dashed lines) are shown. [Symmetry code: (iv) $-x + 1, -y + 1, -z + 1$; for other symmetry designations, see Table 4.]

The comparable planar groups in (I) and (II) are the ‘CDFP’ five-membered ring (atoms O1 and C4–C7), with an r.m.s. deviation (r.m.s.d.) of 0.0018 (11) Å for (I) and 0.0099 (7) Å for (II), and the ‘polyene’ plane defined by atoms N4, C11, C12 and C4 [r.m.s.d. of 0.0023 (9) Å for (I) and 0.0019 (6) Å for (II)]. These two planes are twisted slightly with respect to each other by 2.56 (6) and 2.31 (16)° for (I) and (II), respectively. The phenyl ring in (I) makes an angle of 82.99 (11)° with the polyene plane. The piperidinyl group in (II) adopts a pure chair conformation [Cremer & Pople (1975) parameters $Q = 0.5611$ (14) Å, $\theta = 179.00$ (14)° and $\varphi = 358$ (12)°], with an r.m.s.d. of 0.0003 (7) Å for the ‘seat’ atoms C13, C14, C16 and C17, and with the head and foot atoms N4 and C15 lying on opposite sides of this plane at distances of 0.6307 (16) and 0.664 (2) Å. The ‘seat’ atom plane forms an angle of 53.48 (6)° with the CDFP plane. The angle between the mean plane through the piperidinyl ring and the CDFP plane is 36.02 (5)°.

The essentially planar 2-dicyanomethylene-4,5,5-trimethyl-2,5-dihydrofuran-3-carbonitrile fragments (*i.e.* excluding the phenyl ring) in (I) form layers approximately parallel to the *ac* plane linked by the phenyl–carbonyl C18–H18···O2($x, -y + \frac{3}{2}, z - \frac{1}{2}$) interaction (Table 2 and Fig. 3). Intralayer binding is provided by one phenyl–cyano C–H···N and one phenyl–carbonyl C–H···O=C hydrogen bond. Both of these interaction types have been observed before. Few *meta*-phenyl C–H···N interactions have been reported [*e.g.* from the Cambridge Structural Database (Version 5.28 with May 2007 updates; Allen, 2002), refcodes ETIDAM (Lu *et al.*, 2004) with H···N = 2.59 Å and C–H···N = 145°, and SOXRAY (Quinn *et al.*, 1991) with H···N = 2.52 Å and C–H···N = 130°]. However, there are many examples of the phenyl–carbonyl C–H···O=C interaction (see Gainsford *et al.*, 2007, and references therein). There are no intermolecular interactions in (I) involving the vinyl H atoms (H11 and H12), as both are effectively shielded by the adjacent atoms.

The crystal packing in (II) is dominated by strong C–H···N(cyano) hydrogen bonds, which link molecules into undulating layers approximately parallel to the *ac* plane (Table 4 and Fig. 4). The C11–H11···N1($x, -y + \frac{1}{2}, z - \frac{1}{2}$) interaction binds molecules into these layers; we have observed this strong interaction before (H···N = 2.57 Å and C–H···N = 156°; Gainsford *et al.*, 2007). A hydrogen bond involving a methylene group, *viz.* C13–H13A···N1($-x + 1, -y, -z + 1$), provides a strong crosslink to the layers. Atom N1 also has two further

contacts (not shown in Fig. 4 for clarity) to the same molecule as the stronger hydrogen bond (entry 3, Table 4) which are shorter than the sum of the van der Waals radii (2.75 Å), viz. to methylene atom H17A (entry 5, Table 4) on the piperidinyll ring and to methyl atom H8B [entry 6, Table 4; this interaction type is observed in the packing of the parent structure PANLUM (Li *et al.*, 2005), (III), with H...N = 2.55 Å]. The water molecule is bound between molecules in adjacent layers by cyano N-donor atoms; it does not provide the key attractive binding force, but fits neatly into a hole in the crystal structure (Fig. 4), which explains its partial occupancy of 0.376 (6).

A comparison of key bond lengths and angles with those in (III) is given in Table 5. Note that all the atoms of (III) are constrained to a crystallographic mirror plane, except for the (mirror-related) methyl groups in the 5-position. Examination of the endocyclic dihydrofuranylidene double bonds (C4=C7) shows that in (I) and (II) these bonds exhibit more single-bond character than the corresponding bond in (III). On the other hand, the adjacent endocyclic nominally single bond (C6–C7) in (II) is shorter than that in (III) by 0.035 (5) Å. Notably, when comparing these two bonds (within each structure), we find that in (II) they are indistinguishable in length, while they differ significantly in (I) and (III), viz. by 0.069 (4) and 0.102 (6) Å, respectively. Furthermore, the dicyanomethylidene bonds (C2=C6) in both (I) and (II) are longer than those reported for (III); again the difference is marginal in (I) but significant in (II) [0.031 (4) Å]. The exocyclic nominally single bond in (I) (C4–C11) is some 0.039 (3) Å longer than the analogous bond in (II). The polyene double bond in (I) is shorter [0.053 (4) Å] than the analogous bond in (II). Finally the C–N bond (C12–N4) in (I) is longer by 0.069 (3) Å than the C–N bond in (II) (Tables 1 and 3).

Taken together, these observations clearly indicate that charge from the N-donor atoms in (I) and (II) is delocalized across the molecules to the dicyanomethylidene C atom, the delocalization being more pronounced in (II), as reflected in the larger changes in bond length and hence bond order observed for this molecule. This is to be expected given the greater donor strength of the piperidine nucleus in comparison with the acetanilido functional group. Indeed, the virtual homogeneity of bond orders across the π -conjugated system in (II) would suggest that the charge is evenly delocalized, and hence the ground state is moderately (~50%) zwitterionic. We are currently undertaking theoretical studies to model the geometries of these molecules in order to establish the efficacy of the (DFT) calculations and to predict the hyperpolarizabilities of these, and related, systems.

Experimental

Compound (I) was prepared as described previously (compound 11a; Kay *et al.*, 2004) and recrystallized from ethanol. To a solution of (I) (5.8 mmol) in ethanol (30 ml) was added an equimolar quantity of piperidine. The solution was refluxed for 1 h and cooled. The product, (II), was collected by filtration, washed with ethanol and recrystallized from ethanol.

Compound (I)

Crystal data

$C_{20}H_{16}N_4O_2$	$V = 1772.5 (6) \text{ \AA}^3$
$M_r = 344.37$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 14.417 (3) \text{ \AA}$	$\mu = 0.09 \text{ mm}^{-1}$
$b = 6.9224 (12) \text{ \AA}$	$T = 120 (2) \text{ K}$
$c = 18.508 (4) \text{ \AA}$	$0.53 \times 0.15 \times 0.04 \text{ mm}$
$\beta = 106.334 (6)^\circ$	

Data collection

Bruker–Nonius APEXII CCD area-detector diffractometer	5152 independent reflections
19450 measured reflections	2017 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.174$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.060$	233 parameters
$wR(F^2) = 0.132$	H-atom parameters constrained
$S = 0.83$	$\Delta\rho_{\text{max}} = 0.47 \text{ e \AA}^{-3}$
5152 reflections	$\Delta\rho_{\text{min}} = -0.39 \text{ e \AA}^{-3}$

Compound (II)

Crystal data

$C_{17}H_{18}N_4O \cdot 0.376H_2O$	$V = 1672.53 (9) \text{ \AA}^3$
$M_r = 301.13$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 11.3193 (3) \text{ \AA}$	$\mu = 0.08 \text{ mm}^{-1}$
$b = 8.8981 (3) \text{ \AA}$	$T = 99 (2) \text{ K}$
$c = 16.9338 (5) \text{ \AA}$	$0.65 \times 0.32 \times 0.15 \text{ mm}$
$\beta = 101.298 (2)^\circ$	

Data collection

Bruker–Nonius APEXII CCD area-detector diffractometer	28794 measured reflections
Absorption correction: multi-scan (Blessing, 1995)	4855 independent reflections
$T_{\text{min}} = 0.775, T_{\text{max}} = 0.988$	3607 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.035$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.118$	$\Delta\rho_{\text{max}} = 0.41 \text{ e \AA}^{-3}$
$S = 1.05$	$\Delta\rho_{\text{min}} = -0.19 \text{ e \AA}^{-3}$
4855 reflections	
217 parameters	

Table 1

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

N4–C12	1.382 (2)	C4–C11	1.423 (2)
C2–C6	1.363 (3)	C11–C12	1.342 (3)
C7–C4–C11–C12	–178.49 (19)	C4–C11–C12–N4	–179.55 (17)

Table 2

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C16–H16...O2 ⁱ	0.95	2.60	3.448 (3)	149
C18–H18...O2 ⁱⁱ	0.95	2.58	3.385 (3)	143
C19–H19...N2 ⁱⁱⁱ	0.95	2.54	3.315 (3)	139

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

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

N4—C12	1.3130 (14)	C4—C11	1.3837 (15)
C2—C6	1.3899 (15)	C11—C12	1.3951 (16)
C7—C4—C11—C12	−0.9 (2)	C12—N4—C13—C14	−123.80 (12)
C4—C11—C12—N4	−179.60 (11)	C12—N4—C17—C16	123.93 (13)

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O2—H2A...N3	0.80 (7)	2.11 (7)	2.864 (4)	158 (7)
O2—H2B...N2 ⁱ	0.75 (8)	2.22 (8)	2.951 (4)	167 (8)
C11—H11...N1 ⁱⁱ	0.95	2.53	3.4725 (16)	172
C13—H13A...N1 ⁱⁱⁱ	0.99	2.52	3.4997 (17)	169
C17—H17A...N1 ⁱⁱ	0.99	2.68	3.6584 (17)	172
C8—H8B...N1 ⁱⁱ	0.98	2.69	3.5900 (16)	153

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

Table 5
Selected bond lengths and angles (Å, °) in (I), (II) and (III) at various temperatures *T* (K).

	(I) <i>T</i> = 120	(II) <i>T</i> = 99	(III) <i>T</i> = 298
C4—C7	1.372 (3)	1.4070 (15)	1.343 (4)
C6—C7	1.441 (2)	1.4099 (15)	1.445 (4)
C2—C6	1.363 (3)	1.3899 (15)	1.359 (4)
C6—O1	1.329 (2)	1.3410 (13)	1.333 (3)
C5—O1	1.492 (2)	1.4742 (13)	1.481 (4)
C10—N3	1.147 (2)	1.1502 (15)	1.131 (4)
C4—C11	1.423 (2)	1.3837 (15)	1.472 (4)
C11—C12	1.342 (3)	1.3951 (16)	—
C12—N4	1.382 (2)	1.3130 (14)	—
C4—C7—C6	109.00 (18)	108.75 (9)	109.4 (2)
C7—C6—C2	131.2 (2)	131.51 (10)	131.1 (3)
C5—C4—C7	108.60 (16)	106.65 (9)	109.0 (2)
C7—C4—C11	123.95 (18)	133.61 (11)	128.6 (3)

All H atoms bound to C atoms were constrained to their expected geometries (C—H = 0.95–0.99 Å). The positions of H atoms on water atom O2 in (II) were refined freely after assignment from difference

maps, consistent with O—H...N hydrogen bonds. The occupancy of the water molecule was found by refinement with an isotropic $U_{\text{iso}}(\text{O})$ value of 0.03 Å²; this parameter was then refined, with O2 allowed anisotropic displacement parameters. Attempts to force the O2—H distances to longer values were not supported by the data. All $U_{\text{iso}}(\text{H})$ values were set at 1.5 (methyl) or 1.2 (other H atoms) times U_{eq} of the parent atom. Outlier reflections in (I) (020 and 040) and (II) ($\bar{1}12$) were omitted from the refinements.

For both compounds, data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT* and *SADABS* (Sheldrick, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3054). Services for accessing these data are described at the back of the journal.

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