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Induction of chirality in 4,4'-azopyridine by halogen-bonding interaction with optically active ditopic donors

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Optically active ditopic halogen bond donors bearing two 4-iodotetrafluorophenyl groups were obtained by reaction of chiral diols with iodopentafluorobenzene. Co-crystallization of these donors with *anti*-4,4'-azopyridine afforded binary complexes containing infinite chains of the alternating component molecules connected by halogen bonds. The solid state CD measurements confirmed that complexation induces optical activity of the azo chromophore due to the twisting of the aryl–N=N system or external chiral perturbation exerted by host molecules.

host and guest molecules.¹³

state CD measurements.

Introduction

The controlled arrangement of molecules in a predictable fashion to generate supramolecular assemblies that can exhibit properties not presented by isolated components long has been an area of interest in material chemistry.1 Many multicomponent supramolecular structures have been designed and obtained using non-covalent interactions such as hydrogen and halogen bonds or π - π interactions.²⁻⁴ Particularly, halogen bonding has attracted intense interest in recent years as an useful tool in the field of crystal engineering.⁴ It has been presented as an attractive interaction between an electrophilic region of halogen atom (o-hole) and nucleophilic region of another molecule.⁵ Due to the strength and directionality of halogen bonding interactions they could be used as an alternative to hydrogen bonding.⁴ Thus many new examples of halogen bond donors have been developed as substrates in preparation of ordered solids with designed architecture. Among variety of structures chiral components able to engage in halogen bonds are extremely rare.⁶ Crystalline materials with chiral framework are of interest because of their potential application in the field of optical resolution,⁷ asymmetric syntheses,⁸ photochirogenesis,⁹ nonlinear optics¹⁰ or chiral molecular conductors.¹¹ Furthermore, chiral solid phases exhibit intriguing spectroscopic properties. A phenomenon of induced optical activity arises when an achiral guest molecule is complexed by a chiral host. Optical activity can be induced upon dissolution of an achiral solute in a chiral solvent, by inclusion complexation of achiral guest in the cavity of a chiral host or by chirality transfer between chiral and achiral components in supramolecular polymers.¹² The guest becomes optically active

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due to a dissymmetry created by a chiral environment or upon

assuming a chiral conformation. An asymmetric perturbation of the chromophore leads to induced circular dichroism (ICD),

whose magnitude depends on the mutual arrangement of the

inducing optical activity in the azo chromophore by using

halogen bonded assemblies of *anti*-4,4'-azopyridine (**apy**) with

chiral ditopic halogen bond donors **1–3** (Scheme 1). The induced

optical activity of the azo chromophore was detected by solid

photoinduced syn-anti isomerization that is responsible for

their potential application in optical switches and sensors,

reversible data storage,¹⁴ photoresponsible supramolecular

systems,¹⁵ or liquid crystalline polymers.¹⁶ Photochromic

Azo-dyes, particularly those related to azobenzene, undergo

In this account, we wish to report a new possibility of

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⁺ Electronic Supplementary Information (ESI) available: NMR spectra (¹H, ¹³C, ¹⁹F) and HRMS for all final products, experimental details, geometry of halogen bonds

and crystal structures of all complexes. See DOI: 10.1039/x0xx00000x

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properties of crystalline azobenzenes are inspiring for interest in structural investigations of azobenzene solids. In that context, we have recently demonstrated induced optical activity of the azobenzene chromophore by inclusion complexation by chiral hosts as well as by hydrogen-bonded assembly with optically active dicarboxylic acids.¹⁷

Results and discussion

Ditopic halogen bond donors **1–3** were obtained by reaction of chiral diols with iodopentafluorobenzene in DMF solution using NaH or Cs_2CO_3 as a base following literature procedures.^{6a-b} Optically active diols **(S,S)-4** and **(S,S)-5** were prepared by LiAlH₄ reduction of corresponding dicarboxylic esters (Scheme 2 and Scheme 3). 4,4'-Azopyridine (**apy**) was obtained by oxidative coupling of 4-aminopyridine with sodium hypochlorite solution.¹⁸

Single crystals of the molecular complexes were grown by a slow evaporation of an equimolar amounts of the components from a CH₂Cl₂-heptane solution. Diffraction quality crystals were obtained for the complexes **apy**·(*S*,*S*)-1b, **apy**·(*S*,*S*)-2 and **apy**·(*R*)-3 and their crystal structures were determined by single-crystal X-ray diffraction. Unfortunately the complex **apy**·(*S*,*S*)-1a did not afford any good quality crystals, however, it does not pose any difficulty in the solid state CD measurements.



Scheme 2. The synthesis of ditopic halogen bond donors **(5,5)-1a-b**: (*a*) 2,2-dimethoxypropane (for **(5,5)-1a**) or cyclohexanone (for **(5,5)-1b**), *p*TSA; (*b*) LiAlH₄, THF, then H₂O; (*c*) Cs₂CO₃, CF₅I; (*d*) NaH, CF₅I.



infinite almost linear chains of the alternating component molecules connected by halogen bonds (Fig. 1) and spreading in [-3 1 1] direction. Asymmetric unit contains two independent apy and two (S,S)-1b molecules. Substantial differences between symmetry independent (S,S)-1b molecules can be found in conformation of 5-membered C₃O₂ rings: one is close to envelope on C8 (see Figure S13, ESI) while the second is rather twisted on C40-O9 (found by Platon¹⁹ program). The halogen bonds connecting apy with (S,S)-1b are nearly linear (see Table 1) and quite strong as evidenced by the I...N distances of ca 2.8 Å (80% of the sum of the van der Waals radii of I and N).²⁰ The molecule of (S,S)-1b adopts a partially folded conformation where one of the iodotetrafluorophenyl rings is located over the central cyclohexane ring and the second one pointing outside. The azopyridine apy molecule is slightly deviated from planarity caused by twisting of one the pyridine rings from the plane of the azo group (the corresponding C=C-N=N torsional angles are below 9° for both entities, see Table 2). The parallel orientation of the halogen bonded chains of **apy**·(*S*,*S*)-1**b** enable face-to-face π - π stacking interactions between the fluoroaryl rings of (S,S)-1b between two neighbour molecules (the distance between the centroids of the

Triclinic crystals of apy (S,S)-1b, space group R 1 art contain

additional stabilization of the structure. The complex **apy**·(*S*,*S*)-2 crystallizes in the orthorhombic system, space group $P2_12_12_1$, and is composed of infinite zig-zag chains of halogen bonded alternating component molecules (the I···N distances of *ca* 2.8 Å and the C–I···N angles of *ca* 173°). The cyclohexane ring of (*S*,*S*)-2 adopts a chair conformation with equatorially oriented aryloxymethyl groups (Fig. 2).

neighbouring rings is of ca 3.7 Å, see Fig. 4a) that results in an



Fig. 1. Molecular structure of **apy-(5,5)-1b**. Hydrogen atoms omitted, atom labelling scheme given for selected atoms in the asymmetric unit. Four symmetry equivalent atoms (N4, N8, I2 and I4) added to show chains of halogen bonding, pointed by dotted lines. Symmcodes for N4 and N8: (3+x, -1+y, -1+z), for I2 and I4: (-3+x, 1+y, 1+z).

Table 1. Halogen bonding parameters: contact lengths I···N [Å] (upper value) and angles

 $C-I\cdots N$ [°] (lower value), found in the investigated structures. Symmetry equivalent atoms were used for N4 and N8.

	apy∙(<i>S,S</i>)-1b	apy∙(<i>S,S</i>)-2	apy∙(<i>R</i>)-3
Independent entities Z'	2	1	1
C-I1N3	2.826 (7)	2.814 (5)	2.800 (7)
	175.2 (2)	172.7 (2)	171.2 (3)
C–I2…N4	2.844 (8)	2.815 (5)	2.813 (7)
	170.1 (3)	173.2 (3)	173.1 (3)
C–I3…N7	2.850 (7)		
	172.4 (3)	-	-
C–I4…N8	2.777(7)		
	179.0 (3)	-	-

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The **apy** molecule adopts almost exactly the C_i ($\overline{1}$) symmetry with the pyridine rings twisted from the azo group plane by alternating angles *ca* 13° and very small dihedral angle between the aromatic rings (see Table 2). The 1D chains of **apy**·(*S*,*S*)-2 are further organized into dense packed 2D corrugated layers by face-to-face π - π stacking interactions between the fluoroaryl units of (*S*,*S*)-2 and pyridine rings of **apy** (the distance between the centroids of the rings is of *ca* 4.25 Å, see Fig. 4*b*) occurring between the neighbouring chains. The pyridyl–perfluoroaryl stacking interactions are important stabilizing forces for various supramolecular structures which are capable in cooperation with halogen bonding to direct the crystal packing of binary molecular complexes.^{21,22}

The crystal structure of the complex **apy**·(*R*)-**3** (space group $P2_12_12_1$) revealed infinite chains of halogen bonded component molecules (the I···N distances are of *ca* 2.8 Å and the C–I···N angle is above 170°) (Fig. 3). The molecules of (*R*)-**3** adopt strongly folded conformation resulting from a pair of face-to-face π - π stacking interactions between the fluoroaryl and naphthalene rings (the distance between the centroids of the neighbouring 6-membered fused rings is of *ca* 3.5 Å, see Table 1 in ESI) which is very similar to that reported for the isolated (*R*)-**3** molecule.^{6a}

The guest **apy** molecule assumes a twisted conformation of almost C_2 symmetry (the corresponding C=C–N=N torsional angles are of 13.09 and 14.00°, see Table 2). The crystal packing reveals face-to-face π - π stacking interactions between the fluoroaryl units and pyridine rings and also between the naphthalene and pyridine rings of the host and guest molecules (Table 1, ESI).

Due to different conformational geometry of the ditopic donors, packing of chains of the compounds is different in each case. Crystal packing in **apy**·(*S*,*S*)-1b, can be described as stacking of



parallel straight chains within the entire structure eapy: $(S_{0})_{1}$ as stacking of parallel zig-zag chains and $apy \cdot (R)^{1}$ as stacking of layers with parallel chains, but with alternating direction of chains every second layer (see Fig. 4). Zig-zag chains of $apy \cdot (S,S)$ -2 spread along screw axis, so they obey \mathcal{P}_{1} rod group symmetry.^{23a} Table 3 lists the relevant crystallographic data for the complexes $apy \cdot (S,S)$ -1b, $apy \cdot (S,S)$ -2 and $apy \cdot (R)$ -3.







Fig. 4. Crystal packing of **apy** complexes: *a*) **apy·**(*S*,*S*)**-1b**, view perpendicular to the chains (green and red **apy**, blue and yellow (*S*,*S*)**-1b** symmetry independent molecules), all the chains are parallel to [3 1 1] in the entire structure, *b*) **apy·**(*S*,*S*)**-2**, viewed along [100] direction, parallel zig-zag chains clearly dominate the packing with translation period along [001] *c*) **apy·**(*R*)**-3**, viewed along [001], two linear chains spread in parallel layers in directions [2 1 0] and [2 1 0].

Table 2. Geometrical parameters indicating conformational changes of apy molecules in crystalline state. (Crystals with only apy molecules²⁶ contain inversion centre between N

apy∙(*R*)-3

apy·(*S*,*S*)-2

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apy (298K)²⁶

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molecules.

Syntheses of the host compounds 1-3 are described in

ару (190К)²⁶

The solid state CD spectra were taken with freshly prepared KBr disks and recorded with a Jasco J-715 dichrograph. A mixture of 2–5 mg of the sample and 250 mg of dried KBr was ground and formed into a disk 0.5 mm thick and with radius of 15 mm. The disk was rotated around the optical axis and the CD recordings were made for several positions in order to check a reproducibility of the spectra. The solid state UV-vis spectra were measured with a Unicam SP-300 spectrophotometer.

Diffraction intensity data were collected on an IPDS 2T dualbeam diffractometer (STOE & Cie GmbH, Darmstadt, Germany) at 120.0(2) K with MoKa radiation of a microfocus X-ray source (GeniX 3D Mo High Flux, Xenocs, Sassenage, 50 kV, 1.0 mA, λ = 0.71069 Å). The investigated crystal was thermostated in nitrogen stream at 120 K using CryoStream-800 device (Oxford CryoSystem, UK) during the entire experiment.

Data collection and data reduction were controlled by X-Area 1.75 program (STOE, 2015). An absorption correction was performed on the integrated reflections by a combination of frame scaling, reflection scaling and a spherical absorption correction. The structures were solved by direct methods and refined anisotropically using the program packages Olex2²⁸ and SHELX-2015.23b Positions of the C-H hydrogen atoms were calculated geometrically and taken into account with isotropic temperature factors. All H-atoms were refined as riding on their parent atoms with the usual restraints.

Conclusions

Optically active ditopic halogen bond donors bearing two 4iodotetrafluorophenyl groups were successfully obtained by nucleophilic substitution of iodopentafluorobenzene with chiral diolate anions. Co-crystallization of these donors with anti-4,4'azopyridine afforded binary complexes containing infinite chains of the alternating component molecules connected by halogen bonds. These structures are additionally stabilized by face-to-face π - π stacking interactions between the aryl and fluoroaryl rings. The complexation of the azopyridine molecule induces optical activity of the azo chromophore due to the twisting of the aryl-N=N system or external chiral perturbation exerted by host molecules, which is manifested by solid state CD spectra.

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Such measurements are possible since the long-wavelength

absorption bands of the azo chromophore remain outside of the

absorption range of the host compounds 1-3. The solid state

UV-vis spectra of the complexes closely resemble that of anti-

azobenzene and are characterized by a weak absorption near

460 nm, corresponding to the forbidden n– π^* transition, and a

strong one near 320 nm that can be assigned to the allowed π –

 π^* transition.²⁷ It has been shown that the positive n- π^* Cotton

effect sign can be correlated with the left-handed chirality (M-

helicity) of the skewed aryl-N=N system, and the negative one

with the right-handed chirality (P-helicity).17 Thus the CD

spectrum of apy-(R)-3 featured negative Cotton effect in the

region of the long-wavelength excitation that remains in

accordance with the X-ray structure revealing right-handed

twist of the guest molecule. In the case of apy-(S,S)-1b and

apy-(S,S)-2 (Figure S16 and Figure S17, ESI) the long-wavelength

CD is very weak because the guest molecule is only slightly

twisted from planarity or as in the case of apy-(S,S)-2 assumes

achiral conformation. Instead the weak Cotton effects were

observed near 300 nm in the region of the electronic $\pi - \pi^*$

transition, which are caused by external perturbation of the

chromophore by chiral environment created by the host

spectra of the complexes apy·(S,S)-1a, apy·(S,S)-1b, apy·(S,S)-2

apy·(S,S)-1b



atoms in the azo group, exactly C_i symmetry, causing alternation the torsions and setting the dihedral angle between aromatic rings to zero).

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apy·(S,S)-1b apy•(*S*,*S*)-2 apy•(*R*)-3 $C_{22}H_{16}F_8I_2O_4 \cdot C_{10}H_8N_4$ Chemical formula $C_{20}H_{14}F_8I_2O_2{\cdot}C_{10}H_8N_4$ $C_{32}H_{12}F_8I_2O_2{\cdot}C_{10}H_8N_4$ 934.35 876.31 1018.42 Mr Crystal system Triclinic Orthorhombic Orthorhombic Space group P212121 $P2_{1}2_{1}2_{1}$ Ρ1 10.4002 (10) a [Å] 5.2031 (2) 11.5438 (5) b [Å] 13.3883 (13) 17.8566 (4) 14.8242 (7) c [Å] 14.2970 (14) 32.8945 (8) 21.8290 (17) α [°] 68,135 (8) 90 90 в [°] 70.540 (8) 90 90 69.104 (7) 90 v [°] 90 V [ų] 1679.3 (3) 3056.22 (15) 3735.5 (4) Ζ 2 4 4 Number of measured and 44176, 17217 38579, 8255 54653, 10101 independent reflections 0.054 0.047 0.052 Rint $R[F^2>2\sigma(F^2)],\,wR(F^2),\,S$ 0.046, 0.137, 1.07 0.036, 0.091, 1.08 0.046, 0.123, 1.09 Flack parameter 0.05 (2) -0.018 (15) -0.030 (14) CCDC 1868141 1868142 1868143

Conflicts of interest

There are no conflicts to declare.

Notes and references

- (a) G. R. Desiraju, Crystal Engineering: The Design of Organic Solids, Elsevier, Amsterdam, 1989; (b) G. R. Desiraju, The Crystal as a Supramolecular Entity, Wiley, Chichester, 1995; (c) W. Jones, Organic Molecular Solids. Properties and Applications, CRC Press, Boca Raton, 1997; (d) G. R. Desiraju, J. J. Vittal, A. Ramanan, Crystal Engineering: A Textbook, World Scientific, Singapore, 2011.
- (a) T. Steiner, Angew. Chem. Int. Ed., 2002, 41, 49; (b) C. B. Aakeröy and K. R. Seddon, Chem. Soc. Rev., 1993, 397; (c) J. Bernstein, M. C. Etter and L. Leiserowitz, in Structure Correlation, Vol. 1, ed. J. D. Dunitz and H.-B. Burgi, VCH, New York, 1995, chap. 11.
- 3 (a) G. R. Desiraju and T. Steiner, *The Weak Hydrogen Bond in Structural Chemistry and Biology*, Oxford University Press, Oxford, 1999; (b) C. A. Hunter, K. R. Lawson, J. Perkins and C. J. Urch, *J. Chem. Soc., Perkin Trans.* 2, 2001, 651; (c) E. A. Meyer, R.K. Castellano and F. Diederich, *Angew. Chem. Int. Ed.*, 2003, **42**, 1210.
- 4 (a) P. Metrangolo and G. Resnati, Halogen Bonding: Fundamentals and Applications (Structure and Bonding), Springer: Heidelberg, 2010; (b) A. Priimagi, G. Cavallo, P. Metrangolo and G. Resnati, Acc. Chem. Res., 2013, 46, 2686; (c) L. C. Gilday, S. W. Robinson, T. A. Barendt, M. J. Langton, B. R. Mullaney and P. D. Beer, Chem. Rev., 2015, 115, 7118; (d) G. Cavallo, P. Metrangolo, R. Milani, T. Pilati, A. Priimagi, G. Resnati and G. Terraneo, Chem. Rev., 2016, 116, 2478.
- 5 (a) P. Politzer, J. S. Murray, T. Clark, *Phys. Chem. Chem. Phys.*, 2013, **15**, 11178; (b) H. Wang, W. Wang and W. J. Jin, *Chem. Rev.*, 2016, **116**, 5072.
- (a) J. Lieffrig, A. G. Niassy, O. Jeannin and M. Fourmigue, *CrystEngComm*, 2015, **17**, 50; (b) P. Metrangolo, F. Meyer, T. Pilati, D.M. Proserpio, G. Resnati, *Chem. Eur. J.*, 2007, **13**, 5765-5772. (c) M. Kaasik, S. Kaabel, K. Kriis, I. Järving, R. Aav, K. Rissanen and T. Kanger, *Chem. Eur. J.*, 2017, **23**, 7337.
- 7 (a) G. Li, W. Yu and Y. Cui, J. Am. Chem. Soc., 2008, 130, 4582;
 (b) K. Mishiro, T. Furuta, T. Sasamori, K. Hayashi, N. Tokitoh,

S. Futaki and T. Kawabata, *J. Am. Chem. Soc.*, 2013, **135**, 13644; (c) Z.-X. Xu, Y.-X. Tan, H.-R. Fu, Y. Kanga and J. Zhang, *Chem. Commun.*, 2015, **51**, 2565.

- 8 (a) B. Kesanli and W. Lin, W. Coord. Chem. Rev., 2003, 246, 305; (b) C.-D. Wu and W. Lin, Chem. Commun., 2006, 3673; (c) C.-D. Wu, A. Hu, L. Zhang and W. Lin, J. Am. Chem. Soc., 2005, 127, 8940.
- 9 C. Yang and Y. Inoue, Chem. Soc. Rev., 2014, 43, 4123.
- 10 T. P. Radhakrishnan, Acc. Chem. Res., 2008, 41, 367.
- (a) N. Avarvari and J. Wallis, J. Mater. Chem., 2009, 19, 4061;
 (b) M. Brezgunova, K.-S. Shin, P. Auban-Senzier, O. Jeannin and M. Fourmigue, Chem. Commun. 2010, 46, 3926; (c) J. Lieffrig, R. Le Pennec, O. Jeannin, P. Auban-Senzier and M. Fourmigue, CrystEngComm, 2013, 15, 4408.
- 12 A. Rodger and B. Norden, *Circular Dichroism and Linear Dichroism*, Oxford University Press, Oxford, 1997.
- 13 (a) H. G. Brittain, In Analytical Applications of Circular Dichroism, N. Purdie and H. G. Brittain, Eds.; Elsevier: New York, 1994, Chap. 11. (b) S. Allenmark, Chirality, 2003, 15, 409.
- 14 B. L. Feringa, R. A. van Delden, N. Koumura and E. M. Geertsema, *Chem. Rev.*, 2000, **100**, 1789.
- 15 (a) S. Yagai, T. Karatsu and A. Kitamura, *Chem. Commun.*, 2003, 1844; (b) Y. Saiki, H. Sugiura, K. Nakamura, M. Yamaguchi, T. Hoshi and J. Anzai, *J. Am. Chem. Soc.*, 2003, **125**, 9268; (c) Y. Norikane, K. Kitamoto and N. Tamaoki, *J. Org. Chem.*, 2003, **68**, 8291; (d) F. Rakotondradany, M. A. Whitehead, A.-M. Lebuis and H. F. Sleiman, *Chem. Eur. J.*, 2003, **9**, 4771.
- (a) K. Ichimura, *Chem. Rev.*, 2000, **100**, 1847; (b) J. Barbera, L. Giorgini, F. Paris, E. Salatelli, R. M. Tejedor and L. Angiolini, *Chem. Eur. J.*, 2008, **14**, 11209.
- (a) M. Szyrszyng, E. Nowak, M. Gdaniec, M. J. Milewska and T. Połoński, *Terahedron: Asymm.*, 2004, **15**, 3257; (b) A. Wasilewska, M. J. Milewska, M. Gdaniec and T. Połoński, *Terahedron: Asymm.*, 2009, **20**, 1472.
- 18 E. V. Brown and G. R. Granneman, J. Am. Chem. Soc., 1975, **97**, 621.
- 19 A. L. Spek, J. Appl. Crystallogr., 2003, 36, 7.
- 20 A. Bondi, J. Phys. Chem., 1964, 68, 441.
- 21 M. Gdaniec, W. Jankowski, M. J. Milewska and T. Połoński, Angew. Chem. Int. Ed., 2003, 42, 3903 and references therein.
- 22 A. Wasilewska, M. Gdaniec and T. Połoński, *CrystEngComm*, 2007, **9**, 203.
- 23 (a) V. Kopsky and D. B. Litvin (eds) International Tables for Crystallography, Subperiodic Groups, 2nd ed. Chichester,

View Article Online DOI: 10.1039/C8NJ05750H

Wiley, 2010. Vol. E; (*b*) G. M. Sheldrick, *Acta Crystallogr.*, 2015 A71, 3.

- 24 K. Tanaka, M. Kato and F. Toda, *Chirality*, 2001, **13**, 347 and references therein.
- (a) M. Gdaniec and T. Połoński, J. Am. Chem. Soc., 1998, 120, 7353; (b) M. Gdaniec, M. J. Milewska and T. Połoński, Angew. Chem. Int. Ed., 1999, 38, 392; (c) M. Szyrszyng, E. Nowak, M. Gdaniec, M. J. Milewska, A. Herman and T. Połoński, J. Org. Chem., 2001, 66, 7380; (d) T. Połoński, M. Szyrszyng, M. Gdaniec, E. Nowak and A. Herman, Tetrahedron: Asymmetry, 2001, 12, 797. (e) M. Szyrszyng, E. Nowak, M. Gdaniec, M. J. Milewska and T. Połoński, Tetrahedron: Asymmetry, 2004, 15, 103.
- 26 K. M. Hutchins, K. A. Kummer, R. H. Groeneman, E. W. Reinheimer, M. A. Sinnwell, D. C. Swenson and L. R. Mac Gillivray, *CrystEngComm*, 2016, **18**, 8354.
- 27 H. Suzuki, Electronic Absorption Spectra and Geometry of Organic Molecules. An Application of Molecular Orbital Theory, Academic Press, New York, 1967, Chap. 23.3.
- 28 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, J. Appl. Cryst., 2009, **42**, 339.