(Z)-3-Methyl-N-(7-nitroacridin-3-yl)-2,3-dihydro-1,3-benzothiazol-2-imine from laboratory powder diffraction data

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The title compound, $C_{21}H_{14}N_4O_2S$, belongs to a family of molecules possessing nonlinear optical properties in solution. Its structure has been solved from laboratory X-ray powder diffraction data using a new direct-space structure solution method, where the atomic coordinates are directly used as parameters and the molecular geometry is described by restraints. The molecular packing is controlled by two systems of π–π interactions and one weak edge-to-face interaction.

Comment

Organic materials exhibiting nonlinear optical (NLO) properties are generally constituted by conjugated organic compounds. Molinos-Gómez et al. (2005) described a new family of NLO push–pull D–L–A chromophores composed of a donor group (D) derived from 1,3-benzothiazol-2-amine, an acceptor group (A), viz. a nitro group, and a linker (L), viz. acridine, which also enhances the electron-withdrawing effect of the nitro group. To explain the unexpectedly high NLO response of these molecules, a tautomeric equilibrium between the amino and imino forms was proposed (see Scheme). The two forms would possess different NLO properties, with the higher response being due to the imino form. In order to prove this hypothesis, the methyl-blocked compounds were synthesized, namely N-methyl-N-(2-nitroacridin-6-yl)-1,3-benzothiazol-2-amine [amino form, (IA)] and (Z)-3-methyl-N-(7-nitroacridin-3-yl)-2,3-dihydro-1,3-benzothiazol-2-imine [imino form, (IB)].

As predicted, (IB) exhibits the higher NLO response of this pair of chromophores in solution (Latorre et al., 2010). It also presents other interesting properties, such as fluorescence and thermal stability. For a better understanding of the properties

of this molecule, microcrystals of (IB) were grown and their crystal structure was solved from powder diffraction data (Fig. 1) as no suitable crystals could be obtained for single-crystal diffraction. This previously unknown structure also served as a test case for a new structure solution method for molecular compounds from powder diffraction data (TALP program; Rius et al., 2011). The structure determination of (IB) was challenging due to the size of the unit cell, which caused severe peak overlaps in the powder pattern. TALP uses a global optimization technique based on the incremental least-squares refinement of randomly positioned fragments using a very fast Rietveld refinement program (Rius et al., 1990). Unlike most direct-space structure solution programs [for a review of direct-space methods, see Černý & Favre-Nicolin (2007)], it directly refines the atomic coordinates and not the torsion angles.

Amino form   Imino form

Methyl-blocked tautomers

(IA)   (IB)
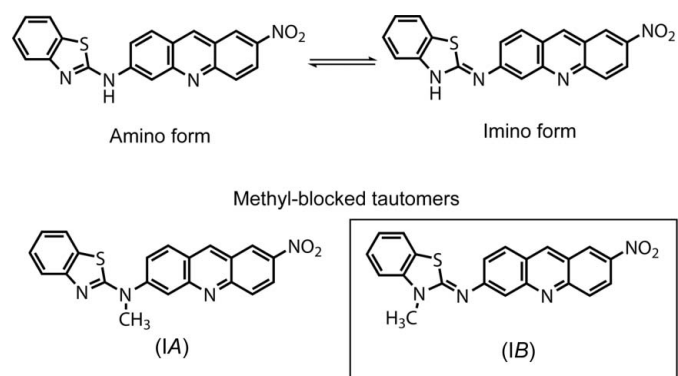
The starting molecular model was obtained by energy minimization using molecular mechanics with an MM2 force field (Allinger, 1977). The geometry of the complete molecule was described in terms of distance and plane restraints: distance restraints were obtained from the Cambridge Structural Database (Version 5.32; Allen, 2002) using Mogul (Bruno et al., 2004) and from International Tables for Crystallography (Vol. C; Allen et al., 2006); plane restraints were applied to the acridine (Acr) and benzothiazole (Bt) rings and to the nitro group. The E–Z isomerism of the imine double bond was not fixed, starting randomly in each cycle and being free to evolve towards the E or Z isomer during iteration. The C11—N10 and C18—N26 bonds were also left completely free to rotate, so that no restriction was imposed on the planarity of the whole molecule. Using these conditions, 10 out of 50 TALP trials (40 000 least-squares cycles per trial at ~25 min each) were correct solutions. A crystal structure proposal was
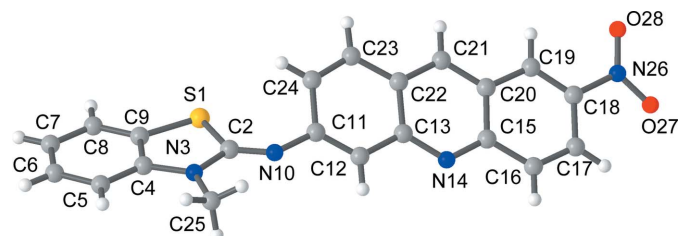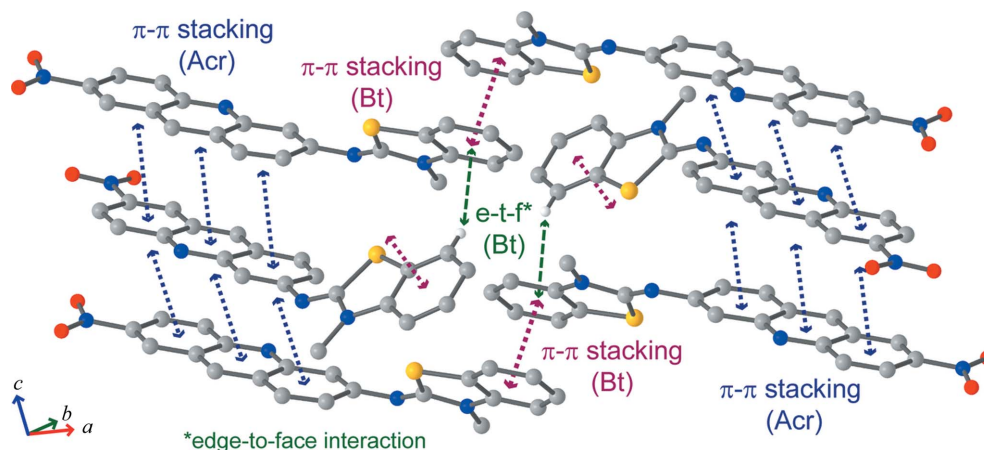

Figure 1
The molecular structure of isomer (IB), showing the atom-numbering scheme.

organic compounds
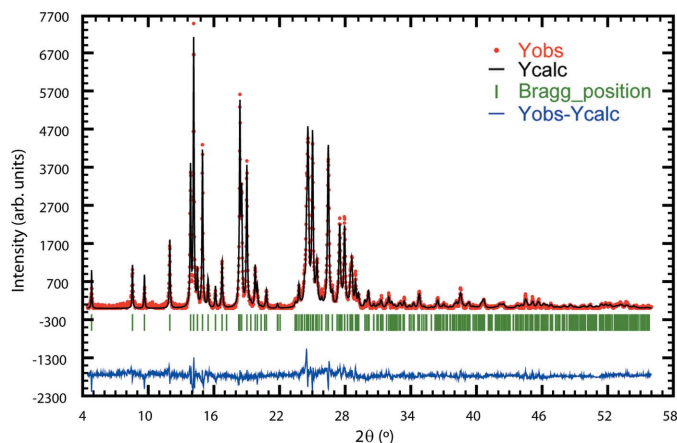
Figure 2
The observed (points) and calculated (line) patterns, with the difference profile (bottom), obtained from Rietveld refinements of (IB).

given at the end of each *TALP* trial with an internal figure of merit (FoM), which essentially measures the discrepancy between the observed and calculated intensity profiles at the Bragg positions. The most probable solutions were identified by their low FoM values [in the case of (IB), the FoM values were ~1.3 times larger for wrong solutions than for correct ones]; the correctness of each solution was also checked by a visual inspection of observed and calculated powder patterns, and finally by checking the chemical sense of the proposed structure. Then, starting from any of the correct solutions, a final restrained Rietveld refinement could be performed using the program *RIBOLS* (Rius, 2009); the observed and calculated powder patterns are shown in Fig. 2.

In crystalline form, (IB) consists of two noncoplanar aromatic ring systems [2-nitroacridin-6-amine (Acr) groups and 1,3-benzothiazol-2-imine groups (Bt)], with the respective mean planes forming a dihedral angle of 42.0 (2)°. The imine double bond has a slight planar distortion [torsion angle C11—N10—C2—S1 = −3.9 (17)°] and the nitro substituent is almost in the Acr plane, with a dihedral angle between their mean planes of 6.9 (5)°.

The molecular packing is controlled by π–π interactions (π stacking) between the aromatic systems in the molecule (Fig. 3). The π stacking of the Acr rings along *c* is characterized by: (i) a distance between central six-membered-ring centroids of 3.831 (4) Å; (ii) an angle of 23.3° between the centroid–centroid vector and the vector normal to the plane; and (iii) a dihedral angle of 1.5° (*i.e.* almost coplanar) between Acr mean planes. On the other hand, each Bt ring forms two types of arrangements with neighbouring Bt rings. The first allows π stacking between Bt rings, giving rise to molecular pairs which determine the unit-cell size in the *a* direction. This π stacking is characterized by: (i) a distance of 3.796 (6) Å between six-membered-ring centroids; (ii) an angle of 23.4° between the centroid–centroid vector and the vector normal to the plane; and (iii) a dihedral angle of 0° between the mean planes, imposed by the inversion centre. In the second arrangement, the Bt rings of adjacent molecules along the *c* axis form a dihedral angle of 73.0°, and the C8—H8 bond of one Bt ring points to the six-membered ring of the other at a distance of 2.80 Å (H8 to phenyl centroid) and an angle of 155° (C8—H8···centroid), allowing a weak intermolecular edge-to-face interaction (Jennings *et al.*, 2001). The nitro O atoms interact weakly with neighbouring molecules; there is a weak C7—H7 hydrogen bond to atom O27 at $(x + \frac{1}{2}, y, -z + \frac{1}{2})$, and another from C23—H23 to atom O28 at $(-x + \frac{1}{2}, -y, -\frac{1}{2} + z)$, although the π stackings are the most significant interactions in the crystal structure of (IB).

Experimental

Compound (IB) was prepared following the procedure described in previous work (Latorre *et al.*, 2010) and the orange powder obtained was loaded into a 0.3 mm Lindemann glass capillary.

Diffraction data were collected on a PANalytical X'Pert PRO MPD diffractometer (45 kV/40 mA) with Cu $K\alpha_1$ radiation selected by a primary hybrid monochromator (X-ray mirror and channel-cut 220 Ge crystal) in transmission geometry, with the sample in a 0.3 mm glass capillary, using an X'Celerator multistrip detector with an active detection length of 2.122°. The measured 2θ interval was 3.5–56.0°,

Figure 3
A simplified scheme showing the π–π interactions (π stacking) between 2-nitroacridin-6-amine (Acr) groups and 1,3-benzothiazol-2-imine groups (Bt), and the edge-to-face interactions in the crystal structure of (IB).

with a step size of 0.017° and an effective counting time (including the sweep of the strip detector) of 8955 s per step (72 h of total measuring time). In the refinement, data in the interval 4.41–55.97° were used. No absorption correction was applied due to the low absorption coefficient and small capillary diameter. A cylindrical correction (Rouse *et al.*, 1970) was tested and showed no improvement.

The powder pattern was indexed using *DICVOL04* (Boultif & Louër, 2004), with figures of merit of M_{20} = 44.4 (de Wolff, 1968) and F_{20} = 96.7 (0.0029, 71) (Smith & Snyder, 1979). The large cell volume is consistent with Z = 8 and the systematic absences indicate the *Pbca* space group. Unit-cell parameter refinement and subsequent extraction of intensities (used for the structure solution with *TALP*; Rius *et al.*, 2011) were performed with the whole-pattern matching program *DAJUST2* (Rius, 2010).

Crystal data

$C_{21}H_{14}N_4O_2S$
$M_r = 386.43$
Orthorhombic, *Pbca*
$a = 36.627 (4)$ Å
$b = 12.5071 (10)$ Å
$c = 7.5769 (4)$ Å

$V = 3470.9 (4)$ Å^3
$Z = 8$
Cu $K\alpha_1$ radiation, $\lambda = 1.54059$ Å
$\mu = 1.88$ mm^{-1}
$T = 298$ K

Data collection

PANalytical X'Pert PRO MPD diffractometer
Specimen mounting: glass capillary
Data collection mode: transmission

Scan method: step
$2\theta_{min} = 4.41°$, $2\theta_{max} = 55.97°$, $2\theta_{step} = 0.017°$

Refinement

$R_p = 0.034$
$R_{wp} = 0.044$
$R_{exp} = 0.026$
$R_{Bragg} = 0.075$
$\chi^2 = 2.779$

3034 data points
91 parameters
109 restraints
H-atom parameters constrained

The initial structure model supplied by *TALP* (Rius *et al.*, 2011) was optimized by restrained Rietveld refinement (*RIBOLS* program; Rius, 2009). A total of 91 parameters were refined (atomic coordinates, scale factor, overall displacement parameter, profile coefficients, cell parameters and zero shift). 109 restraints were added, 32 for bond distances, 47 for bond angles and 30 to define three planes, one for the acridine ring, one for the benzothiazole ring and the last for the nitro group. The same restraints were used for structure solution and for the final Rietveld refinement, and these are detailed in the CIF. The planarity of the imine double bond was indirectly imposed by the addition of atom N10 to the definition of both the Acr and Bt planes.

H atoms were placed at calculated positions and constrained to ride on the corresponding C atoms in the final refinement cycles. In the case of the methyl group, several orientations for the H atoms were tested and the more sterically favourable orientation was selected. For all atoms, an overall displacement parameter was used.

Data collection: *X'pert Data Collector* (PANalytical, 2003); cell refinement: *DAJUST2* (Rius, 2010); data reduction: *X'pert Highscore* (PANalytical, 2003); program(s) used to solve structure: *TALP* (Rius *et al.*, 2011); program(s) used to refine structure: *RIBOLS* (Rius, 2009); molecular graphics: *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010) and *PLATON* (Spek, 2009).

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Allen, F. H., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (2006). *Typical Interatomic Distances: Organic Compounds. International Tables for Crystallography*, Vol. C, *Mathematical, Physical and Chemical Tables*, 1st online ed., edited by E. Prince, ch. 9.5, pp. 790–811. Chester: International Union of Crystallography. [doi:10.1107/97809553602060000103]
Allinger, N. L. (1977). *J. Am. Chem. Soc.* **99**, 8127–8134.
Boultif, A. & Louër, D. (2004). *J. Appl. Cryst.* **37**, 724–731.
Bruno, I. J., Cole, J. C., Kessler, M., Luo, J., Motherwell, W. D. S., Purkis, L. H., Smith, B. R., Taylor, R., Cooper, R. I., Harris, S. E. & Orpen, A. G. (2004). *J. Chem. Inf. Comput. Sci.* **44**, 2133–2144.
Černý, R. & Favre-Nicolin, V. (2007). *Z. Kristallogr.* **222**, 105–113.
Jennings, W. B., Farrell, B. M. & Malone, J. F. (2001). *Acc. Chem. Res.* **34**, 885–894.
Latorre, S., Moreira, I. de P. R., Villacampa, B., Julià, L., Velasco, D., Bofill, J. M. & López-Calahorra, F. (2010). *ChemPhysChem*, **11**, 912–919.
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.
Molinos-Gómez, A., Vidal, X., Maymó, M., Velasco, D., Martorell, J. & López-Calahorra, F. (2005). *Tetrahedron*, **61**, 9075–9081.
PANalytical (2003). *X'pert Data Collector* and *X'pert Highscore*. PANalytical BV, Almelo, The Netherlands.
Rius, J. (2009). *RIBOLS*. Institut de Ciència de Materials de Barcelona (CSIC), Catalunya, Spain.
Rius, J. (2010). *DAJUST2*. Institut de Ciència de Materials de Barcelona (CSIC), Catalunya, Spain.
Rius, J., Miravitlles, C., Molins, E., Crespo, M. & Veciana, J. (1990). *Mol. Cryst. Liq. Cryst.* **187**, 155–163.
Rius, J., Vallcorba, O., Frontera, C. & Miravitlles, C. (2011). *TALP*. Institut de Ciència de Materials de Barcelona (CSIC), Catalunya, Spain.
Rouse, K. D., Cooper, M. J., York, E. J. & Chakera, A. (1970). *Acta Cryst.* A**26**, 682–691.
Smith, G. S. & Snyder, R. L. (1979). *J. Appl. Cryst.* **12**, 60–65.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
Wolff, P. M. de (1968). *J. Appl. Cryst.* **1**, 108–113.