

Accurate atomic displacement parameters from time-of-flight neutron-diffraction data at TOPAZ

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Accurate atomic displacement parameters (ADPs) are a good indication of high-quality diffraction data. Results from the newly commissioned time-of-flight Laue diffractometer TOPAZ at the SNS are presented. Excellent agreement is found between ADPs derived independently from the neutron and X-ray data emphasizing the high quality of the data from the time-of-flight Laue diffractometer.

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1. Introduction

While atomic coordinates derived independently from X-ray and neutron data generally agree very well, significant differences between the atomic displacement parameters (ADPs) are often observed (Coppens *et al.*, 1984). In particular, X-ray-derived ADPs may be biased by chemical bonding effects, while differences in a range of systematic errors between the two methods add to the discrepancies, as the ADPs are prone to absorb the errors (Blessing, 1995; Iversen *et al.*, 1996, 1999). In addition, X-ray data are not able to provide accurate knowledge of the position and thermal motion of hydrogen atoms (Madsen *et al.*, 2007). Thus, for electron-density studies where separation of thermal and electronic effects is absolutely essential, not least for hydrogen, it is therefore important to have independent access to accurate ADPs for all atoms.

The best approach to achieve unbiased ADPs, for the non-H atoms only, is by explicitly modelling the bonding electron density using the so-called multipole model (MM; Hansen & Coppens, 1978). Otherwise an independent atom model (IAM) refined against high-order data only can be used (Jeffrey & Cruickshank, 1953). A recent alternative approach using X-ray data alone and which also provides anisotropic hydrogen ADPs is known as Hirshfeld atom refinement (HAR). This method is based on a Hirshfeld partitioning of a theoretical density and from this molecule-specific non-spherical scattering factors are calculated and implemented in refinement (Jayatilaka & Dittrich, 2008; Capelli *et al.*, 2014). This method is so far only applicable with one molecule in the asymmetric unit (Woińska *et al.*, 2014). Finally, the SHADE approach (Madsen, 2006) estimates hydrogen ADPs for hydrogen atoms as a sum of the TLS (translation–libration–screw) (Schomaker & Trueblood, 1968) motion of the rigid non-H-atom groups, to which they are attached, and the internal motion from a database of neutron-diffraction experiments.

Hitherto, the drawback of neutron diffraction has been the requirement for large crystals and limited beam and instrument availability. To remedy this situation, the newly commissioned time-

of-flight (TOF) Laue diffractometer TOPAZ (Schultz *et al.*, 2014) has been designed to take full advantage of the high flux of the Spallation Neutron Source (SNS) and it thus facilitates the use of smaller samples, potentially minimizing the systematic effects such as absorption and extinction in the data. The use of TOF methods leads to higher signal-to-noise ratios, compared with monochromatic instruments, as the incoherent scattering contributing to the overall background is distributed in both space and time.

To demonstrate the data quality at TOPAZ, single-crystal diffraction data of orthorhombic rubrene, 5,6,11,12-tetraphenyl-tetracene (Jurchescu *et al.*, 2006), and a co-crystal of betaine, imidazole and picric acid (BIPa) (Overgaard *et al.*, 1999) have been measured. Both of these compounds pose challenges for neutron diffraction as they have high hydrogen contents, 40%_{atom} in rubrene and 33%_{atom} in BIPa. Furthermore, BIPa crystallizes with a 24 Å axis in the Niggli cell and 75 atoms in the asymmetric unit.

Reference ADPs were modelled using high-resolution, conventional X-ray data for the two systems collected at the same temperature. From these X-ray data, ADPs from MM, IAM, high-order IAM, HAR and SHADE models were obtained.

2. Neutron data collection details

A rubrene crystal with a volume of approximately 2.25 mm³ was used and data were collected in 23 settings for 3.5 h each, a total of approximately 80 h. The settings were selected for maximum coverage using an evolutionary algorithm in the program *CrystalPlan* (Zikovskiy *et al.*, 2011). The data were indexed and integrated using the program *Mantid* (Taylor *et al.*, 2012). Corrections for wavelength-dependent effects, absorption and Lorentz factor were done in *ANVRED2* (Schultz *et al.*, 1984). The structural model was refined against the neutron data using the program *GSAS* (Larson & Von Dreele, 1994; Toby, 2001) with a published 100 K X-ray structure as the starting model (Jurchescu *et al.*, 2006). All coordinates and anisotropic temperature parameters along with a secondary type I

Table 1
Comparison of ADPs.

HO refers to high-order refinement with $\sin \theta/\lambda \geq 0.8 \text{ \AA}^{-1}$.

Compound	Type	No. (and type) of atoms compared	$\langle U_X^i/U_N^i \rangle$	$\frac{\langle \Delta U \rangle}{\langle U_X^i - U_N^i \rangle} (\text{\AA}^2)$
Rubrene	X _{MM} -N	11 (C)	1.01 (3)	0.00021 (17)
	X _{IAM} -N	11 (C)	0.99 (3)	0.00034 (25)
	X _{IAM, HO} -N	11 (C)	1.05 (3)	0.00038 (31)
	X _{HAR} -N	11 (C)	0.98 (16)	0.00175 (203)
	X _{HAR} -N	7 (H)	1.07 (13)	0.00810 (880)
	X _{MM, SHADE} -N	7 (H)	0.98 (6)	0.00104 (157)
BIPa	X _{MM} -N	50 (C, N, O)	1.00 (3)	0.00036 (30)
	X _{IAM} -N	50 (C, N, O)	1.04 (6)	0.00062 (52)
	X _{IAM, HO} -N	50 (C, N, O)	1.03 (4)	0.00041 (33)
	X _{MM, SHADE} -N	25 (H)	1.06 (41)	0.00753 (869)

Lorentzian spread extinction model were refined. Additional experimental details and full lists of refined parameters have been deposited in the supporting information.¹

An irregular BIPa crystal was ground to a sphere with a volume of approximately 0.91 mm³ in a pneumatic grinder based on an original design by Cordero-Borboa (1985). The data were collected using 17 crystal settings for 6.5 h each, a total of approximately 110 h. The data were processed using the same procedure outlined for rubrene above. The starting model for the structural refinement was the one reported by Overgaard *et al.* (1999) at 28 K. Experimental details for both the X-ray and the neutron data sets are provided in the supporting information.

3. X-ray and neutron ADP comparison

Both neutron and X-ray diffraction data are sensitive to a range of systematic effects which can lead to erroneous values for the ADPs (Blessing, 1995; Iversen *et al.*, 1996, 1999). However, if the ADPs for the non-H atoms are obtained from high-quality and properly corrected data, these values from the two independent experiments may be compared and their similarity may serve as an accuracy indicator of the data sets. Additionally, it is possible to obtain accurate values for hydrogen positional and vibrational parameters from the neutron data, which can be subsequently included in the X-ray model, with or without scaling, in an X-N approach (Coppens, 1967). In certain situations it has proven important to include accurate hydrogen positions and thermal parameters to obtain a reliable description of chemical bonding, also for interactions not involving the hydrogen atoms (Madsen *et al.*, 2004).

Previous X-N studies have shown excellent agreement between neutron and X-ray ADPs for very simple compounds and/or for studies carried out at helium temperatures (see *e.g.* Table 2 in Morgenroth *et al.*, 2008 and references therein). Besides the systematic effects described above other effects may influence the results, *e.g.* poor absolute temperature calibration and less exhaustive experimental effort during ‘cheaper’ 100 K experiments. At liquid-nitrogen temperatures the reported studies, except the one for alloxan (Swaminathan *et al.*, 1985), result in larger deviations; in particular the average value of the ratio of diagonal values of the *U* tensor, $\langle U_X^i/U_N^i \rangle$, deviates significantly from unity. The average difference between the parameters, $\langle |\Delta U| \rangle$, generally increases at liquid-nitrogen temperatures or above, concurrent with a higher e.s.d. indicating that the differences between the X-ray and neutron values

are still random. That the difference is random seems to indicate that the deconvolution of thermal motion is not the problem, as this would cause the ADPs from X-ray to be systematically larger than those from neutron data.

The $\langle |\Delta U| \rangle$ and $\langle U_X^i/U_N^i \rangle$ values for both rubrene and BIPa are tabulated in Table 1 for comparison of the six different methods (N, X_{MM}, X_{IAM}, X_{IAM, HO}, X_{HAR}, X_{MM, SHADE}). It is immediately obvious that the X_{MM} and N ADPs compare very well, with ratios of unity for both crystals. CIF files including anisotropic parameters are included in the supporting information. Of particular importance are the values for $\langle |\Delta U| \rangle$, which are among the lowest ever reported, especially when the relatively high temperature of 100 K and the size of the systems are taken into account (Morgenroth *et al.*, 2008). The X_{IAM} comparisons are slightly worse, with both higher ratio and differences, than the multipole comparison. These values, however, are still among the lowest in the literature. It is somewhat surprising to observe very little difference between X_{IAM} refinement against all data and high-order data. The X_{HAR}-N comparison is clearly inferior to the X_{MM} and X_{IAM} methods (an order of magnitude in $\langle |\Delta U| \rangle$) and the values of $\langle U_X^i/U_N^i \rangle$ have significant e.s.d.’s indicative of substantial scatter of values. This is also reflected in the significantly different hydrogen ADPs that result from the X_{HAR} and N refinements, respectively. Finally, it is also observed that the X_{MM, SHADE} approach is unable to reproduce the hydrogen ADPs found from the N data, although performing significantly better than the X_{HAR} approach in this case. This is illustrated in Fig. 1 where the r.m.s.d.’s between X_{MM, SHADE} and N ADPs are displayed, clearly showing the excellent match of non-H atoms ($\langle |\Delta U| \rangle = 0.00021 \text{ \AA}^2$), and the similarly poor match for the hydrogen atoms ($\langle |\Delta U| \rangle = 0.00104 \text{ \AA}^2$).

In most cases it is advantageous to measure diffraction data at the lowest possible temperature to avoid thermal diffuse scattering, which for most systems is very difficult, if not practically impossible, to correct for (Willis & Pryor, 1975). The estimated Debye temperature of rubrene is 63 K (Okada *et al.*, 2011), *i.e.* TDS could be a problem at 100 K. However, the excellent agreement between the data sets for X_{MM}-N and X_{IAM, HO}-N indicates that this is not the case.

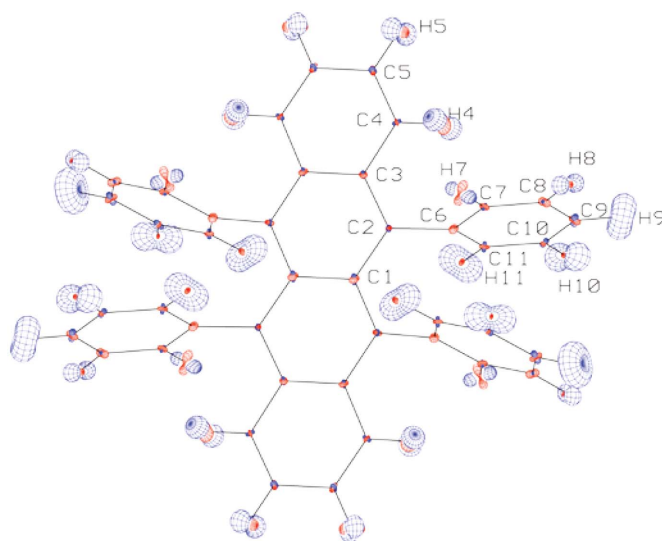


Figure 1
PEANUT (Hummel *et al.*, 1990) plots of r.m.s.d. surfaces for X_{MM, SHADE}-N for rubrene r.m.s.d.’s scaled up by 1.54.

¹ Supporting information for this paper is available from the IUCr electronic archives (Reference: PC5039).

4. Conclusion

Comparison of ADPs from modelling of neutron-diffraction data with ADPs obtained from multipole electron-density modelling against high-resolution X-ray data has clearly shown that the newly commissioned time-of-flight Laue diffractometer, TOPAZ, at the SNS is capable of measuring very high quality data with minimal systematic errors. This is the case even on organic crystals containing a very large amount of hydrogen. On the other hand, the HAR approach provides much inferior ADPs for rubrene. Similarly the commonly used SHADE approach is observed for both crystals to be inferior to neutron-diffraction data. The ADPs for rubrene are actively being used in a full electron-density study with focus on its semiconducting properties.

5. Supporting information

Crystallographic data in CIF format and details of neutron and X-ray data collection and Hirshfeld atom refinement are given in the supporting information. Programs used for the X-ray data collection and refinement included *CrysAlisPro* (Agilent Technologies UK Ltd, 2013), *SORTAV* (Blessing, 1995), *SHELXS* and *SHELXL97* (Sheldrick, 2008), *Olex2* (Dolomanov *et al.*, 2009) and *XD2006* (Volkov *et al.*, 2006). Core and valence scattering factors were derived from Su & Coppens (1998) and Macchi & Coppens (2001). The final multipole model was subjected to a Hirshfeld (1976) rigid-bond test to all covalent bonds involving non-hydrogen atoms and a residual density analysis (Meindl & Henn, 2008). Hirshfeld atom refinement used the program *TONTO* (Jayatilaka & Grimwood, 2001).

This research was supported by the Danish National Research Foundation (Center for Materials Crystallography, DNRF93). Research conducted at ORNL's Spallation Neutron Source was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, US Department of Energy. We would like to thank the referees for their useful comments.

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