
Supporting information for: Accurate Atomic Displacement Parameters from Time-of-Flight Neutron Diffraction Data at TOPAZ

Authors

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S1. Neutron Data Collection and Refinement

S1.1. Rubrene

A block shaped crystal with clearly visible facets and dimensions of 1.5 x 1.5 x 1.0 mm³ was fixed to the end of a thin polyamide tube using cyanoacrylate glue. The low hydrogen contents of the glue and the thin walls of the tube minimize background scattering while ensuring a rigid and stable mount. This assembly was mounted on the single crystal time of flight Laue diffractometer, TOPAZ, at the Spallation Neutron Source at Oak Ridge National Laboratory during the final commissioning. The sample was cooled from room temperature to 100(1) K, at a rate of 180 K/h, using an Oxford Cryosystems Liquid Nitrogen Cryostream. The data were collected using 13 Anger cameras, each with an active area of approximately 15 x 15 cm², arranged on a nearly spherical tank around the sample. A total of 23 settings, exposed for approximately 3.5 hours each, were collected. The settings were calculated to optimize the coverage using the evolutionary algorithm in the program CrystalPlan (Zikovsky *et al.*, 2011). All detected neutrons are stored with an associated detector ID, position on detector, time, and other experimental data. The stored events are transformed to Q-space and integrated using an ellipsoids fitted to each peak (Shultz *et al.*, 2014) in the program Mantid (Taylor *et al.*, 2012). A total of 98478 reflections (98% completeness, excluding detector edges and negative reflections) were integrated up to a resolution of 0.4 Å.

The integrated data was scaled to correct for the incident beam spectrum, see Figure S1 and the detector efficiency in the program ANVRED (Shultz *et al.*, 1984). This program also corrects the data

for absorption assuming a spherical shape of the crystal. Besides these corrections, reflections were rejected based on a $I/\sigma(I) < 1$ criteria or if they were collected close to the edge of one of the Anger cameras. This results in a total of 24945 reflections up to a maximum resolution of 0.4 Å.

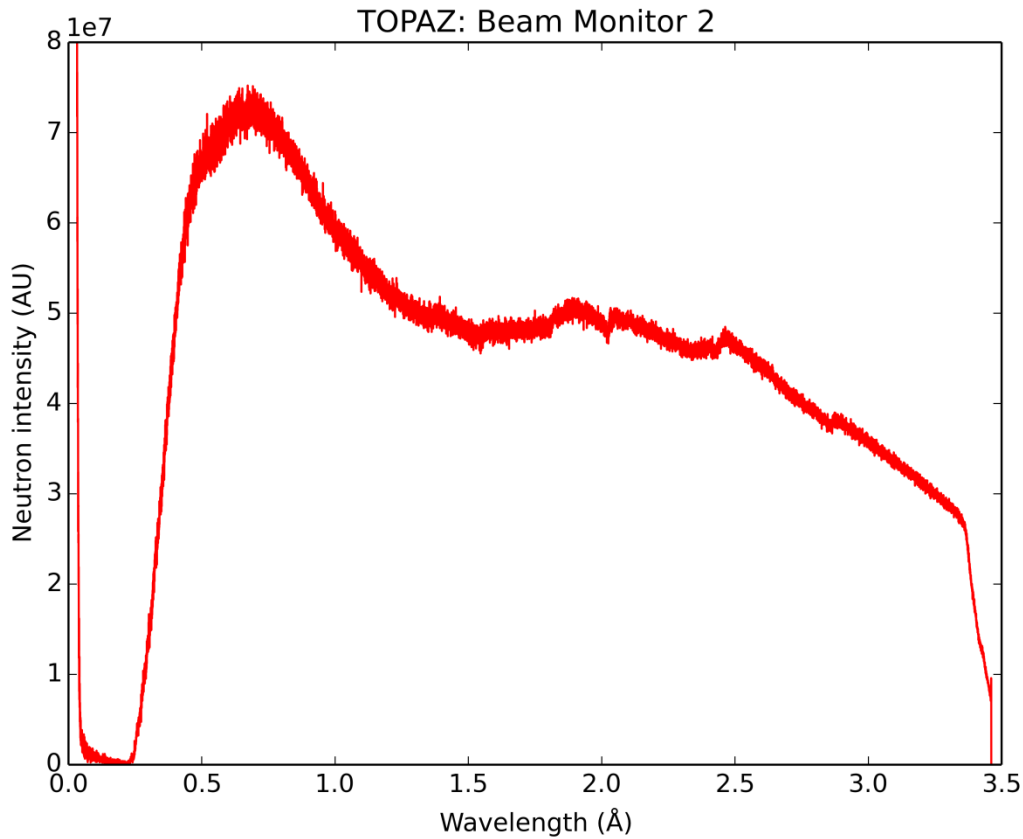


Figure S1 Beam spectrum from TOPAZ.

The 100 K structure reported by Jurchescu *et al.* (2006) was used as a starting model. All coordinates and anisotropic temperature parameters along with a secondary type I Lorentzian spread extinction model was refined using GSAS (Larson & Von Dreele, 1994, Toby, 2001). Based on this model 572 reflections were rejected using the following criteria $F_o^2/F_c^2 > 10$, $F_c^2/F_o^2 > 10$ and $|F_o^2 - F_c^2|/\sigma(F_o^2) > 10$. In addition to these, 1599 additional reflections with $I/\sigma(I) < 3$ was rejected leading to 22775 reflections against which the final model was refined. This does not significantly affect the parameters but does improve the residuals significantly. Crystallographic details are tabulated in Table S1.

S1.2. BIPa

A single crystal was ground from an irregular shape to a 1.2 mm diameter sphere in an air-powered crystal grinder based on the original design by Cordero-Borboa (1985). This sample was mounted in

the same way as rubrene. The sample was cooled to 100 (1) K at a ramp rate of 360 K/h. 17 crystal orientations were measured for approximately 6.5h per orientation. The data was processed as described above for rubrene. 73225 reflections (excluding negative intensities and edges of detectors) were integrated up to a resolution of $d = 0.5\text{\AA}$ corresponding to a coverage of 95%. After corrections in ANVRED 32750 reflections were used in the first refinement cycles starting from the geometry reported by Overgaard *et al.* (1999). 901 outliers were rejected based on the criteria described above. Additionally 6862 weak reflections, $I/\sigma(I) < 3$, were removed. This cut off does not significantly affect the parameters but does improve the residuals significantly. The final model was refined against 25886 reflections. Crystallographic data and refinement details are listed in Table S3.

S2. X-ray Data Collection and Refinement

S2.1. Rubrene

A good quality single crystal of rubrene with dimensions $0.24 \times 0.22 \times 0.18 \text{ mm}^3$ was selected under a polarizing microscope and mounted on the tip of a glass pin attached to goniometer-head using Paratone-N oil. The crystal was slowly cooled to 100(1) K at the rate of 60 K/h with a liquid nitrogen stream using an Oxford cryosystems Cryostream 700 device. High resolution X-ray data up to $(\sin\theta/\lambda)_{\text{max}} = 1.1 \text{ \AA}^{-1}$ with high redundancy (~ 10) and high completeness ($\sim 100\%$) were collected on an Agilent Technologies SuperNova diffractometer fitted with a microfocus Mo K_α source at the Department of Chemistry, Aarhus University. The data was collected using ω -scans 1 degree wide with an exposure time of 25 seconds at low order and 150 seconds at high order.

Cell refinement, data integration and reduction were carried out using the CrysAlisPRO software (Agilent Technologies UK Ltd., 2013). The crystal faces were indexed and used for a numerical absorption correction. Sorting, scaling and merging of the collected data sets were carried out using the SORTAV program (Blessing, 1995). The crystal structure was solved by direct methods in SHELXS and refined by using SHELXL97 (Sheldrick, 2008) in the Olex2 package (Dolomanov *et al.*, 2009). All hydrogen atoms were located from the difference Fourier analysis.

The spherical atom refinement parameters were used as a starting input for the multipole refinement. The multipolar non-spherical atom refinements were performed with XD2006 (Volkov *et al.*, 2006) using the Hansen-Coppens multipole formalism (Hansen & Coppens, 1978). The core and valence scattering factors in the model were derived from Su, Coppens and Macchi wave functions (Su & Coppens, 1998, Macchi & Coppens, 2001). The C-H bond distances were constrained to standard values from neutron experiments, but the positions were otherwise refined freely. Suitable symmetry constraints, separate κ and κ' to define different atom types based chemical environment were applied in the refinement. The refined parameters for the carbon atoms were P_{val} , P_{lm} , κ and κ' in a stepwise manner (monopoles, dipoles, quadrupoles, octopoles, hexadecapoles and kappa parameters) until the

convergence was reached. For hydrogens, P_{val} , bond directed dipole (d_z) and a bond directed quadrupole (q_{3z^2-1}) components were allowed to refine. In the final refinement cycles all parameters were co-refined.

The final multipole model was subjected to a Hirshfeld rigid bond test to all covalent bonds involving non-hydrogen atoms (Hirshfeld, 1976). The maximum difference of mean-square displacement amplitudes (DMSDA) was found to be very low at $3 \times 10^{-4} \text{ \AA}^2$ for the C(3)-C(4) pair. Further, the correctness of the multipole model was tested by the residual density analysis (Meindl & Henn, 2008). It resulted in a flat and parabolic shaped fractal dimension plot (Fig S1). The minimum and maximum residual electron density peaks calculated over the asymmetric unit were -0.18 and 0.18 e \AA^{-3} . Residual density plots in the plane of the molecule and the phenyl ring are included in the supporting information (Fig S2). The crystallographic details are listed in Table S1.

The multipole model was used to estimate anisotropic thermal displacement parameters were calculated with the SHADE server (Madsen, 2006). This model is referred to as $X_{MM, SHADE}$ in the main text. The whole molecule was used for the TLS fit. The four phenyl rings were treated as rigid groups rotating around the C-C bond connecting to the molecular backbone. The weighted R-value for the TLS fit was 0.099. Attempts to allow a second axis of liberation for the phenyl rings were unsuccessful with much higher R-values and non-positive definite hydrogen ADPs. The parameters were evaluated based on the multipolar model with isotropic hydrogen, no iterative procedure were performed.

Refinements of the independent atom models were done in XD2006 using the full multipole model as a starting geometry. Using neutral, spherical-atom model with HF scattering factors generated from Slater-type wave functions, all heavy atom coordinates and thermal parameters were refined against all data and data with $\sin \theta / \lambda \geq 0.8 \text{ \AA}^{-1}$ for IAM and high order IAM, respectively.

Table S1 Crystallographic and refinement data Rubrene.

Radiation	Neutron	X-ray
Empirical Formula	$\text{C}_{42}\text{H}_{28}$	
Formula Weight, g mol^{-1}	535.64	
Crystal size	1.5 x 1.5 x 1.0	0.24 x 0.22 x 0.18
Crystal system	Orthorhombic	
Space Group	Cmca	
λ , \AA	0.4-3.4	0.7107
a, \AA	26.7972(3)	26.8106(3)

b, Å	7.1617(1)	7.1602(1)
c, Å	14.1940(2)	14.2029(1)
V, Å ³	2724.05(5)	2726.52(5)
Z	4	
F(000)	697.76	1120
T, K	100(1)	
ρ, g cm ⁻³	1.299	1.298
μ	1.189 + 0.789λ cm ⁻¹	0.073 mm ⁻¹
T _{max} , T _{min}	0.848, 0.646	0.987, 0.983
sin(θ)/λ _{max} , Å ⁻¹	1.25	1.1
N _{meas} , N _{uniq}	98478, -	83536, 7703
Redundancy	N/A†	10.84
Completeness (%)	98	100
R _{int}	N/A†	0.0328
N _{obs} , N _{var} , (3σ)	22775, 182	6070, 383
R _w (F), R _w (F ²)	0.046, 0.091	0.031, 0.055
R(F), R(F ²),	0.055, 0.088	0.022, 0.025
Goodness of fit	2.46	1.49
Δρ	-0.31, 0.23 fmÅ ⁻³	-0.18, 0.18 eÅ ⁻³

†Each reflection collected in different settings are collected at different wavelength thus all measurements are independent and e.g. absorption and extinction has to be corrected before R_{int} can be calculated. Since R_{int} will be model dependent we do not report it here.

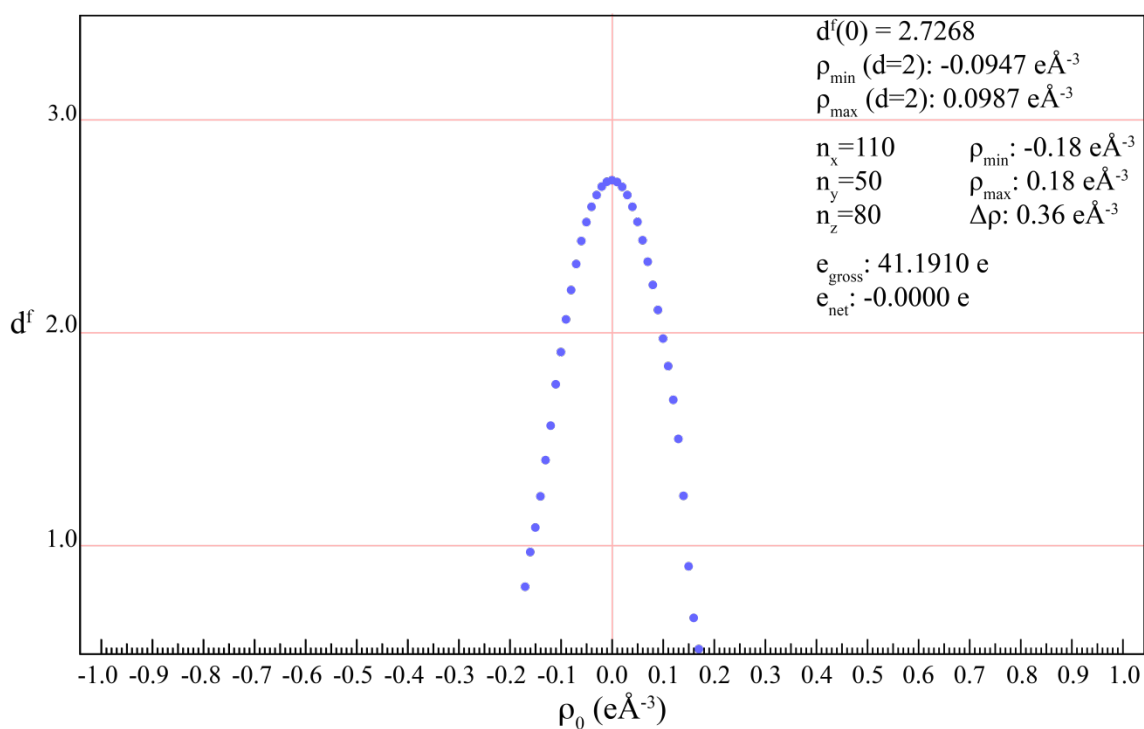


Figure S2 Fractal dimension (d^f) as a function of residual density (ρ_0).

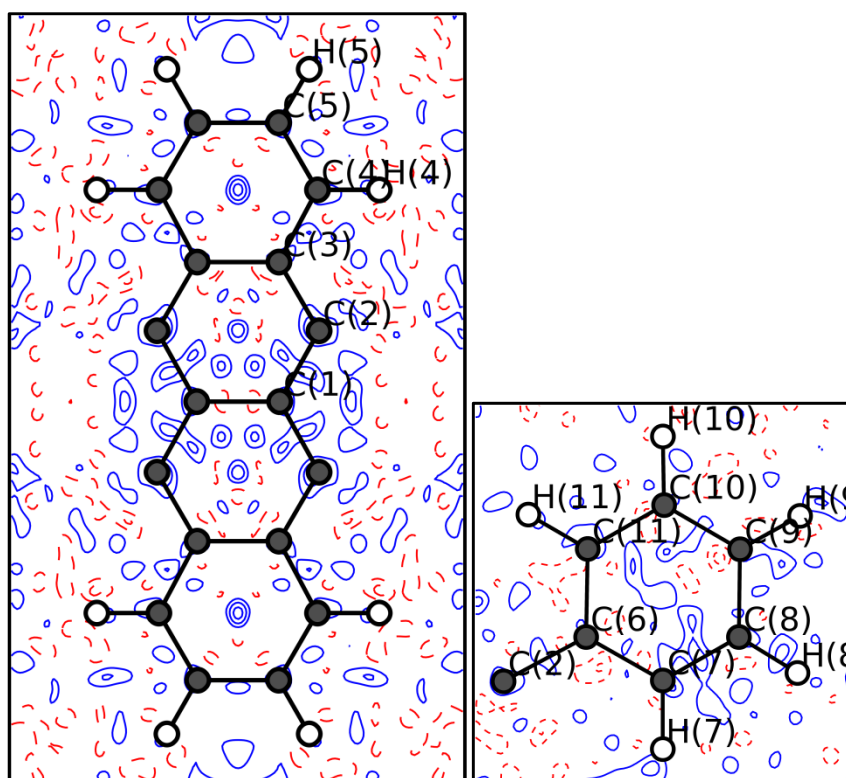


Figure S3 Residual density ($\rho_{\text{obs}}(\mathbf{r}) - \rho_{\text{model}}(\mathbf{r})$) in $0.05 \text{ e}\text{\AA}^{-3}$ steps. Positive and negative contours are represented by full blue lines and dashed red lines, respectively. Maps calculated using a data up to 1.10 \AA^{-1} .

S2.2. BIPa

A yellow block shaped crystal with dimensions of 0.16 x 0.20 x 0.29 mm³ was mounted on a thin glass fiber using epoxy resin on the end of a standard goniometer head. The assembly was mounted on the SuperNova instrument (see above). The sample was flash cooled to 100(1) K. A total of 162776 (41957 unique, 98.4% completeness) reflections up to a maximum resolution of 1.2 Å⁻¹ were integrated using the program CrysAlisPRO. The data was collected using ω -scans 1 degree wide with an exposure time of 30 or 300 seconds at low and high order, respectively. Equivalent reflections were merged in SORTAV yielding an R_{int} value of 3.81%. 27262 reflections with three or more independent measurements and a max resolution of 1.1 Å⁻¹ were used in the refinement.

The structure was refined in SHELXL-97 using the reported structure by Overgaard *et al.* (1999). This model was imported into the XD2006 program suite. Coordinates and thermal parameters of the heavy atoms were refined against the high order reflections ($\sin \theta / \lambda \geq 0.80$ Å⁻¹) to get unbiased positions. In the subsequent refinements cycles the multipoles were gradually added and refined against all data in the same way outlined for BIPa above. For all heavy atoms all symmetry allowed poles up to octupoles were included. For hydrogen a monopole and a bond directed dipole were refined. Separate κ and κ' parameters were refined for C, O and N. All parameters were co-refined until convergence.

The Hirshfeld rigid body test yields an average DMSDA of 3.0×10^{-4} Å². One atom pair, N(4B) and O(3B) shows a high value of 20×10^{-4} Å², all other values are low. The highest/lowest peak in the residual density is 0.31/-0.26 eÅ⁻³ at full resolution ($\sin \theta / \lambda \leq 1.10$ Å⁻¹). At reduced resolution ($\sin \theta / \lambda \leq 0.80$ Å⁻¹) it is reduced to 0.17/-0.16 eÅ⁻³.

Anisotropic thermal displacement parameters for the hydrogen atoms were calculated with the SHADE server (Madsen, 2006) using the coordinates and ADPs from the heavy atoms from the final multipole model. The parameters were calculated separately for each molecule. For imidazole B the TLS analysis didn't converge leading to non-positive definite hydrogen ADPs. The hydrogen parameters therefore were calculated as the sum of a riding motion and the internal motion. The weighted R-values for the TLS fits are listed below in Table S2. The R-values for the two Picric acid molecules are quite high, indicating that the molecule does not behave completely as a rigid group. An attempt to treat the three nitro groups as separate rigid units lead to an even higher R-value. As for rubrene, only one SHADE cycle were performed.

Table S2 Weighted R-values of the TLS fits for the molecules in BIPa.

Molecule	wR _{TLS}
Betaine	0.073

Imidazole A	0.009
Imidazole B	N/A (See text)
Picric acid A	0.158
Picric acid B	0.167

Refinement of the independent atom models were done in XD2006 using the full multipole model as a starting geometry. Using neutral, spherical-atom model with HF scattering factors generated from Slater-type wave functions, all heavy atom coordinates and thermal parameters were refined against all data and data with $\sin \theta / \lambda \geq 0.8 \text{ \AA}^{-1}$ for IAM and high order IAM, respectively.

Table S3 Crystallographic and refinement data BIPa.

Radiation	Neutron	X-ray
Empirical Formula	$\text{C}_{25}\text{N}_{11}\text{O}_{16}\text{H}_{25}$ ($\text{C}_5\text{NO}_2\text{H}_{11}$, 2 $\text{C}_3\text{N}_2\text{H}_5$, 2 $\text{C}_6\text{N}_3\text{O}_7\text{H}_2$)	
Formula Weight, g mol ⁻¹	535.64	
Crystal size	Sphere, r = 0.6 mm	0.29 x 0.20 x 0.16
Crystal system	Monoclinic	
Space Group	C2/c	
λ , Å	0.4-3.4	0.7107
a, Å	33.5759(1)	33.5939(5)
b, Å	7.6607(1)	7.6658(1)
c, Å	25.1114(2)	25.1324(3)
β , °	114.6982(4)	114.716(2)
V, Å ³	5868.14(7)	5879.3(1)
Z	8	
F(000)	2041.53	2944
T, K	100(1)	
ρ , g cm ⁻³	1.624	1.627
μ	$1.220 + 0.639\lambda \text{ cm}^{-1}$	0.077 mm^{-1}
T _{max} , T _{min}	0.888, 0.747	0.990, 0.985
$\sin(\theta)/\lambda_{\text{max}}$, Å ⁻¹	1.00	1.10

$N_{\text{meas}}, N_{\text{uniq}}$	73225, -	41957, 27262
Redundancy	N/A	3.9
Completeness (%)	95.0	98.4
R_{int}	N/A	0.0381
$N_{\text{obs}}, N_{\text{var}}, (3\sigma)$	25886, 693	21277, 1306
$R_w(F), R_w(F^2)$	0.040, 0.078	0.043, 0.072
$R(F), R(F^2)$, all data	0.051, 0.078	0.030, 0.030
Goodness of fit	1.57	0.87
$\Delta\rho$	-0.20, 0.21 $\text{fm}\text{\AA}^{-3}$	-0.26, 0.31 $\text{e}\text{\AA}^{-3}$, (-0.16, 0.17 $\text{e}\text{\AA}^{-3}$ @ $\sin(\theta)/\lambda \leq 0.8\text{\AA}^{-1}$)

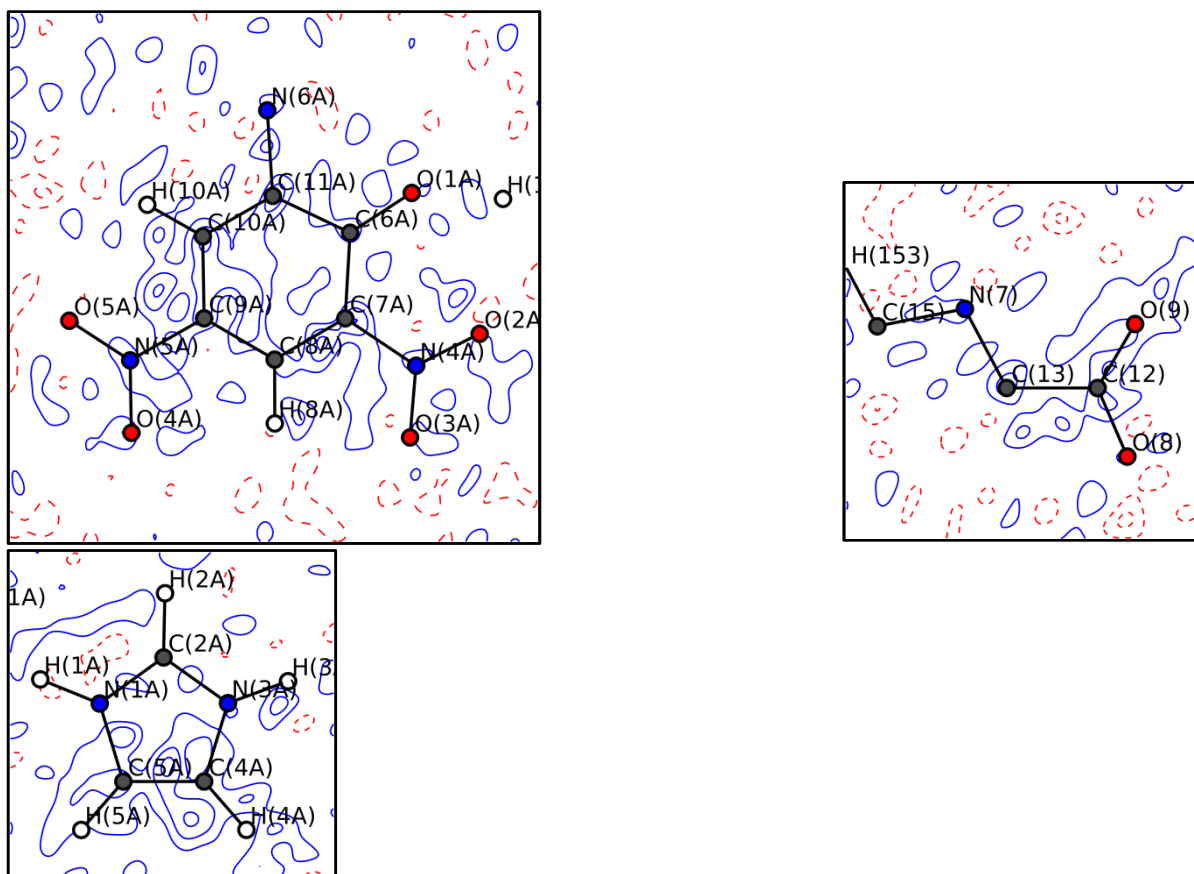


Figure S4 Residual density ($\rho_{\text{obs}}(\mathbf{r}) - \rho_{\text{model}}(\mathbf{r})$) in $0.05 \text{ e}\text{\AA}^{-3}$ steps. Positive and negative contours are represented by full blue lines and dashed red lines, respectively. Maps calculated using a data up to 0.80 \AA^{-1} .

S3. Hirshfeld atom refinement

The Hirshfeld atom refinement (Jayatilaka & Dittrich, 2008) as implemented in the program TONTO (Jayatilaka & Grimwood, 2001) was performed for rubrene using BLYP/cc-pVTZ. The inherent rigid atom constraints in HAR are effectively removed by use of an iterative procedure where the SCF is repeated after convergence is reached and atomic positions are changed. Point charges calculated for atoms in surrounding molecules within a range of 8 Å are used in the SCF cycles, and hydrogen ADPs were refined freely in the process. The HAR is complete when the χ^2 -value is unchanged by refinement of atomic positions and thermal parameters, which in this case took four iterations and a total of almost 7 days on four CPUs. The Table S4 below outlines the results of the refinements.

Table S4 Selected details from Hirshfeld Atom Refinement.

	Rubrene
R(F)	0.0257
No of parameters	159
χ^2	2.96

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