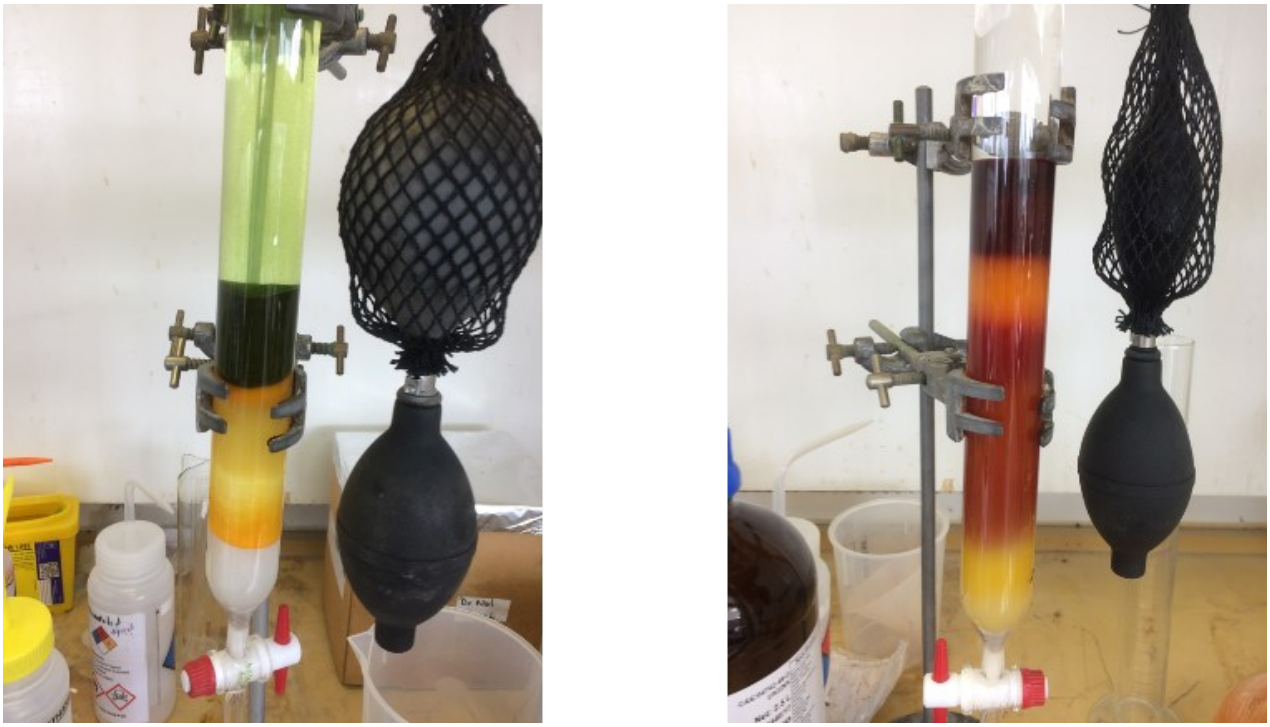
ELECTRONIC SUPPLEMENTARY INFORMATION

Novel Benzothiazole Half-Squaraines: Model Chromophores to Study Dye-TiO_2 Interactions in Dye-Sensitized Solar Cells

Peter J. Holliman,[a*] Christopher P. Kershaw[a], Eurig W. Jones,[a] Diana Meza-Rojas[a], Anthony Lewis[a], James McGettrick[a], Dawn Geatches[b], Kakali Sen[b], Sebastian Metz[b,c], Graham J. Tizzard[d] and Simon J. Coles[d]

[a] College of Engineering, Swansea University, Bay Campus, Swansea SA1 8EN UK.
[b] Scientific Computing Department, STFC Daresbury Laboratory, Daresbury, Warrington, UK
[c] Fraunhofer ISE, Heidenhofstr. 2, 79110 Freiburg, Germany
[d] UK National Crystallography Service, Chemistry, University of Southampton, University Road, Southampton SO17 1BJ UK

S1 - Synthetic data



ESI Figure 1: (left) column chromatography of $C(CH_3)_2$-containing dye **(10)** showing green due to the combination of yellow/red half-squaraine along with a blue full-squaraine impurity and (right) the synthesis of sulphur-containing dye **(3)**, which only shows the red/yellow colour of half-squaraine.

Preparation of 3-dodecyl-2-methylbenzothiazol-3-ium bromide (1)[1]

A mixture of 2-methylbenzothiazole (5.0 g, 33.1 mmol) and 1-bromododecane (16.70 g, 67.02 mmol) was heated for 48 h under N_2 in anhydrous reagent alcohol (80 ml). After cooling, the solvent was removed *in vacuo*. Diethyl ether (100 ml) was added to the round bottom flask and the mixture was refluxed for 8 h. After cooling, the mixture was filtered and the solid was washed with diethyl ether using a soxhlet for 8 h to give a white solid. (Yield 3.31 g, 24.79 %).

^{1}H NMR (400 MHz, DMSO) δ 8.45 (1H, d, J 8.1), 8.34 (1H, d, J 8.4), 7.90 (1H, t, J 7.8), 7.81 (1H, t, J 7.7), 4.71 (2H, t), 3.21 (3H, s), 1.94 – 1.73 (2H, m), 1.43 (2H, dd, J 14.4, 7.2), 1.24 (15H, s), 0.86 (3H, t, J 6.6).

^{13}C NMR (101 MHz, DMSO) δ 177.07, 140.83, 129.36, 129.11, 128.10, 124.64, 116.87, 49.17, 31.28, 28.99, 28.97, 28.91, 28.84, 28.68, 28.57, 27.78, 25.86, 22.08, 16.80, 13.95.

MS (FTMS$^+$) $[M\text{-}Br]^+$ calculated = 318.00, $[M\text{-}Br]^+$ observed = 318.00

Preparation of 3-(2-carboxyethyl)-2-methylbenzothiazol-3-ium bromide (5)[2]

A mixture of 2-methylbenzothiazole (2.00 g, 13.40 mmol) and 3-bromopropionic acid (5.00 g, 32.67 mmol) was heated for 48 h under nitrogen under in anhydrous reagent alcohol (80 ml). After cooling, the solvent was removed *in vacuo*. Diethyl ether (100 ml) was added to the round bottom flask and the mixture was refluxed for 8 h. After cooling the mixture was filtered into a thimble and the solid was washed with diethyl ether using a Soxhlet for 8 h to give a white/ pink solid. (Yield 2.68 g, 66.17 %)

^{1}H NMR (400 MHz, DMSO) δ 8.46 (1H, d, J 8.1), 8.36 (1H, d, J 8.5), 7.88 (1H, t**,** J 7.8), 7.80 (1H, t, J 7.7), 4.90 (2H, t, J 7.2), 3.26 (3H, s), 2.99 (2H, t, J 7.2).

^{13}C NMR (101 MHz, DMSO) δ 178.62, 171.93, 141.20, 129.85, 129.40, 128.53, 125.12, 117.40, 45.46, 32.24, 17.59.

MS (TOF MS ES $^{+}$) $[M]^{+}$ calculated = 222.06, $[M]^{+}$ observed = 222.06, m/e

Preparation of 1-dodecyl-2,3,3-trimethylindol-1-ium bromide (9)[3]

A mixture of 2,3,3-trimethylindolenine (5.00 g, 31.40 mmol) and 1-bromododecane (15.65 g, 62.80 mmol) was heated overnight under nitrogen in anhydrous acetonitrile (80 ml). After cooling, the solvent was removed *in vacuo*. Diethyl ether (100 ml) was added to the round bottom flask and the mixture was refluxed for 8 h. The mixture was filtered through a thimble and the solid was washed with diethyl ether using a soxhlet for 8 h to give a purple solid. (Yield 8.31 g, 64.77 %)

^{1}H NMR (400 MHz, DMSO) δ 8.02 – 7.93 (1 H, m), 7.88 – 7.79 (1 H, m), 7.67 – 7.59 (2 H, m), 4.45 (2 H, t, J 7.7), 2.85 (3 H, s), 1.91 – 1.76 (2 H, m), 1.54 (6 H, s), 1.47 – 1.37 (2 H, m), 1.24 (12 H, s), 0.85 (3 H, t, J 6.6).

^{13}C NMR (101 MHz, DMSO) δ 196.76, 174.93, 138.98, 137.45, 133.51, 131.16, 130.19, 128.88, 127.73, 123.90, 113.83, 55.96, 48.33, 34.12, 29.21, 29.14, 29.07, 28.97, 27.92, 26.31, 24.92, 22.10, 14.30

MS (FTMS $^{+}$) $[M\text{-}C_2H_4]^{+}$ calculated = 300.51, $[M\text{-}C_2H_4]^{+}$ observed = 300.27

Preparation of 3-((1-dodecyl-3,3-dimethylindolin-2-ylidene)methyl)-4-ethoxycyclobut-3-ene-1,2-dione (10)[3]

3.00 g (7.34 mmol) of 1-dodecyl-2,3,3-trimethyl-indol-1-ium bromide **(9)**, 1.25 g (7.34 mmol) of 3,4-Diethoxy-3-cyclobutene-1,2-dione **(2)** and triethylamine (3 ml) were dissolved in ethanol (25 ml) and refluxed for 30 minutes under nitrogen. The solvent was removed from the green solution and the crude product was purified by column chromatography (SiO_2) with petroleum ether and ethyl acetate (80:20) as eluent. (Yield 1.39 g, 41.87 %).

^{1}H NMR (400 MHz, DMSO) δ 7.43 (1H, d, J 7.3), 7.28 (1H, t, J 7.6), 7.17 (1H, d, J 7.9), 7.06 (1H, t, J 7.4), 5.36 (1H, s), 4.81 (2H, q, J 7.1), 3.90 (2H, t, J 7.2), 1.70 – 1.58 (2H, m), 1.54 (6H, s), 1.44 (3H, t, J 7.1), 1.31 (4H, s), 1.21 (10H, s), 0.83 (3H, t, J 6.7).

^{13}C NMR (101 MHz, DMSO) δ 192.16, 187.69, 186.22, 172.55, 167.74, 142.42, 140.31, 127.83, 122.51, 121.93, 109.19, 80.70, 69.72, 47.41, 42.11, 31.24, 28.79, 28.77, 28.60, 28.53, 26.47, 26.03, 25.69, 22.04, 15.64, 13.92

FT-IR (ATR) ν/cm^{-1} 2974 (br), 2958 (br), 2924 (br), 2845 (br), 1770 (s), 1717 (s), 1687 (s), 1534 (s), 1514 (s), 1424 (s), 1290 (s).

UV-visible λ_{max} 424 nm (71,704 M^{-1} cm^{-1} ± 1,993 M^{-1} cm^{-1}) in ethanol.

Preparation of 3-((1-dodecyl-3,3-dimethylindolin-2-ylidene)methyl)-4-hydroxycyclobut-3-ene-1,2-dione (11)[3]

3-((1-dodecyl-3,3-dimethylindolin-2-ylidene)methyl)-4-ethoxycyclobut-3-ene-1,2-dione (**10**) (1.00 g, 2.21 mmol) was dissolved in ethanol (10 ml) and heated under reflux. Tetrabutylammonium hydroxide solution (2 ml, 40 %) was added and the mixture was refluxed for 1 h. After cooling the solvent was removed *in vacuo* and the product was obtained as a red solid after purification by column chromatography (SiO_2) with ethyl acetate and petroleum ether as eluent to remove impurities. Pure product can then be run off the column with a dichloromethane: methanol mix (90:10). Yield (0.48 g, 32.65 %).

^{1}H NMR (500 MHz, DMSO) δ 7.23 (1H, d, J 7.3), 7.13 (1H, td, J 7.8, 1.2), 6.82 (2H, t, J 7.5), 5.39 (1H, s), 3.69 (2H, t, J 7.3), 1.59 (8H, m, J 7.3, 6.2), 1.55 (6H, s), 1.22 (12H, s), 0.85 (3H, t, J 6.9).

^{13}C NMR (126 MHz, DMSO) δ 210.50, 195.58, 179.18, 157.86, 144.52, 140.30, 127.68, 122.00, 119.85, 107.08, 84.66, 49.06, 46.21, 41.93, 31.75, 29.46, 29.43, 29.37, 29.31, 29.15, 28.06, 26.86, 26.17, 23.53, 22.56, 19.68, 14.42, 13.96.

MS (FTMS$^-$) $[M\text{-}TBA]^-$ calculated = 422.27, $[M\text{-}TBA]^-$ observed = 422.85, m/e

FT-IR (ATR) ν/cm^{-1} 2954 (m), 2924 (m), 2856 (m), 1748 (s), 1552 (vs), 1460 (m), 1360 (m), 1308 (m)

UV-visible λ_{max} 423 nm (38,218 M^{-1} cm^{-1} ± 478 M^{-1} cm^{-1}) in ethanol.

Preparation of 1-(2-carboxyethyl)-2,3,3-trimethyl-indol-1-ium bromide (13)[2]

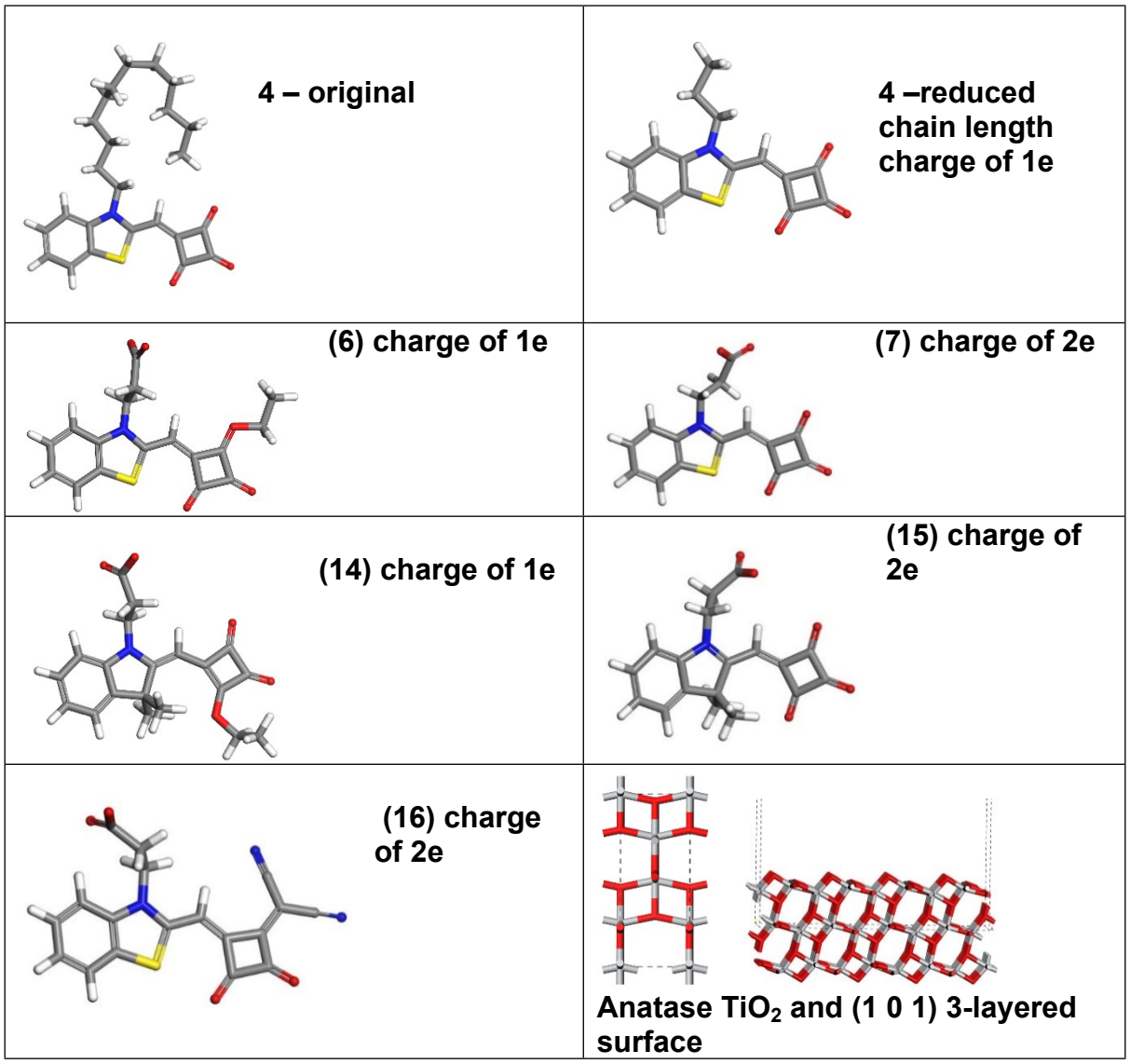
A mixture of 2,3,3-trimethylindolenine (5.0 g, 31.40 mmol) and 3-bromopropionic acid (10.00 g, 65.37 mmol) was heated overnight under nitrogen in anhydrous toluene (80 ml). After cooling, the solvent was removed *in vacuo.* Diethyl ether (100 ml) was added to the round bottom flask and the mixture was refluxed for 8 h. After cooling the mixture was filtered into a thimble and the solid was washed with diethyl ether using a soxhlet for 8 h to give a purple solid. (Yield 7.13 g, 72.76 %)

^{1}H NMR (400 MHz, DMSO) δ 8.00 (1H, dd, J 6.0, 2.9), 7.85 (1H, dd, J 5.3, 3.3), 7.67 – 7.58 (2H, m), 4.66 (2H, t, J 7.0), 2.99 (2H, t, J 7.0), 2.87 (3H, s), 1.54 (6H, s).

^{13}C NMR (101 MHz, DMSO) δ 198.38, 171.99, 142.23, 141.30, 129.82, 129.39, 123.96, 116.04, 54.74, 44.03, 31.58, 22.35, 14.90.

MS (FTMS $^+$) $[M^+]$ calculated = 232.30, $[M^+]$ observed = 232.13, m/e

S2 – Modelling data



ESI Figure 2: Six half-squaraine dyes and the final TiO_2 model. Grey - carbon; white - hydrogen; red -oxygen; blue - nitrogen; yellow – sulphur; silver - Ti. We added one or two hydrogens to the dyes to make then neutral for both gas-phase calculations and surface adsorption.

Analytical methods

Relative total energies: AutoDock (release 4.2.6) (release 4.2.6)[4,5] produced total energies for optimised, dye-plus-TiO_2-surface configurations that were compared for same-molecule systems, from which subsets of the lowest total energy configurations were identified.

Absolute adsorption energies: Absolute adsorption energy (E_{AA}) is the energy difference between the total energy of the combined, relaxed dye-plus-TiO_2-surface configuration ($E_{slab+mol}$) and the sum of the energies of a relaxed TiO_2 slab ($E_{slab\text{-}relxd}$) and a relaxed dye molecule in vacuum ($E_{gp.mol\text{-}relxd}$):

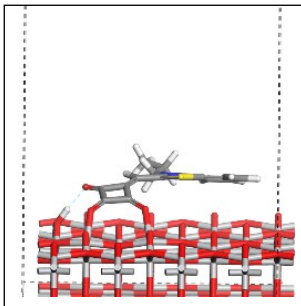
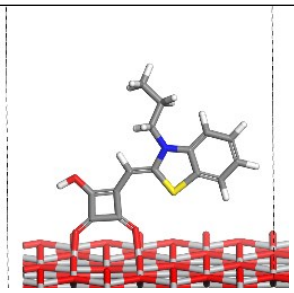
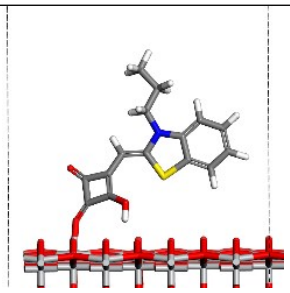
$$E_{AA} = E_{slab+mol} - (E_{slab-relxd} + E_{gp.mol-relxd})$$

E_{AA} were calculated for the subsets of lowest energy, dye-plus-TiO_2-surface configurations obtained from AutoDock, that were further optimised under the periodic, DFT parameters and convergence criteria detailed in the main manuscript, section: 'Modelling Procedure'.

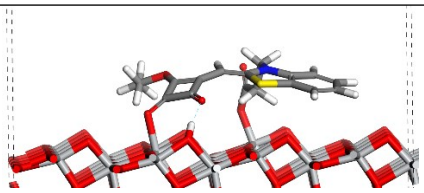
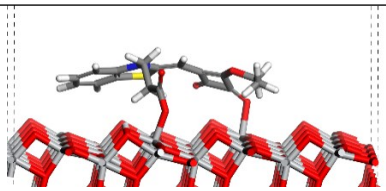
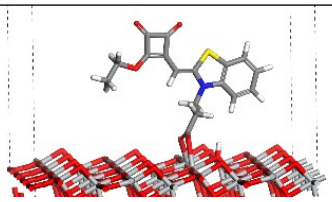
Simulated AR-XPS: Simulated Angle Resolved X-ray Photo-Spectroscopy provides a comparison with experimental, AR-XPS, which is a useful indicator of the orientation of the dye molecules on the physical, TiO_2 surface. The highest-lying Ti in the surface was taken as the datum and the perpendicular, z-distances of the dye's nitrogen (indole and cyano-), oxygen (squaraine and carboxylic) and sulphur atoms were calculated; plotting these produced simulated AR-XPS analagous to experimental spectra.

Results

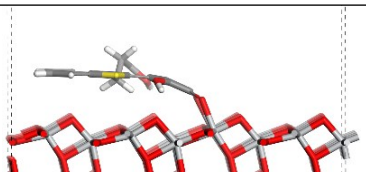
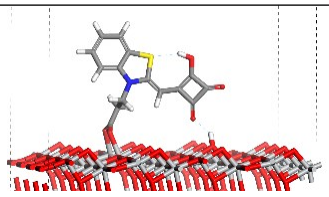
AutoDock produced configurations with relatively low energy; however, it is heavily dependent on the force field parameters of the dyes and surface; acknowledging the production of unphysical configurations, we added configurations where the dyes were oriented vertically and, where applicable, on their 'side' to the TiO_2 surface. This produced 19 dye-plus-TiO_2-surface configurations that were fully geometry optimised according to the convergence criteria (detailed in the section: 'Modelling Procedure' of the main manuscript); their final configurations (excluding the constrained configurations) are shown in Figure S3-S8

		
m04_horz -3.313	m04_vert-a -2.205	m04_vert-b -1.794

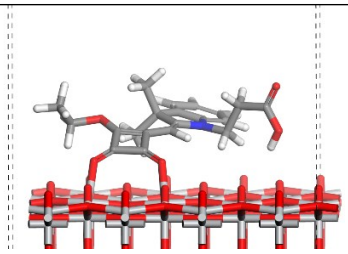
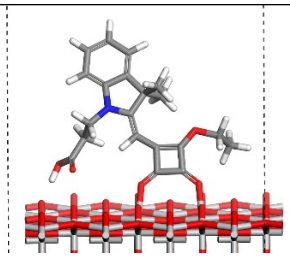
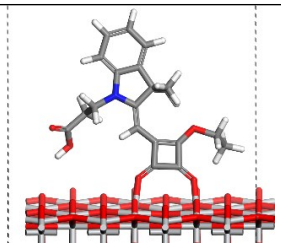
ESI Figure 3: Final, lowest total energy configurations of TiO_2 surface-adsorbed dye **(4)** (corresponding to the AR-XPS graphs shown in the main manuscript, section: 'Simulated AR-XPS') and absolute adsorption energies (eV) to 3 d.p.

		
m06_horz-a -3.052	m06_horz-b -2.320	m06_vert -1.158

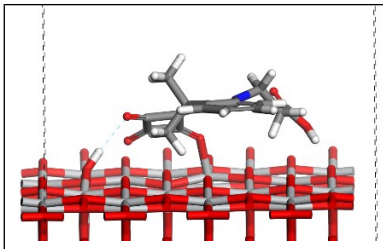
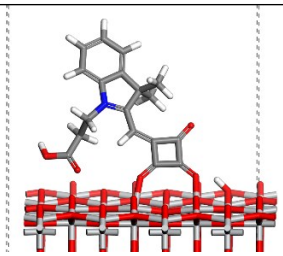
ESI Figure 4: Final, lowest total energy configurations of TiO_2 surface-adsorbed dye **(6)** (corresponding to the AR-XPS graphs shown in the main manuscript, section: 'Simulated AR-XPS') and absolute adsorption energies (eV) to 3 d.p.

		
m07_horz -3.214	m07_vert -1.635	

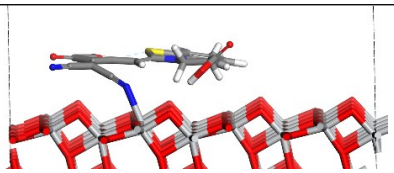
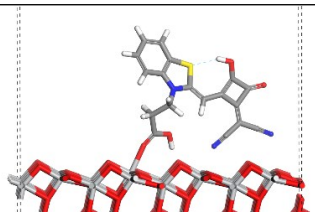
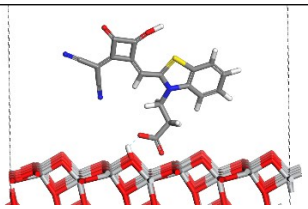
ESI Figure 5: Final, lowest total energy configurations of TiO_2 surface-adsorbed dye **(7)** (corresponding to the AR-XPS graphs shown in the main manuscript, section: 'Simulated AR-XPS') and absolute adsorption energies (eV) to 3 d.p.

		
m14_horz -2.957	m14_side -2.791	m14_vert -2.289

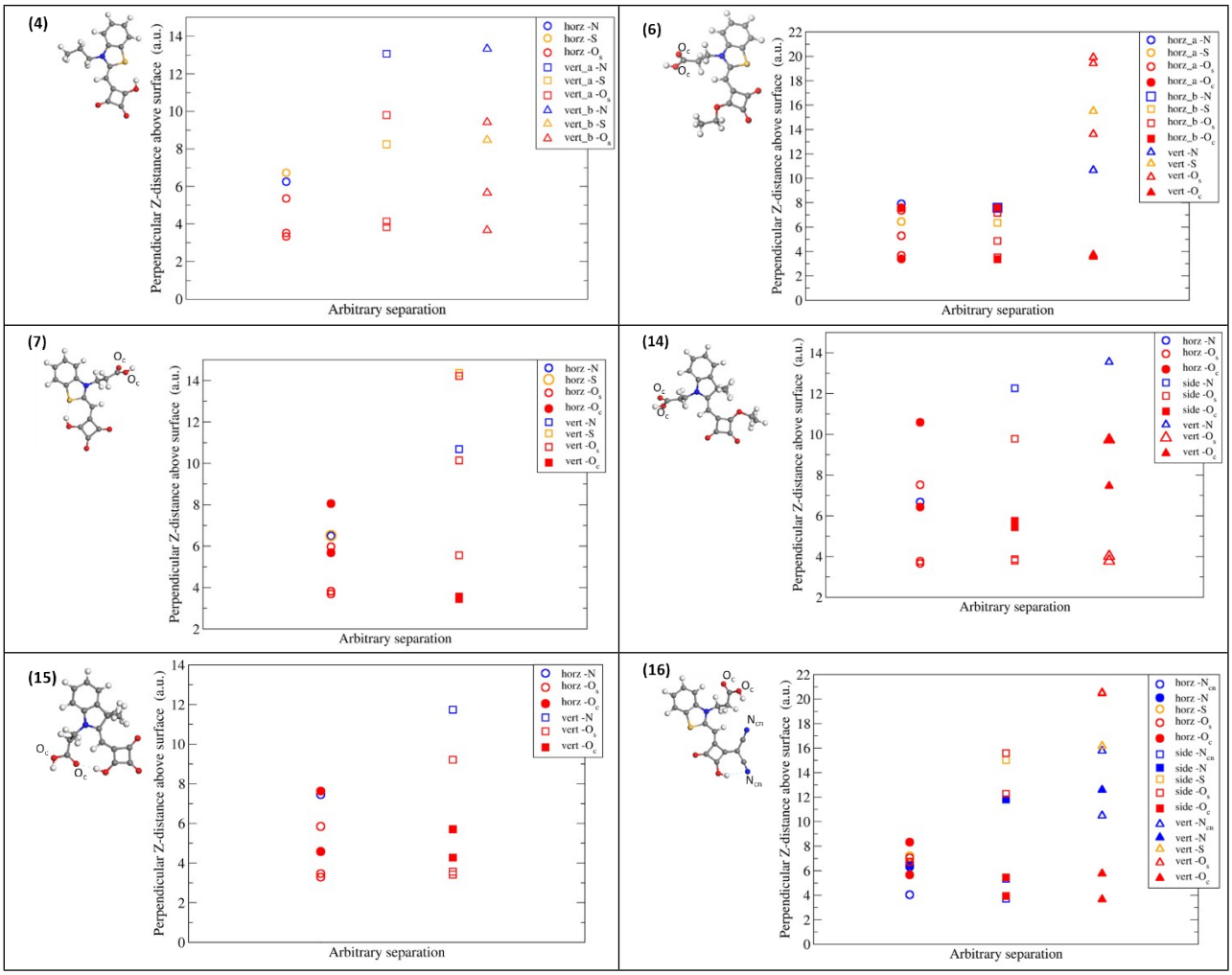
ESI Figure 6: Final, lowest total energy configurations of TiO_2 surface-adsorbed dye **(14)** (corresponding to the AR-XPS graphs shown in the main manuscript, section: 'Simulated AR-XPS') and absolute adsorption energies (eV) to 3 d.p.

		
m15_horz -3.034	m15_vert -2.365	

ESI Figure 7: Final, lowest total energy configurations of TiO_2 surface-adsorbed dye **(15)** (corresponding to the AR-XPS graphs shown in the main manuscript, section: 'Simulated AR-XPS') and absolute adsorption energies (eV) to 3 d.p.

		
m16_horz -2.320	m16_side -2.100	m16_vert -0.938

ESI Figure 8: Final, lowest total energy configurations of TiO_2 surface-adsorbed dye **(16)** (corresponding to the AR-XPS graphs shown in the main manuscript, section: 'Simulated AR-XPS') and absolute adsorption energies (eV) to 3 d.p.



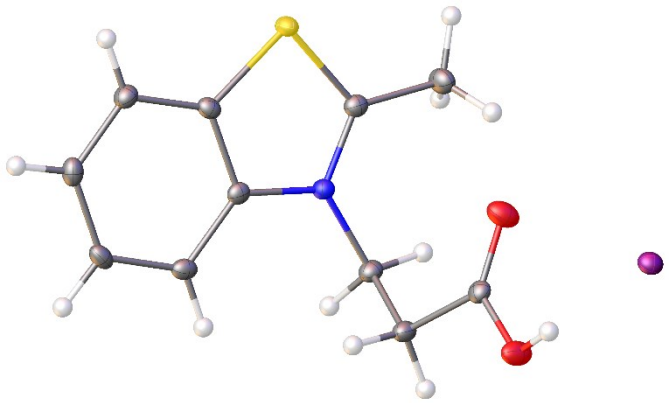
ESI Figure 9: AR-XPS of all low-energy configurations - horizontal (horz), vertical (vert) and side (between horizontal and vertical) - for each dye/TiO_2 system. The y-axis (note the different scales) shows the perpendicular distance above the highest Ti in the surface of (in atomic units): indole nitrogen (N), cyano nitrogen (N_{cn}), sulphur (S), oxygens of the squaraine moiety (O_s), oxygens of the carboxyl group (O_c).

S3 – X-ray crystallography

UK National Crystallography Service
www.ncs.ac.uk | info@ncs.ac.uk | 023 8059 6722

Submitted by: **Peter J. Holliman**
Swansea University
Solved by: **Graham J. Tizzard**
Sample ID: **15CHK-05-E1**

Crystal Data and Experimental



Experimental. Single colourless plate-shaped crystals of **5** were supplied. A suitable crystal 0.10×0.05×0.02 mm^3 was selected and mounted on a suitable support on a Rigaku FRE+ equipped with VHF Varimax confocal mirrors and an AFC12 goniometer and HG Saturn 724+ detector. The crystal was kept at a steady T = 100(2) K during data collection. The structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program using the Intrinsic Phasing solution method and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The model was refined with version 2018/3 of **ShelXL** (Sheldrick, 2015) using Least Squares minimisation.

Crystal Data. $C_{11}H_{12}NO_2SI$, M_r = 349.18, monoclinic, $C2/c$ (No. 15), a = 14.2803(3) Å, b = 10.7176(2) Å, c = 16.7845(4) Å, β = 108.662(2)°, α = γ = 90°, V = 2433.81(9) Å^3, T = 100(2) K, Z = 8, Z' = 1, μ(MoK$_\alpha$) = 2.788 mm^{-1}, 10576 reflections measured, 2789 unique (R_{int} = 0.0203) which were used in all calculations. The final wR_2 was 0.0405 (all data) and R_1 was 0.0168 (I > 2(I)).

Compound	**5**
CCDC	1908056
Formula	$C_{11}H_{12}NO_2SI$
$D_{calc.}$/ g cm^{-3}	1.906
μ/mm^{-1}	2.788
Formula Weight	349.18
Colour	colourless
Shape	plate
Size/mm^3	0.10×0.05×0.02
T/K	100(2)
Crystal System	monoclinic
Space Group	$C2/c$
a/Å	14.2803(3)
b/Å	10.7176(2)
c/Å	16.7845(4)
α/°	90
β/°	108.662(2)
γ/°	90
V/Å^3	2433.81(9)
Z	8
Z'	1
Wavelength/Å	0.71075
Radiation type	MoK$_\alpha$
Θ_{min}/°	2.424
Θ_{max}/°	27.485
Measured Refl.	10576
Independent Refl.	2789
Reflections with I > 2(I)	2606
R_{int}	0.0203
Parameters	149
Restraints	0
Largest Peak	0.538
Deepest Hole	-0.338
GooF	1.052
wR_2 (all data)	0.0405
wR_2	0.0398
R_1 (all data)	0.0192
R_1	0.0168

Structure Quality Indicators

Reflections:	d min (Mo) 0.77	I/σ 59.0	Rint 2.03%	complete 100% (IUCr) 100%
Refinement:	Shift -0.002	Max Peak 0.5	Min Peak -0.3	GooF 1.052

A colourless plate-shaped crystal with dimensions 0.10×0.05×0.02 mm^3 was mounted on a suitable support. X-ray diffraction data were collected using a Rigaku FRE+ equipped with VHF Varimax confocal mirrors and an AFC12 goniometer and HG Saturn 724+ detector equipped with an Oxford Cryosystems low-temperature device, operating at T = 100(2) K.

Data were measured using profile data from ω-scans of 1.0 ° per frame for 7.0 s using MoK_α radiation (Rotating Anode, 45.0 kV, 55.0 mA). The total number of runs and images was based on the strategy calculation from the program **CrystalClear** (Rigaku).The maximum resolution achieved was Θ = 27.485°.

Cell parameters were retrieved using the **CrysAlisPro** (Rigaku, V1.171.40.45a, 2019) software and refined using **CrysAlisPro** (Rigaku, V1.171.40.45a, 2019) on 8227 reflections, 78 % of the observed reflections. Data reduction was performed using the **CrysAlisPro** (Rigaku, V1.171.40.45a, 2019) software which corrects for Lorentz polarisation. The final completeness is 99.90 % out to 27.485° in Θ.

A multi-scan absorption correction was performed using CrysAlisPro 1.171.40.45a (Rigaku Oxford Diffraction, 2019) using spherical harmonics as implemented in SCALE3 ABSPACK. The absorption coefficient μ of this material is 2.788 mm^{-1} at this wavelength (λ = 0.71075Å) and the minimum and maximum transmissions are 0.836 and 1.000.

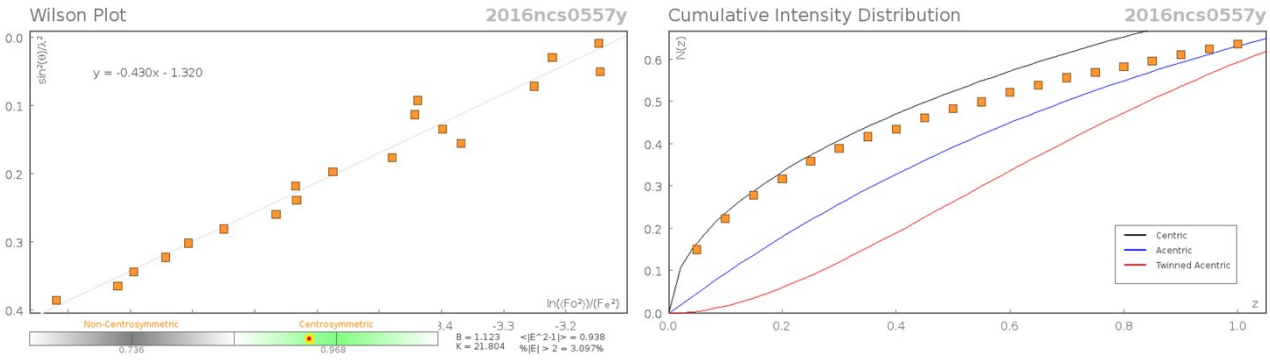
The structure was solved in the space group $C2/c$ (# 15) by Intrinsic Phasing using the **ShelXT** (Sheldrick, 2015) structure solution program and refined by Least Squares using version 2018/3 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Most hydrogen atom positions were calculated geometrically and refined using the riding model, but some hydrogen atoms were refined freely (see below).

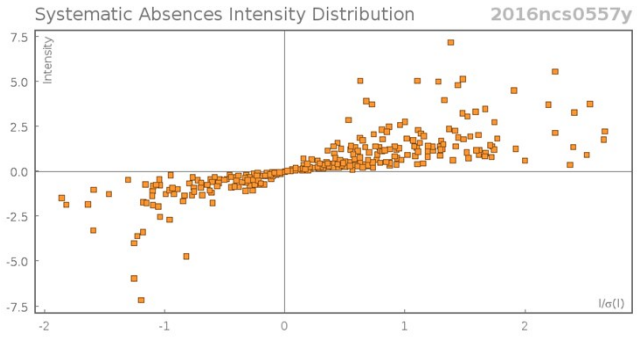
_refine_special_details: Hydrogen atom positions were calculated geometrically except H2 (bound to O2) which was located from the difference map and refined using the riding model.

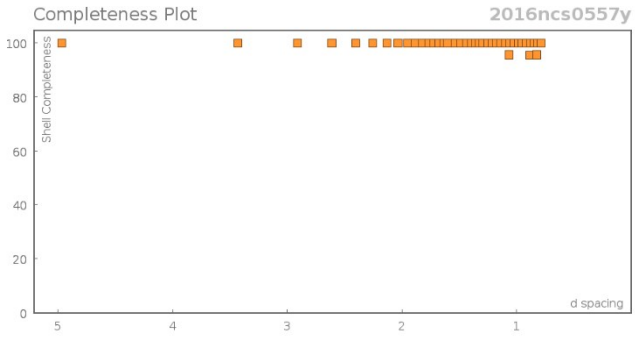
_exptl_absorpt_process_details: CrysAlisPro 1.171.40.45a (Rigaku Oxford Diffraction, 2019) using spherical harmonics as implemented in SCALE3 ABSPACK.

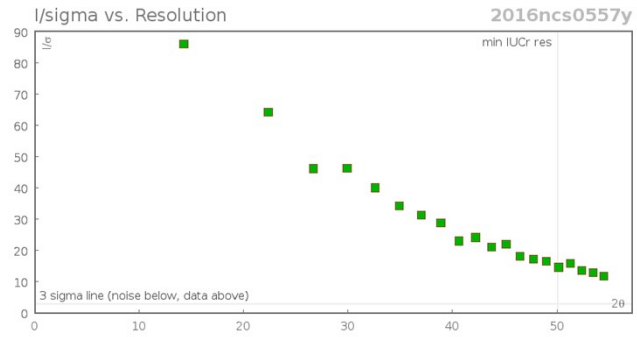
There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 8 and Z' is 1.

Data Plots: Diffraction Data

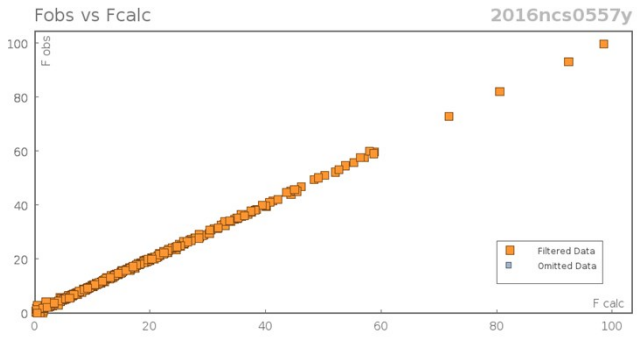


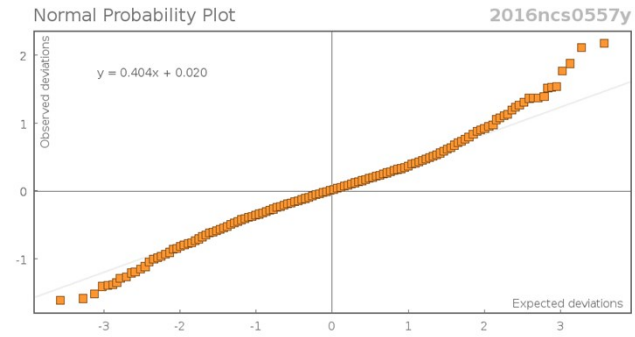






Data Plots: Refinement and Data





Reflection Statistics

Total reflections (after filtering)	10960	Unique reflections	2789
Completeness	0.999	Mean I/σ	49.05
hkl_{max} collected	(18, 13, 21)	hkl_{min} collected	(-17, -8, -18)
hkl_{max} used	(17, 13, 21)	hkl_{min} used	(-18, 0, 0)
Lim d_{max} collected	100.0	Lim d_{min} collected	0.36
d_{max} used	8.4	d_{min} used	0.77
Friedel pairs	1584	Friedel pairs merged	1
Inconsistent equivalents	12	R_{int}	0.0203
R_{sigma}	0.0169	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	0
Multiplicity	(2721, 3210, 434, 118, 9)	Maximum multiplicity	16
Removed systematic absences	384	Filtered off (Shel/OMIT)	0

Table 1: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **5**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
I1	6647.9(2)	8449.5(2)	6119.8(2)	13.84(5)
S1	11361.9(3)	10172.8(4)	5134.8(3)	12.91(9)
O1	9548.4(10)	8435.9(11)	6460.6(10)	21.3(3)
O2	8694.0(9)	6663.0(12)	6376.5(10)	20.4(3)
N1	11311.8(9)	8085.5(13)	5836.7(9)	11.0(3)
C1	11391.2(11)	9308.1(16)	5992.3(11)	12.6(3)
C2	11247.9(11)	8836.3(16)	4527.7(11)	12.1(3)
C3	11199.2(12)	8740.7(17)	3687.9(11)	14.4(3)
C4	11170.3(11)	7560.0(17)	3350.0(11)	15.1(3)
C5	11204.7(12)	6496.3(15)	3842.0(12)	14.3(4)
C6	11244.3(12)	6580.1(15)	4677.2(12)	13.3(3)
C7	11253.8(10)	7773.9(16)	5011.9(11)	11.3(3)
C8	11510.8(13)	9898.2(17)	6817.7(11)	17.3(4)
C9	11300.1(11)	7125.5(16)	6468.9(11)	13.4(3)
C10	10300.4(12)	6488.3(15)	6292.0(12)	14.2(4)
C11	9492.3(11)	7319.7(16)	6390.1(11)	12.8(3)

Table 2: Anisotropic Displacement Parameters (×10⁴) **5**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + \ldots + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I1	13.07(6)	11.94(7)	16.02(7)	0.85(4)	4.00(5)	1.96(4)
S1	16.73(18)	9.5(2)	12.7(2)	0.11(16)	4.93(16)	0.01(15)
O1	18.0(6)	14.7(7)	31.1(9)	-2.7(5)	7.9(6)	1.1(5)
O2	15.1(6)	14.4(7)	35.4(9)	2.8(6)	13.0(6)	2.9(5)
N1	10.9(6)	10.4(7)	11.0(7)	0.7(6)	2.7(5)	0.1(5)
C1	10.3(6)	12.8(9)	14.4(9)	1.4(7)	3.6(6)	0.7(6)
C2	10.2(7)	10.5(8)	15.1(9)	-0.9(7)	3.5(6)	0.8(6)
C3	15.0(7)	14.5(9)	14.0(9)	2.6(7)	5.2(6)	1.2(6)
C4	12.8(7)	20.0(10)	12.9(9)	-2.8(7)	4.8(6)	-0.3(6)
C5	11.9(7)	12.2(9)	19.5(10)	-4.8(7)	5.9(7)	-0.6(6)
C6	10.0(7)	11.2(9)	18.6(10)	1.1(7)	4.7(7)	-0.2(6)
C7	7.9(6)	12.4(9)	13.7(9)	1.2(7)	3.6(6)	0.1(6)
C8	22.0(8)	15.3(9)	13.8(9)	-2.1(7)	4.7(7)	-1.2(7)
C9	13.8(7)	12.5(9)	14.1(9)	3.0(7)	4.9(6)	1.4(6)
C10	15.1(7)	11.5(9)	18.0(10)	1.9(7)	8.0(7)	0.6(6)
C11	14.3(7)	13.6(9)	10.5(8)	2.1(6)	4.1(6)	0.8(6)

Table 3: Bond Lengths in Å for **5**.

Atom	Atom	Length/Å
S1	C1	1.7011(17)
S1	C2	1.7351(18)
O1	C11	1.202(2)
O2	C11	1.334(2)
N1	C1	1.334(2)
N1	C7	1.401(2)
N1	C9	1.482(2)
C1	C8	1.482(2)
C2	C3	1.393(2)
C2	C7	1.397(2)
C3	C4	1.382(3)
C4	C5	1.399(3)
C5	C6	1.388(3)
C6	C7	1.396(2)
C9	C10	1.524(2)
C10	C11	1.508(2)

Table 4: Bond Angles in ° for **5**.

Atom	Atom	Atom	Angle/°
C1	S1	C2	91.11(8)
C1	N1	C7	113.72(14)
C1	N1	C9	124.17(14)
C7	N1	C9	122.11(14)
N1	C1	S1	113.08(13)
N1	C1	C8	125.40(15)
C8	C1	S1	121.51(13)
C3	C2	S1	128.32(14)
C3	C2	C7	121.18(16)
C7	C2	S1	110.43(13)
C4	C3	C2	117.91(17)
C3	C4	C5	120.87(17)
C6	C5	C4	121.72(15)
C5	C6	C7	117.25(15)
C2	C7	N1	111.60(15)
C6	C7	N1	127.32(16)
C6	C7	C2	121.02(16)
N1	C9	C10	113.34(14)
C11	C10	C9	114.58(14)
O1	C11	O2	123.81(15)
O1	C11	C10	124.71(15)
O2	C11	C10	111.48(15)

Table 5: Torsion Angles in ° for **5**.

Atom	Atom	Atom	Atom	Angle/°
S1	C2	C3	C4	176.04(12)
S1	C2	C7	N1	2.24(15)
S1	C2	C7	C6	-175.25(12)
N1	C9	C10	C11	-68.0(2)
C1	S1	C2	C3	-178.19(15)
C1	S1	C2	C7	-1.01(12)
C1	N1	C7	C2	-2.71(18)
C1	N1	C7	C6	174.58(15)
C1	N1	C9	C10	110.95(17)
C2	S1	C1	N1	-0.52(12)
C2	S1	C1	C8	178.54(14)
C2	C3	C4	C5	-1.0(2)
C3	C2	C7	N1	179.65(14)
C3	C2	C7	C6	2.2(2)
C3	C4	C5	C6	1.6(2)
C4	C5	C6	C7	-0.3(2)
C5	C6	C7	N1	-178.58(14)
C5	C6	C7	C2	-1.5(2)
C7	N1	C1	S1	1.94(16)
C7	N1	C1	C8	-177.07(14)
C7	N1	C9	C10	-70.04(18)
C7	C2	C3	C4	-0.9(2)
C9	N1	C1	S1	-178.97(11)
C9	N1	C1	C8	2.0(2)
C9	N1	C7	C2	178.18(13)
C9	N1	C7	C6	-4.5(2)
C9	C10	C11	O1	12.2(3)
C9	C10	C11	O2	-168.77(15

Atom	Atom	Atom	Atom	Angle/°
				)

Table 6: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **5**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H2	8262(18)	7090(20)	6353(15)	31
H3	11186.18	9464.33	3357.67	17
H4	11126.47	7469.31	2776.21	18
H5	11200.78	5695.89	3597.8	17
H6	11264.08	5854.72	5007.55	16
H8A	11535.01	10806.98	6762.85	26
H8B	12126.19	9606.04	7230.29	26
H8C	10950.43	9671.67	7005.58	26
H9A	11483.74	7521.69	7030.73	16
H9B	11805.19	6485.4	6483.64	16
H10A	10092.02	6158.94	5710.39	17
H10B	10378.55	5768.44	6677.43	17

Citations

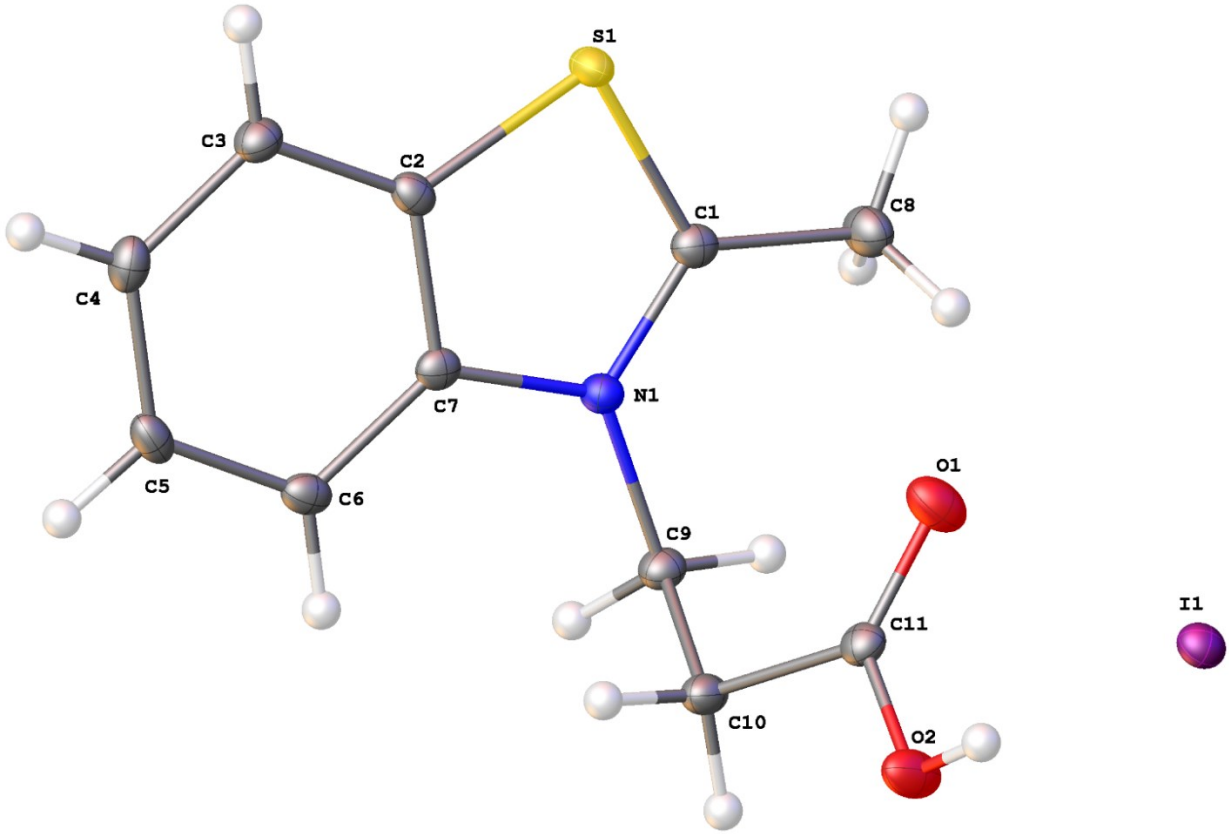
CrysAlisPro Software System, Rigaku Oxford Diffraction, (2019).

CrystalClear, Rigaku Corporation, The Woodlands, Texas, U.S.A., (2008-2014).

O.V. Dolomanov and L.J. Bourhis and R.J. Gildea and J.A.K. Howard and H. Puschmann, Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.*, (2009), **42**, 339-341.

Sheldrick, G.M., Crystal structure refinement with ShelXL, *Acta Cryst.*, (2015), **C27**, 3-8.

Sheldrick, G.M., ShelXT-Integrated space-group and crystal-structure determination, *Acta Cryst.*, (2015), **A71**, 3-8.



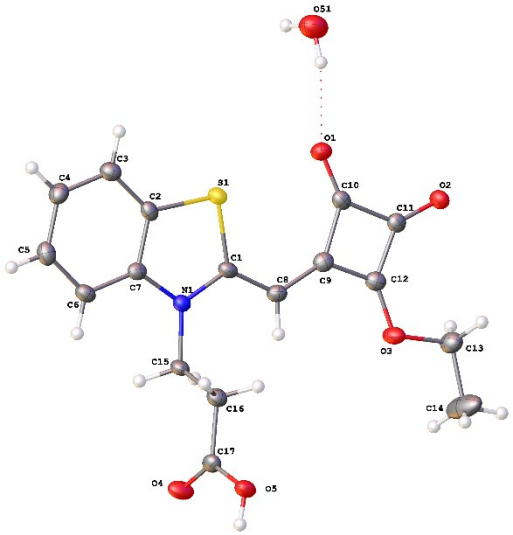
Submitted by: **Peter J. Holliman**

Swansea University

Solved by: **Graham J. Tizzard**

Sample ID: **15CK-05-E2**

Crystal Data and Experimental



Experimental. Single yellow block-shaped crystals of **6** were supplied. A suitable crystal 0.10×0.10×0.06 mm^3 was selected and mounted on a MITIGEN holder in perfluoroether oil on a Rigaku FRE+ equipped with HF Varimax confocal mirrors and an AFC12 goniometer and HG Saturn 724+ detector. The crystal was kept at a steady T = 100(2) K during data collection. The structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program using the Intrinsic Phasing solution method and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The model was refined with version 2018/3 of **ShelXL** (Sheldrick, 2015) using Least Squares minimisation.

Crystal Data. $C_{17}H_{17}NO_6S$, M_r = 363.37, triclinic, P-1 (No. 2), a = 9.4467(7) Å, b = 9.8579(7) Å, c = 10.8912(8) Å, α = 114.208(7)°, β = 113.622(7)°, γ = 91.306(6)°, V = 826.02(12) $Å^3$, T = 100(2) K, Z = 2, Z' = 1, μ(MoK_α) = 0.231 mm^{-1}, 10889 reflections measured, 3776 unique (R_{int} = 0.0429) which were used in all calculations. The final wR_2 was 0.1309 (all data) and R_1 was 0.0531 (I > 2(I)).

Compound	**6**
CCDC	1908057
Formula	$C_{17}H_{17}NO_6S$
$D_{calc.}$/ g cm^{-3}	1.461
μ/mm^{-1}	0.231
Formula Weight	363.37
Colour	yellow
Shape	block
Size/mm^3	0.10×0.10×0.06
T/K	100(2)
Crystal System	triclinic
Space Group	P-1
a/Å	9.4467(7)
b/Å	9.8579(7)
c/Å	10.8912(8)
α/°	114.208(7)
β/°	113.622(7)
γ/°	91.306(6)
V/$Å^3$	826.02(12)
Z	2
Z'	1
Wavelength/Å	0.71075
Radiation type	MoK_α
Θ_{min}/°	2.296
Θ_{max}/°	27.484
Measured Refl.	10889
Independent Refl.	3776
Reflections with I > 2(I)	2693
R_{int}	0.0429
Parameters	233
Restraints	0
Largest Peak	0.528
Deepest Hole	-0.367
GooF	1.024
wR_2 (all data)	0.1309
wR_2	0.1182
R_1 (all data)	0.0865
R_1	0.0531

Structure Quality Indicators

Reflections:		I/σ 16.7	Rint 4.29%	
Refinement:	Shift 0.001		Min Peak -0.4	GooF 1.024

A yellow block-shaped crystal with dimensions 0.10×0.10×0.06 mm^3 was mounted on a MITIGEN holder in perfluoroether oil. X-ray diffraction data were collected using a Rigaku FRE+ equipped with HF Varimax confocal mirrors and an AFC12 goniometer and HG Saturn 724+ detector equipped with an Oxford Cryosystems low-temperature device, operating at T = 100(2) K.

Data were measured using profile data from ω-scans of 1.0 ° per frame for 20.0 s using MoK_α radiation (Rotating Anode, 45.0 kV, 55.0 mA). The total number of runs and images was based on the strategy calculation from the program **CrystalClear** (Rigaku).The maximum resolution achieved was Θ = 27.484°.

Cell parameters were retrieved using the **CrysAlisPro** (Rigaku, V1.171.40.45a, 2019) software and refined using **CrysAlisPro** (Rigaku, V1.171.40.45a, 2019) on 4993 reflections, 46 % of the observed reflections. Data reduction was performed using the **CrysAlisPro** (Rigaku, V1.171.40.45a, 2019) software which corrects for Lorentz polarisation. The final completeness is 100.00 % out to 27.484° in Θ.

A multi-scan absorption correction was performed using CrysAlisPro 1.171.40.45a (Rigaku Oxford Diffraction, 2019) using spherical harmonics as implemented in SCALE3 ABSPACK. The absorption coefficient μ of this material is 0.231 mm^{-1} at this wavelength (λ = 0.71075Å) and the minimum and maximum transmissions are 0.921 and 1.000.

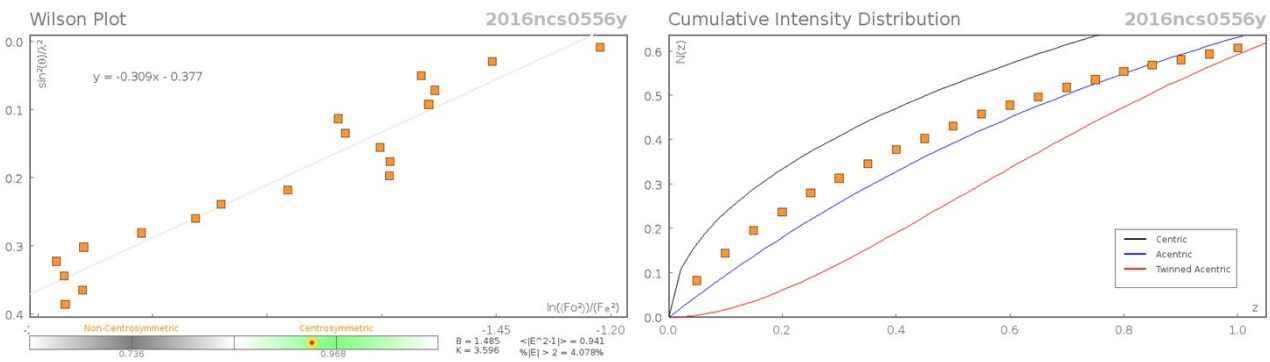
The structure was solved in the space group P-1 (# 2) by Intrinsic Phasing using the **ShelXT** (Sheldrick, 2015) structure solution program and refined by Least Squares using version 2018/3 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Most hydrogen atom positions were calculated geometrically and refined using the riding model, but some hydrogen atoms were refined freely.

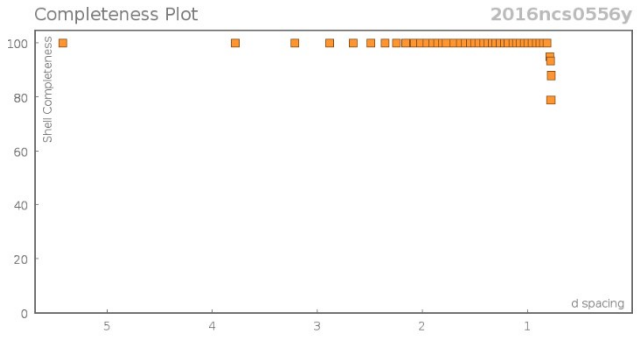
_refine_special_details: Hydrogen atom positions were calculated geometrically except H5 (bound to O5) which was located from the difference map and refined using the riding model. The solvent water molecule was refined with rigid body restraints.

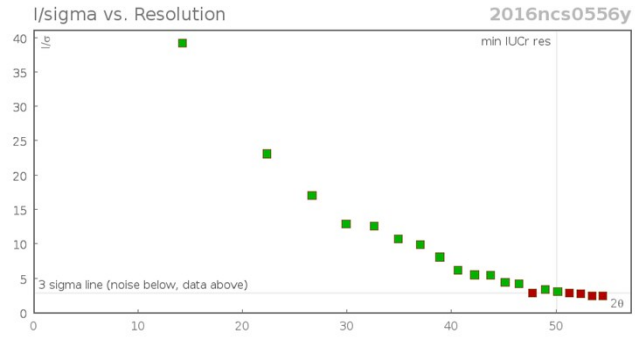
_exptl_absorpt_process_details: CrysAlisPro 1.171.40.45a (Rigaku Oxford Diffraction, 2019) using spherical harmonics as implemented in SCALE3 ABSPACK.

There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 2 and Z' is 1.

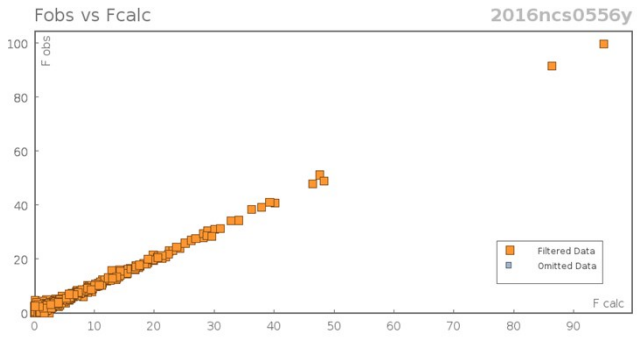
Data Plots: Diffraction Data

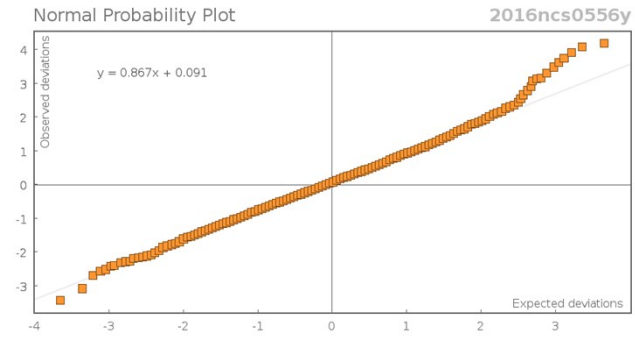






Data Plots: Refinement and Data





Reflection Statistics

Total reflections (after filtering)	10889	Unique reflections	3776
Completeness	0.997	Mean I/σ	15.08
hkl_{max} collected	(12, 12, 14)	hkl_{min} collected	(-12, -12, -14)
hkl_{max} used	(10, 11, 14)	hkl_{min} used	(-12, -12, 0)
Lim d_{max} collected	100.0	Lim d_{min} collected	0.36
d_{max} used	8.87	d_{min} used	0.77
Friedel pairs	2648	Friedel pairs merged	1
Inconsistent equivalents	5	R_{int}	0.0429
R_{sigma}	0.0597	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	0
Multiplicity	(3314, 2122, 692, 233, 55, 8)	Maximum multiplicity	11
Removed systematic absences	0	Filtered off (Shel/OMIT)	0

Table 1: Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for **6**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
S1	-13366.3(8)	-16505.7(7)	-13869.6(7)	20.43(17)
O1	-10763(2)	-13955.9(18)	-12966.6(18)	23.6(4)
O2	-9393(2)	-12335.3(18)	-14451.2(18)	22.0(4)
O3	-12496(2)	-14513.0(19)	-17742.5(18)	24.9(4)
O4	-19030(2)	-19621(2)	-21064.1(19)	29.3(4)
O5	-17378(2)	-21076(2)	-21602(2)	24.6(4)
N1	-15891(2)	-17749(2)	-16394(2)	18.3(4)
C1	-14460(3)	-16759(3)	-15700(3)	18.8(5)
C2	-14889(3)	-17737(3)	-14065(3)	18.9(5)
C3	-14923(3)	-18150(3)	-13003(3)	23.5(6)
C4	-16268(3)	-19152(3)	-13407(3)	24.1(6)
C5	-17537(3)	-19736(3)	-14843(3)	24.0(6)
C6	-17504(3)	-19336(3)	-15915(3)	20.9(5)

Atom	x	y	z	U_{eq}
C7	-16162(3)	-18322(3)	-15504(3)	18.5(5)
C8	-13961(3)	-16077(3)	-16395(3)	19.9(5)
C9	-12570(3)	-14997(3)	-15730(3)	20.2(5)
C10	-11206(3)	-14074(3)	-14231(3)	19.3(5)
C11	-10570(3)	-13327(3)	-14927(3)	19.1(5)
C12	-11929(3)	-14279(3)	-16337(3)	20.8(5)
C13	-11546(3)	-13641(3)	-18069(3)	28.4(6)
C14	-12369(5)	-14145(4)	-19720(3)	60.1(11)
C15	-17038(3)	-18211(3)	-17967(3)	19.6(5)
C16	-16579(3)	-19446(3)	-19055(3)	22.0(5)
C17	-17801(3)	-20040(3)	-20665(3)	20.2(5)
O51	-8908(3)	-12350(3)	-9749(2)	43.8(5)

Table 2: Anisotropic Displacement Parameters (×10⁴) **6**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	17.3(3)	22.2(3)	18.1(3)	9.4(3)	4.7(3)	1.5(2)
O1	23.7(10)	25.6(9)	17.7(9)	8.2(8)	7.7(8)	3.6(8)
O2	20.2(10)	20.0(9)	20.6(9)	7.4(7)	6.7(8)	-0.4(7)
O3	25.3(10)	25.3(9)	18.5(9)	11.2(8)	3.8(8)	-0.7(8)
O4	22.3(11)	33.2(10)	22.6(10)	9.4(8)	4.3(9)	11.7(8)
O5	18.8(10)	28.8(10)	17.5(9)	5.5(8)	5.5(8)	3.7(8)
N1	15.5(11)	20.5(10)	16.9(10)	7.9(9)	6.2(9)	4.3(8)
C1	15.4(13)	19.2(12)	16.0(12)	5.6(10)	4.4(11)	4.2(10)
C2	15.0(12)	17.4(11)	22.0(13)	7.1(10)	8.2(11)	4.2(10)
C3	21.2(14)	23.9(13)	22.0(13)	10.1(11)	7.1(12)	5.8(11)
C4	25.5(15)	28.0(13)	25.9(14)	16.7(11)	13.3(12)	9.3(11)
C5	21.6(14)	22.0(12)	32.3(15)	13.9(11)	14.0(12)	6.6(11)
C6	17.1(13)	19.6(12)	19.4(13)	6.2(10)	5.0(11)	3.2(10)
C7	17.7(13)	19.8(12)	18.3(12)	8.8(10)	8.0(11)	8.5(10)
C8	20.5(14)	19.2(12)	17.3(12)	7.4(10)	7.0(11)	5.0(10)
C9	22.9(14)	17.9(12)	21.9(13)	10.5(10)	10.4(11)	8.5(10)
C10	18.2(13)	16.3(11)	20.9(13)	6.1(10)	9.0(11)	5.1(10)
C11	19.4(13)	17.1(11)	20.8(13)	7.6(10)	10.2(11)	6.5(10)
C12	21.5(14)	17.8(12)	20.7(13)	7.8(10)	8.3(11)	5.9(10)
C13	31.1(16)	28.9(14)	25.5(14)	14.5(12)	11.0(13)	1.9(12)
C14	82(3)	54(2)	30.3(18)	21.4(16)	12.5(19)	-22(2)
C15	14.4(13)	23.9(12)	16.2(12)	9.2(10)	3.0(10)	2.4(10)
C16	18.3(14)	23.4(12)	20.9(13)	9.2(11)	6.5(11)	6.1(11)
C17	19.9(14)	17.6(12)	18.5(12)	5.9(10)	7.0(11)	-1.2(10)
O51	36.9(13)	48.8(14)	32.1(12)	10.9(11)	11.2(11)	7.9(11)

Table 3: Bond Lengths in Å for **6**.

Atom	Atom	Length/Å
S1	C1	1.742(2)
S1	C2	1.746(2)
O1	C10	1.220(3)
O2	C11	1.238(3)
O3	C12	1.316(3)
O3	C13	1.464(3)
O4	C17	1.214(3)
O5	C17	1.317(3)
N1	C1	1.367(3)
N1	C7	1.403(3)
N1	C15	1.472(3)
C1	C8	1.391(3)
C2	C3	1.386(3)
C2	C7	1.397(3)
C3	C4	1.386(4)
C4	C5	1.393(4)
C5	C6	1.388(3)
C6	C7	1.388(3)
C8	C9	1.388(3)
C9	C10	1.482(4)
C9	C12	1.410(3)
C10	C11	1.511(3)
C11	C12	1.439(4)
C13	C14	1.487(4)
C15	C16	1.525(3)
C16	C17	1.502(3)

Table 4: Bond Angles in ° for **6**.

Atom	Atom	Atom	Angle/°
C1	S1	C2	91.42(12)
C12	O3	C13	116.55(19)
C1	N1	C7	114.7(2)
C1	N1	C15	122.59(19)
C7	N1	C15	122.7(2)
N1	C1	S1	110.88(17)
N1	C1	C8	123.6(2)
C8	C1	S1	125.52(19)
C3	C2	S1	127.9(2)
C3	C2	C7	121.1(2)
C7	C2	S1	111.01(17)
C2	C3	C4	117.9(2)
C3	C4	C5	120.9(2)
C6	C5	C4	121.4(2)
C5	C6	C7	117.6(2)
C2	C7	N1	111.9(2)
C6	C7	N1	127.0(2)
C6	C7	C2	121.0(2)
C9	C8	C1	126.5(2)
C8	C9	C10	139.7(2)
C8	C9	C12	131.1(2)
C12	C9	C10	89.2(2)
O1	C10	C9	136.2(2)
O1	C10	C11	134.8(2)
C9	C10	C11	88.96(18)
O2	C11	C10	135.0(2)
O2	C11	C12	137.9(2)
C12	C11	C10	87.03(19)
O3	C12	C9	128.2(2)
O3	C12	C11	137.0(2)
C9	C12	C11	94.8(2)
O3	C13	C14	107.0(2)
N1	C15	C16	110.7(2)
C17	C16	C15	112.0(2)
O4	C17	O5	123.7(2)
O4	C17	C16	124.5(2)
O5	C17	C16	111.8(2)

Table 5: Torsion Angles in ° for **6**.

Atom	Atom	Atom	Atom	Angle/°
S1	C1	C8	C9	-5.2(4)
S1	C2	C3	C4	179.94(19)
S1	C2	C7	N1	-1.0(2)
S1	C2	C7	C6	179.62(18)
O1	C10	C11	O2	-0.7(5)
O1	C10	C11	C12	179.4(3)
O2	C11	C12	O3	0.9(5)
O2	C11	C12	C9	-179.5(3)
N1	C1	C8	C9	175.9(2)
N1	C15	C16	C17	175.03(19)
C1	S1	C2	C3	-179.5(2)
C1	S1	C2	C7	0.99(18)
C1	N1	C7	C2	0.4(3)
C1	N1	C7	C6	179.8(2)
C1	N1	C15	C16	79.9(3)
C1	C8	C9	C10	-5.3(5)
C1	C8	C9	C12	177.5(2)
C2	S1	C1	N1	-0.75(18)

Atom	Atom	Atom	Atom	Angle/°
C2	S1	C1	C8	-179.8(2)
C2	C3	C4	C5	0.6(4)
C3	C2	C7	N1	179.5(2)
C3	C2	C7	C6	0.1(4)
C3	C4	C5	C6	-0.1(4)
C4	C5	C6	C7	-0.4(4)
C5	C6	C7	N1	-178.9(2)
C5	C6	C7	C2	0.4(3)
C7	N1	C1	S1	0.3(2)
C7	N1	C1	C8	179.4(2)
C7	N1	C15	C16	-98.4(2)
C7	C2	C3	C4	-0.6(4)
C8	C9	C10	O1	2.7(5)
C8	C9	C10	C11	-177.5(3)
C8	C9	C12	O3	-2.5(4)
C8	C9	C12	C11	177.8(3)
C9	C10	C11	O2	179.5(3)
C9	C10	C11	C12	-0.39(18)
C10	C9	C12	O3	179.2(2)
C10	C9	C12	C11	-0.42(19)
C10	C11	C12	O3	-179.2(3)
C10	C11	C12	C9	0.41(19)
C12	O3	C13	C14	177.2(2)
C12	C9	C10	O1	-179.4(3)
C12	C9	C10	C11	0.40(18)
C13	O3	C12	C9	-177.8(2)
C13	O3	C12	C11	1.7(4)
C15	N1	C1	S1	-178.01(17)
C15	N1	C1	C8	1.0(4)
C15	N1	C7	C2	178.8(2)
C15	N1	C7	C6	-1.9(4)
C15	C16	C17	O4	-1.6(3)
C15	C16	C17	O5	178.29(19)

Table 6: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **6**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H5	-18070(40)	-21480(30)	-22520(30)	37
H3	-14052.35	-17758.55	-12027.86	28
H4	-16325.49	-19445.1	-12696.06	29
H5A	-18444.54	-20423.02	-15093.6	29
H6	-18368.64	-19740.49	-16894.35	25
H8	-14639.06	-16382.5	-17427.92	24
H13A	-10465.98	-13838.94	-17772.64	34
H13B	-11457.83	-12533.89	-17505.01	34
H14A	-13434.89	-13942.78	-19997.72	90
H14B	-12447.09	-15241.61	-20264.1	90
H14C	-11766.46	-13584.75	-19984.42	90
H15A	-17073.09	-17313.56	-18163.11	24
H15B	-18108.2	-18601.41	-18134.96	24
H16A	-15548.32	-19023.43	-18941.91	26
H16B	-16447.07	-20301.02	-18792.87	26
H51A	-9319.49	-12866.68	-10702.86	66
H51B	-9560.22	-11861.13	-9503.85	66

Citations

CrysAlisPro Software System, Rigaku Oxford Diffraction, (2019).

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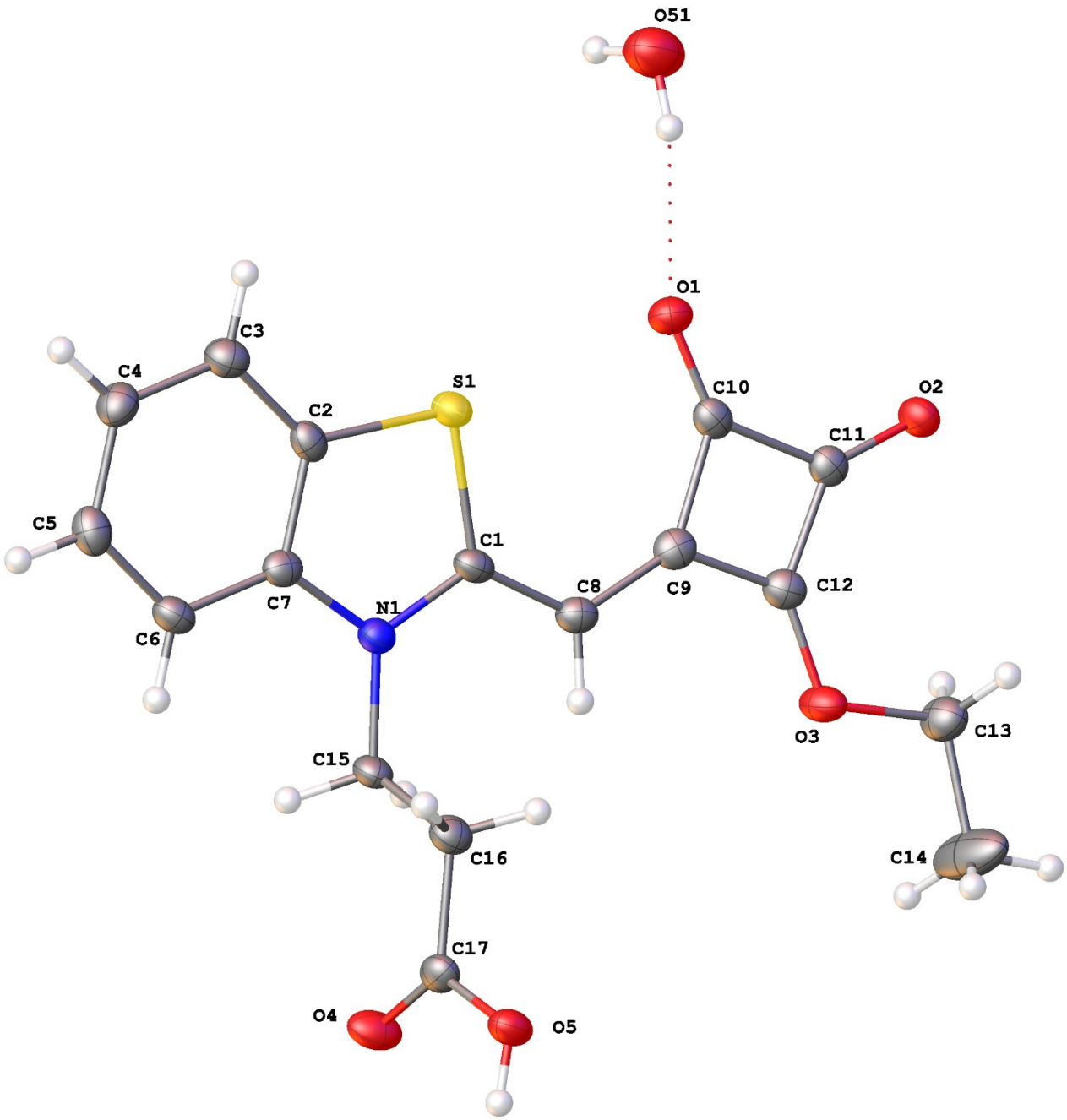
O.V. Dolomanov and L.J. Bourhis and R.J. Gildea and J.A.K. Howard and H. Puschmann, Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.*, (2009), **42**, 339-341.

Sheldrick, G.M., Crystal structure refinement with ShelXL, *Acta Cryst.*, (2015), **C27**, 3-8.

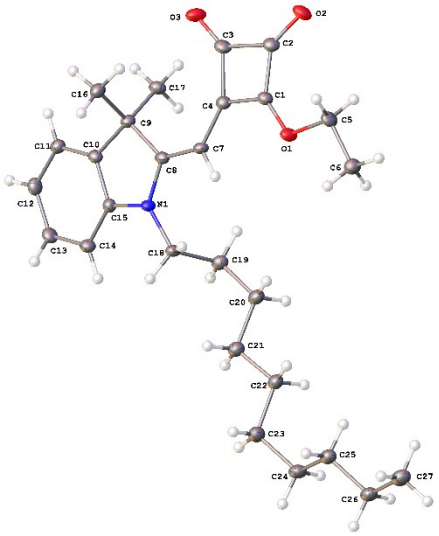
Sheldrick, G.M., ShelXT-Integrated space-group and crystal-structure determination, *Acta Cryst.*, (2015), **A71**, 3-8.



10

Submitted by: **Peter J. Holliman**
Swansea University
Solved by: **Graham J. Tizzard**
Sample ID: **15CK-05-C3**

Crystal Data and Experimental



Experimental. Single yellow shard-shaped crystals of **10** were supplied. A suitable crystal 0.16×0.08×0.04 mm^3 was selected and mounted on a MITIGEN holder in perfluoroether oil on a Rigaku FRE+ equipped with VHF Varimax confocal mirrors and an AFC12 goniometer and HG Saturn 724+ detector. The crystal was kept at a steady T = 100(2) K during data collection. The structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program using the Intrinsic Phasing solution method and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The model was refined with version 2018/3 of **ShelXL** (Sheldrick, 2015) using Least Squares minimisation.

Crystal Data. $C_{27}H_{37}NO_3$, M_r = 423.57, triclinic, P-1 (No. 2), a = 9.2092(4) Å, b = 10.9301(4) Å, c = 12.2653(5) Å, α = 100.390(3)°, β = 99.578(4)°, γ = 92.170(3)°, V = 1194.49(9) Å^3, T = 100(2) K, Z = 2, Z' = 1, μ(MoK$_\alpha$) = 0.075 mm^{-1}, 15143 reflections measured, 5441 unique (R_{int} = 0.0428) which were used in all calculations. The final wR_2 was 0.1179 (all data) and R_1 was 0.0486 (I > 2(I)).

Compound	**10**
CCDC	1908058
Formula	$C_{27}H_{37}NO_3$
$D_{calc.}$/ g cm^{-3}	1.178
μ/mm^{-1}	0.075
Formula Weight	423.57
Colour	yellow
Shape	shard
Size/mm^3	0.16×0.08×0.04
T/K	100(2)
Crystal System	triclinic
Space Group	P-1
a/Å	9.2092(4)
b/Å	10.9301(4)
c/Å	12.2653(5)
α/°	100.390(3)
β/°	99.578(4)
γ/°	92.170(3)
V/Å^3	1194.49(9)
Z	2
Z'	1
Wavelength/Å	0.71075
Radiation type	MoK$_\alpha$
Θ_{min}/°	2.305
Θ_{max}/°	27.485
Measured Refl.	15143
Independent Refl.	5441
Reflections with I > 2(I)	3949
R_{int}	0.0428
Parameters	284
Restraints	0
Largest Peak	0.296
Deepest Hole	-0.199
GooF	1.017
wR_2 (all data)	0.1179
wR_2	0.1051
R_1 (all data)	0.0786
R_1	0.0486

Structure Quality Indicators

Reflections:		I/σ 19.8	Rint 4.28%	complete 99% (IUCr) 100%
Refinement:	Shift 0.000	Max Peak 0.3	Min Peak -0.2	GooF 1.017

A yellow shard-shaped crystal with dimensions 0.16×0.08×0.04 mm^3 was mounted on a MITIGEN holder in perfluoroether oil. X-ray diffraction data were collected using a Rigaku FRE+ equipped with VHF Varimax confocal mirrors and an AFC12 goniometer and HG Saturn 724+ detector equipped with an Oxford Cryosystems low-temperature device, operating at T = 100(2) K.

Data were measured using profile data from ω-scans of 1.0 ° per frame for 20.0 s using MoK_α radiation (Rotating Anode, 45.0 kV, 55.0 mA). The total number of runs and images was based on the strategy calculation from the program **CrystalClear** (Rigaku).The maximum resolution achieved was Θ = 27.485°.

Cell parameters were retrieved using the **CrysAlisPro** (Rigaku, V1.171.40.45a, 2019) software and refined using **CrysAlisPro** (Rigaku, V1.171.40.45a, 2019) on 7175 reflections, 47 % of the observed reflections. Data reduction was performed using the **CrysAlisPro** (Rigaku, V1.171.40.45a, 2019) software which corrects for Lorentz polarisation. The final completeness is 99.90 % out to 27.485° in Θ.

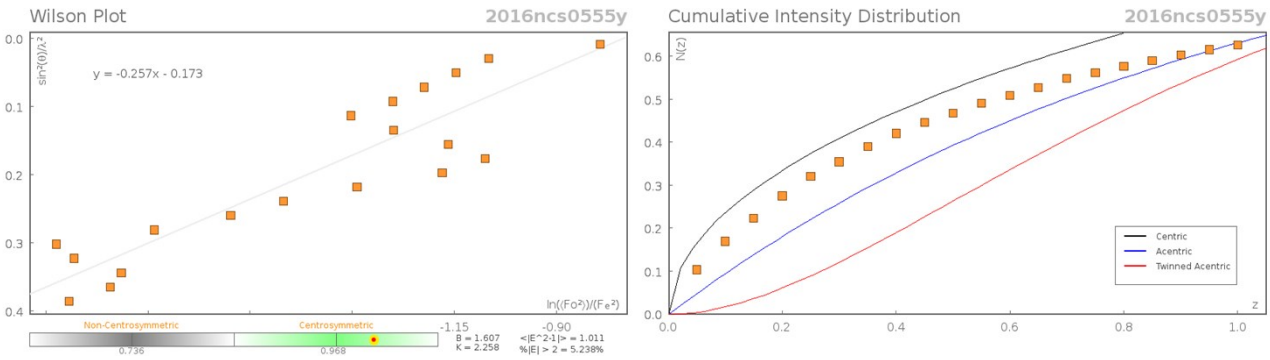
A multi-scan absorption correction was performed using CrysAlisPro 1.171.40.45a (Rigaku Oxford Diffraction, 2019) using spherical harmonics as implemented in SCALE3 ABSPACK. The absorption coefficient μ of this material is 0.075 mm^{-1} at this wavelength (λ = 0.71075Å) and the minimum and maximum transmissions are 0.576 and 1.000.

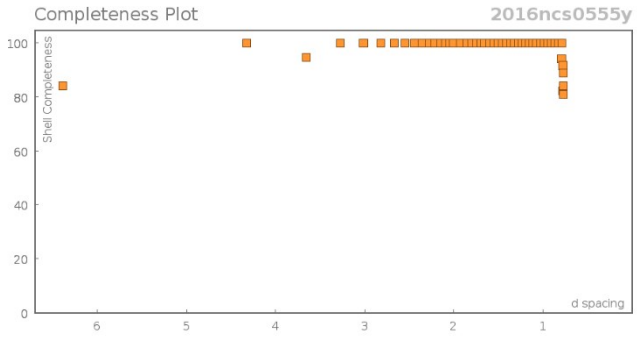
The structure was solved in the space group P-1 (# 2) by Intrinsic Phasing using the **ShelXT** (Sheldrick, 2015) structure solution program and refined by Least Squares using version 2018/3 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

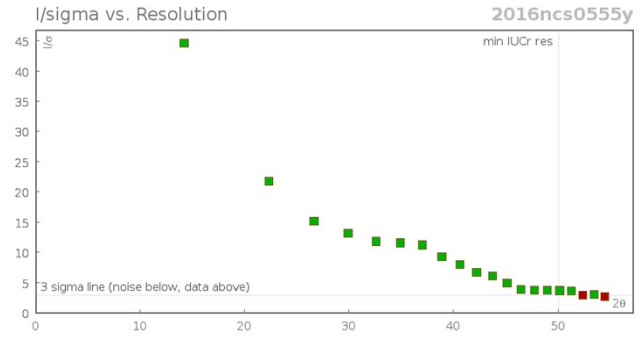
_exptl_absorpt_process_details: CrysAlisPro 1.171.40.45a (Rigaku Oxford Diffraction, 2019) using spherical harmonics as implemented in SCALE3 ABSPACK.

There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 2 and Z' is 1.

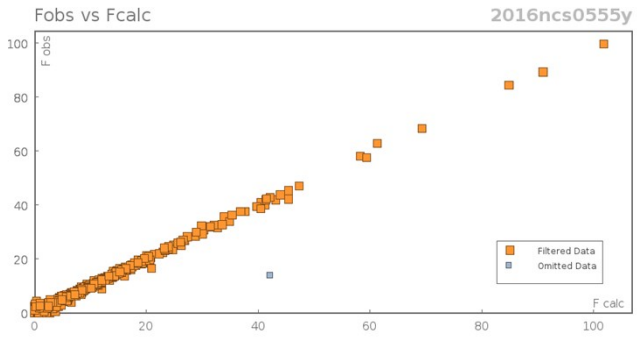
Data Plots: Diffraction Data

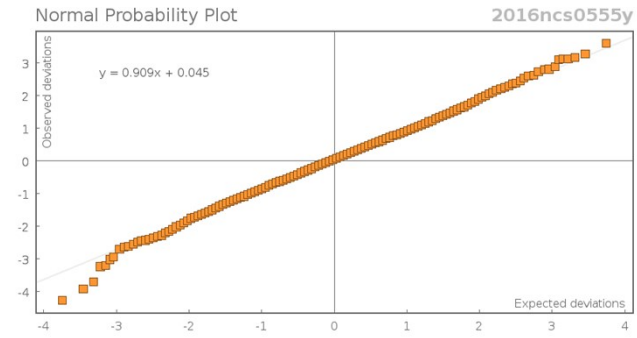






Data Plots: Refinement and Data





Reflection Statistics

Total reflections (after filtering)	15144	Unique reflections	5441
Completeness	0.995	Mean I/σ	15.07
hkl_{max} collected	(11, 14, 15)	hkl_{min} collected	(-11, -12, -15)
hkl_{max} used	(11, 13, 15)	hkl_{min} used	(-11, -14, 0)
Lim d_{max} collected	100.0	Lim d_{min} collected	0.36
d_{max} used	9.06	d_{min} used	0.77
Friedel pairs	3298	Friedel pairs merged	1
Inconsistent equivalents	26	R_{int}	0.0428
R_{sigma}	0.0505	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	1
Multiplicity	(4050, 3154, 1364, 166, 6)	Maximum multiplicity	7
Removed systematic absences	0	Filtered off (Shel/OMIT)	0

Table 1: Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for **10**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	Z	U_{eq}
O1	1800.1(12)	2090.2(9)	4225.0(8)	21.8(3)
O2	1506.0(12)	-178.3(9)	5676.0(9)	25.1(3)
O3	369.7(13)	1848.3(10)	7571.2(9)	27.5(3)
N1	1545.1(13)	6395.0(11)	6776.8(10)	16.3(3)
C1	1465.2(16)	1953.4(13)	5201.9(12)	17.8(3)
C2	1300.2(17)	933.2(13)	5800.3(12)	19.3(3)
C3	845.8(17)	1904.8(13)	6714.1(13)	19.8(3)
C4	1198.8(16)	2890.5(13)	6066.5(12)	16.4(3)
C5	1904.7(19)	933.0(13)	3429.7(13)	22.4(3)
C6	2402.9(18)	1319.5(14)	2428.7(12)	22.2(3)
C7	1371.0(16)	4188.1(13)	6087.5(12)	16.4(3)
C8	1232.8(16)	5196.5(13)	6897.1(12)	15.6(3)
C9	738.8(16)	5233.0(13)	8031.8(12)	16.3(3)

Atom	x	y	Z	U_{eq}
C10	892.7(16)	6621.5(13)	8511.6(12)	16.7(3)
C11	664.9(16)	7265.1(14)	9538.5(12)	18.9(3)
C12	962.5(17)	8558.2(14)	9793.4(13)	21.5(3)
C13	1489.1(17)	9175.7(14)	9028.6(13)	22.1(3)
C14	1721.3(17)	8538.0(13)	7986.2(13)	19.6(3)
C15	1402.4(16)	7259.2(13)	7751.7(12)	16.3(3)
C16	-870.0(17)	4701.4(14)	7847.2(13)	20.6(3)
C17	1783.4(17)	4562.4(14)	8802.0(12)	19.8(3)
C18	2094.3(16)	6738.7(13)	5816.4(12)	16.4(3)
C19	3757.1(16)	6622.6(14)	5906.9(12)	19.9(3)
C20	4288.4(17)	6525.8(15)	4783.0(13)	21.7(3)
C21	4040.7(18)	7643.9(14)	4208.8(13)	22.5(3)
C22	4659.1(17)	7486.5(14)	3112.6(13)	22.1(3)
C23	4435.8(19)	8596.7(15)	2520.2(14)	26.1(4)
C24	5329.3(19)	8605.7(15)	1572.8(14)	26.0(4)
C25	4987.8(18)	7477.0(15)	618.3(13)	23.4(3)
C26	5913.1(18)	7512.6(15)	-298.2(13)	24.9(4)
C27	5625.5(19)	6347.8(16)	-1216.7(13)	27.3(4)

Table 2: Anisotropic Displacement Parameters (×10^4) **10**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + \ldots + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	33.8(7)	12.1(5)	21.0(6)	2.1(4)	10.9(5)	0.4(5)
O2	35.1(7)	12.3(5)	28.4(6)	5.1(4)	5.6(5)	2.5(5)
O3	43.0(7)	16.8(5)	25.5(6)	4.7(4)	14.6(5)	-3.9(5)
N1	20.7(7)	10.9(6)	18.5(6)	3.4(5)	7.0(5)	-0.6(5)
C1	19.6(8)	13.9(7)	20.1(7)	3.9(6)	3.7(6)	-0.6(6)
C2	22.0(8)	14.5(7)	20.8(8)	2.8(6)	3.1(6)	-3.1(6)
C3	21.7(8)	13.3(7)	23.5(8)	3.4(6)	2.5(6)	-2.8(6)
C4	16.2(7)	14.9(7)	17.9(7)	3.2(6)	2.9(6)	-1.0(6)
C5	31.5(9)	12.0(7)	23.8(8)	-0.5(6)	9.2(7)	1.1(6)
C6	25.5(9)	18.9(7)	22.4(8)	2.7(6)	7.0(7)	-0.6(6)
C7	19.4(8)	14.3(7)	17.0(7)	5.5(5)	5.3(6)	-1.0(6)
C8	13.6(7)	14.4(7)	19.5(7)	5.9(6)	2.6(6)	-0.4(6)
C9	17.9(8)	13.8(7)	18.0(7)	3.2(5)	5.2(6)	-1.6(6)
C10	16.3(7)	13.5(7)	20.5(7)	3.9(6)	3.2(6)	0.1(6)
C11	19.7(8)	18.2(7)	20.0(7)	4.4(6)	5.9(6)	0.9(6)
C12	22.9(8)	19.5(8)	21.1(8)	-0.6(6)	5.6(6)	3.3(6)
C13	24.2(8)	13.0(7)	28.5(8)	0.8(6)	6.5(7)	-0.1(6)
C14	22.0(8)	14.7(7)	23.4(8)	5.1(6)	6.7(6)	-0.2(6)
C15	16.8(7)	15.3(7)	17.5(7)	3.1(6)	4.7(6)	2.3(6)
C16	21.4(8)	18.4(7)	22.9(8)	2.4(6)	8.5(6)	-1.6(6)
C17	24.1(8)	15.6(7)	20.5(8)	5.8(6)	3.8(6)	-0.4(6)
C18	21.2(8)	12.1(7)	17.4(7)	4.2(5)	6.2(6)	-0.1(6)
C19	20.8(8)	20.7(8)	19.3(8)	5.7(6)	4.9(6)	-0.2(6)
C20	20.3(8)	24.2(8)	23.7(8)	8.7(6)	7.8(6)	2.0(6)
C21	24.5(8)	20.8(8)	24.2(8)	6.1(6)	8.1(6)	0.7(6)
C22	21.5(8)	23.2(8)	25.2(8)	9.0(6)	9.0(6)	3.3(6)
C23	33.3(9)	21.3(8)	28.0(9)	7.6(7)	13.8(7)	5.0(7)
C24	32.3(9)	21.6(8)	29.0(9)	10.6(7)	12.8(7)	1.9(7)
C25	24.4(8)	23.4(8)	26.0(8)	10.3(7)	8.6(7)	2.4(7)
C26	27.8(9)	23.2(8)	28.3(9)	11.2(7)	11.5(7)	2.5(7)
C27	30.7(9)	29.9(9)	24.0(8)	9.3(7)	8.4(7)	0.6(7)

Table 3: Bond Lengths in Å for **10**.

Atom	Atom	Length/Å
O1	C1	1.3180(17)
O1	C5	1.4683(17)
O2	C2	1.2228(18)

Atom	Atom	Length/Å
O3	C3	1.2149(18)
N1	C8	1.3697(18)
N1	C15	1.4119(18)

Atom	Atom	Length/Å
N1	C18	1.4587(17)
C1	C2	1.458(2)
C1	C4	1.396(2)
C2	C3	1.523(2)
C3	C4	1.505(2)
C4	C7	1.4162(19)
C5	C6	1.502(2)
C7	C8	1.369(2)
C8	C9	1.5289(19)
C9	C10	1.5178(19)
C9	C16	1.536(2)
C9	C17	1.535(2)
C10	C11	1.380(2)
C10	C15	1.389(2)
C11	C12	1.398(2)
C12	C13	1.388(2)
C13	C14	1.395(2)
C14	C15	1.385(2)
C18	C19	1.529(2)
C19	C20	1.525(2)
C20	C21	1.523(2)
C21	C22	1.530(2)
C22	C23	1.526(2)
C23	C24	1.533(2)
C24	C25	1.523(2)
C25	C26	1.524(2)
C26	C27	1.523(2)

Table 4: Bond Angles in ° for **10**.

Atom	Atom	Atom	Angle/°
C1	O1	C5	115.92(11)
C8	N1	C15	111.27(11)
C8	N1	C18	124.76(11)
C15	N1	C18	123.71(11)
O1	C1	C2	137.11(13)
O1	C1	C4	127.29(13)
C4	C1	C2	95.55(12)
O2	C2	C1	137.70(14)
O2	C2	C3	135.94(14)
C1	C2	C3	86.25(11)
O3	C3	C2	133.73(14)
O3	C3	C4	137.74(14)
C4	C3	C2	88.51(11)
C1	C4	C3	89.19(11)
C1	C4	C7	125.41(13)
C7	C4	C3	145.32(13)
O1	C5	C6	106.22(12)
C8	C7	C4	131.46(13)
N1	C8	C9	108.58(12)
C7	C8	N1	122.19(13)
C7	C8	C9	129.23(13)
C8	C9	C16	109.95(12)
C8	C9	C17	111.49(12)
C10	C9	C8	101.63(11)
C10	C9	C16	111.72(12)
C10	C9	C17	109.27(12)
C17	C9	C16	112.31(12)
C11	C10	C9	130.44(13)
C11	C10	C15	120.05(13)
C15	C10	C9	109.45(12)
C10	C11	C12	118.73(14)
C13	C12	C11	120.33(14)
C12	C13	C14	121.59(14)
C15	C14	C13	116.82(13)
C10	C15	N1	108.94(12)
C14	C15	N1	128.58(13)
C14	C15	C10	122.48(13)
N1	C18	C19	111.94(12)
C20	C19	C18	113.53(12)
C21	C20	C19	115.54(13)
C20	C21	C22	111.90(12)
C23	C22	C21	113.15(13)
C22	C23	C24	114.35(13)
C25	C24	C23	114.59(14)
C24	C25	C26	112.97(13)
C27	C26	C25	112.62(13)

Table 5: Torsion Angles in ° for **10**.

Atom	Atom	Atom	Atom	Angle/°
O1	C1	C2	O2	6.7(3)
O1	C1	C2	C3	-177.04(19)
O1	C1	C4	C3	176.61(15)
O1	C1	C4	C7	-6.0(2)
O2	C2	C3	O3	-10.4(3)
O2	C2	C3	C4	171.26(19)
O3	C3	C4	C1	-172.9(2)
O3	C3	C4	C7	10.9(4)
N1	C8	C9	C10	-2.08(15)
N1	C8	C9	C16	116.38(13)
N1	C8	C9	C17	-118.39(13)
N1	C18	C19	C20	159.94(12)
C1	O1	C5	C6	-175.86(13)
C1	C2	C3	O3	173.19(19)
C1	C2	C3	C4	-5.13(11)
C1	C4	C7	C8	-175.76(15)
C2	C1	C4	C3	-5.61(12)
C2	C1	C4	C7	171.80(14)
C2	C3	C4	C1	5.35(11)
C2	C3	C4	C7	-170.9(2)
C3	C4	C7	C8	-0.3(3)
C4	C1	C2	O2	-170.71(19)
C4	C1	C2	C3	5.56(12)
C4	C7	C8	N1	175.59(15)
C4	C7	C8	C9	-4.5(3)
C5	O1	C1	C2	8.1(2)
C5	O1	C1	C4	-175.16(14)
C7	C8	C9	C10	178.00(15)
C7	C8	C9	C16	-63.54(19)
C7	C8	C9	C17	61.69(19)
C8	N1	C15	C10	-3.76(16)
C8	N1	C15	C14	175.02(15)
C8	N1	C18	C19	-80.62(17)
C8	C9	C10	C11	-177.41(15)
C8	C9	C10	C15	-0.14(15)
C9	C10	C11	C12	176.75(15)
C9	C10	C15	N1	2.26(16)
C9	C10	C15	C14	-176.61(14)
C10	C11	C12	C13	-0.6(2)
C11	C10	C15	N1	179.85(13)
C11	C10	C15	C14	1.0(2)
C11	C12	C13	C14	0.7(2)
C12	C13	C14	C15	0.0(2)
C13	C14	C15	N1	-179.44(14)
C13	C14	C15	C10	-0.8(2)
C15	N1	C8	C7	-176.44(13)
C15	N1	C8	C9	3.63(16)
C15	N1	C18	C19	93.10(15)
C15	C10	C11	C12	-0.3(2)

Atom	Atom	Atom	Atom	Angle/°
C16	C9	C10	C11	65.4(2)
C16	C9	C10	C15	-117.33(13)
C17	C9	C10	C11	-59.5(2)
C17	C9	C10	C15	117.78(13)
C18	N1	C8	C7	-2.0(2)
C18	N1	C8	C9	178.03(12)
C18	N1	C15	C10	-178.23(13)
C18	N1	C15	C14	0.5(2)
C18	C19	C20	C21	61.73(18)
C19	C20	C21	C22	177.82(13)
C20	C21	C22	C23	-179.66(14)
C21	C22	C23	C24	167.13(14)
C22	C23	C24	C25	60.1(2)
C23	C24	C25	C26	-179.22(13)
C24	C25	C26	C27	176.86(14)

Table 6: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **10**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	Z	U_{eq}
H5A	932.84	455.73	3202.02	27
H5B	2626.2	404.85	3777.48	27
H6A	2466.05	577.05	1860.78	33
H6B	3375.45	1773.45	2664.85	33
H6C	1692.24	1860.3	2107.52	33
H7	1628.14	4395.85	5421.35	20
H11	312.55	6837.29	10062.14	23
H12	803.49	9016.75	10493.67	26
H13	1696.42	10053.73	9219.25	27
H14	2081.13	8960.75	7462.36	23
H16A	-1487.93	5131.21	7326.18	31
H16B	-1219.04	4825.73	8569.09	31
H16C	-929.53	3808	7528.5	31
H17A	1688.82	3665.62	8493.17	30
H17B	1525	4706.95	9556.08	30
H17C	2803.19	4886.33	8848.51	30
H18A	1872.31	7608.96	5770.48	20
H18B	1575.9	6192.54	5115.48	20
H19A	4281.23	7358.39	6437.06	24
H19B	4020.87	5873.6	6224.92	24
H20A	5357.9	6400.01	4906.44	26
H20B	3779.95	5775.49	4264.24	26
H21A	4522.44	8405.08	4726.65	27
H21B	2969.23	7753.46	4044.18	27
H22A	5728.2	7368.21	3280.11	27
H22B	4173.4	6725.19	2597.23	27
H23A	4710.26	9374.14	3085.94	31
H23B	3374.68	8597.42	2202.62	31
H24A	5139.6	9367.76	1256.22	31
H24B	6392.71	8652.43	1898.74	31
H25A	3929.45	7434.98	278.9	28
H25B	5167.83	6711.21	930.81	28
H26A	5691.12	8252.72	-641.39	30
H26B	6971.92	7601.34	47.1	30
H27A	6290.82	6390.68	-1756.71	41
H27B	4599.47	6294.43	-1606.63	41
H27C	5801.17	5608.53	-877.87	41

Citations

CrysAlisPro Software System, Rigaku Oxford Diffraction, (2019).

CrystalClear, Rigaku Corporation, The Woodlands, Texas, U.S.A., (2008-2014).

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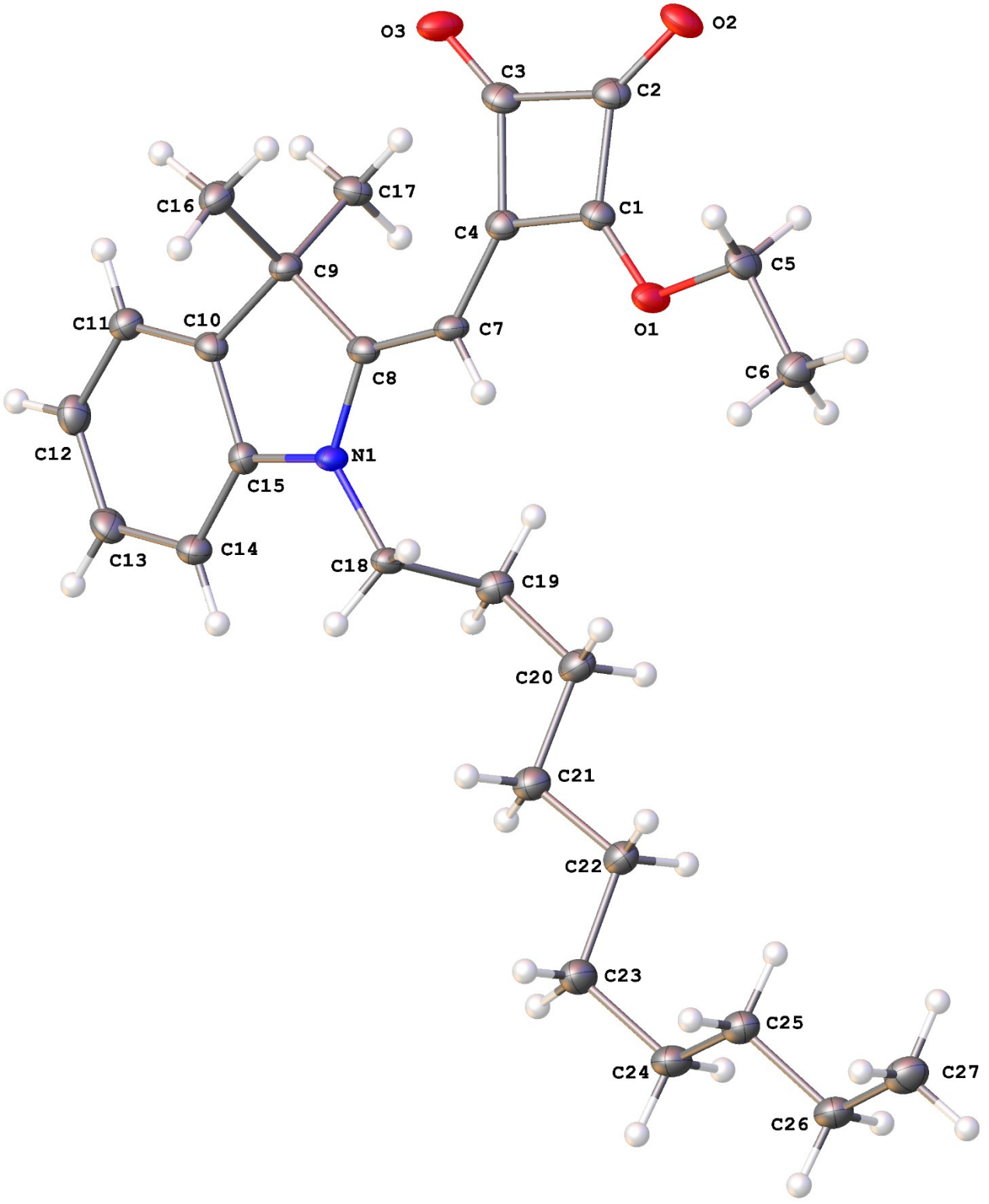
Sheldrick, G.M., Crystal structure refinement with ShelXL, *Acta Cryst.*, (2015), **C27**, 3-8.

Sheldrick, G.M., ShelXT-Integrated space-group and crystal-structure determination, *Acta Cryst.*, (2015), **A71**, 3-8.


O3
O2
C3
C2
C16
C17
C1
C4
C5
C9
C11
C10
C7
O1
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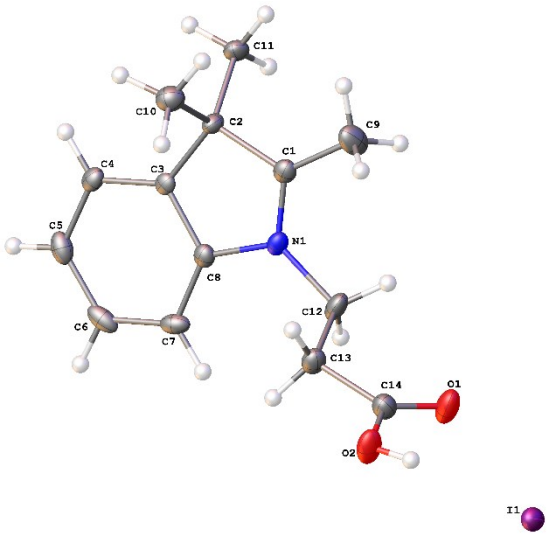
C12
N1
C15
C13
C14
C18
C19
C20
C21
C22
C23
C25
C24
C27
C26

13

Submitted by: **Peter J. Holliman**
Swansea University
Solved by: **Graham J. Tizzard**
Sample ID: **15CK-05-G1**

Crystal Data and Experimental



Experimental. Single colourless plate-shaped crystals of **13** were recrystallised from MeCN. A suitable crystal 0.09×0.07×0.02 mm^3 was selected and mounted on a MITIGEN holder in perfluoroether oil on a Rigaku FRE+ equipped with VHF Varimax confocal mirrors and an AFC12 goniometer and HG Saturn 724+ detector. The crystal was kept at a steady T = 100(2) K during data collection. The structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program using the Intrinsic Phasing solution method and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The model was refined with version 2018/3 of **ShelXL** (Sheldrick, 2015) using Least Squares minimisation.

Crystal Data. $C_{14}H_{18}NO_2I$, M_r = 359.19, orthorhombic, *Pbca* (No. 61), a = 7.3991(2) Å, b = 13.6384(4) Å, c = 29.8148(10) Å, $\alpha = \beta = \gamma = 90^\circ$, V = 3008.67(16) Å^3, T = 100(2) K, Z = 8, Z' = 1, μ(MoK$_\alpha$) = 2.124 mm^{-1}, 25790 reflections measured, 3452 unique (R_{int} = 0.0760) which were used in all calculations. The final wR_2 was 0.0628 (all data) and R_1 was 0.0336 (I > 2(I)).

Compound	**13**
CCDC	1908059
Formula	$C_{14}H_{18}NO_2I$
$D_{calc.}$/ g cm^{-3}	1.586
μ/mm^{-1}	2.124
Formula Weight	359.19
Colour	colourless
Shape	plate
Size/mm^3	0.09×0.07×0.02
T/K	100(2)
Crystal System	orthorhombic
Space Group	*Pbca*
a/Å	7.3991(2)
b/Å	13.6384(4)
c/Å	29.8148(10)
α/°	90
β/°	90
γ/°	90
V/Å^3	3008.67(16)
Z	8
Z'	1
Wavelength/Å	0.71075
Radiation type	MoK$_\alpha$
Θ_{min}/°	2.733
Θ_{max}/°	27.486
Measured Refl.	25790
Independent Refl.	3452
Reflections with I > 2(I)	2583
R_{int}	0.0760
Parameters	169
Restraints	0
Largest Peak	0.453
Deepest Hole	-0.398
GooF	1.035
wR_2 (all data)	0.0628
wR_2	0.0567
R_1 (all data)	0.0583
R_1	0.0336

Structure Quality Indicators

Reflections:		I/σ 23.2	Rint 7.60%	
Refinement:	Shift -0.001	Max Peak 0.5		GooF 1.035

A colourless plate-shaped crystal with dimensions 0.09×0.07×0.02 mm^3 was mounted on a MITIGEN holder in perfluoroether oil. X-ray diffraction data were collected using a Rigaku FRE+ equipped with VHF Varimax confocal mirrors and an AFC12 goniometer and HG Saturn 724+ detector equipped with an Oxford Cryosystems low-temperature device, operating at T = 100(2) K.

Data were measured using profile data from ω-scans of 1.0 ° per frame for 10.0 s using MoK_α radiation (Rotating Anode, 45.0 kV, 55.0 mA). The total number of runs and images was based on the strategy calculation from the program **CrystalClear** (Rigaku).The maximum resolution achieved was Θ = 27.486°.

Cell parameters were retrieved using the **CrysAlisPro** (Rigaku, V1.171.40.45a, 2019) software and refined using **CrysAlisPro** (Rigaku, V1.171.40.45a, 2019) on 9439 reflections, 37 % of the observed reflections. Data reduction was performed using the **CrysAlisPro** (Rigaku, V1.171.40.45a, 2019) software which corrects for Lorentz polarisation. The final completeness is 100.00 % out to 27.486° in Θ.

A multi-scan absorption correction was performed using CrysAlisPro 1.171.40.45a (Rigaku Oxford Diffraction, 2019) using spherical harmonics as implemented in SCALE3 ABSPACK. The absorption coefficient μ of this material is 2.124 mm^{-1} at this wavelength (λ = 0.71075Å) and the minimum and maximum transmissions are 0.484 and 1.000.

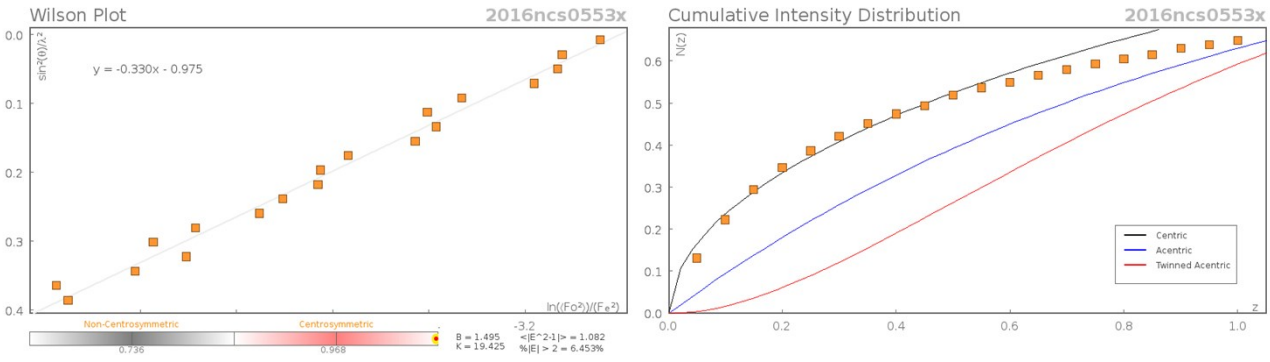
The structure was solved in the space group *Pbca* (# 61) by Intrinsic Phasing using the **ShelXT** (Sheldrick, 2015) structure solution program and refined by Least Squares using version 2018/3 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Most hydrogen atom positions were calculated geometrically and refined using the riding model, but some hydrogen atoms were refined freely.

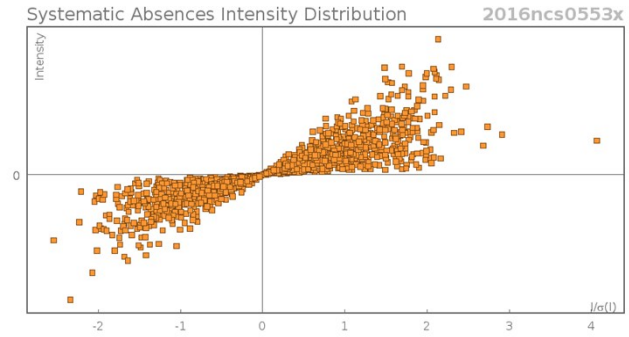
_refine_special_details: Hydrogen atom positions were calculated geometrically except H2 (bound to O2) which was located from the difference map and refined using the riding model (see below).

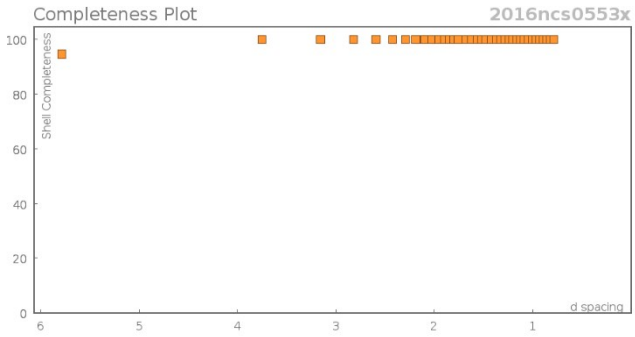
_exptl_absorpt_process_details: CrysAlisPro 1.171.40.45a (Rigaku Oxford Diffraction, 2019) using spherical harmonics as implemented in SCALE3 ABSPACK.

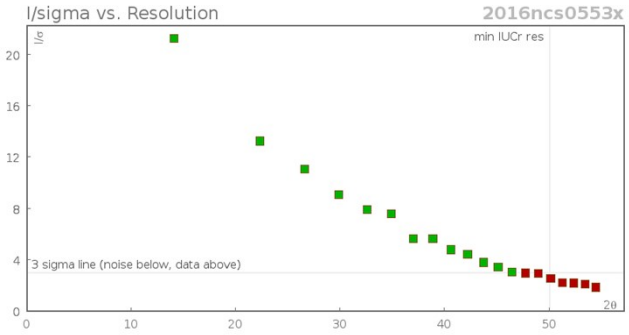
There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 8 and Z' is 1.

Data Plots: Diffraction Data

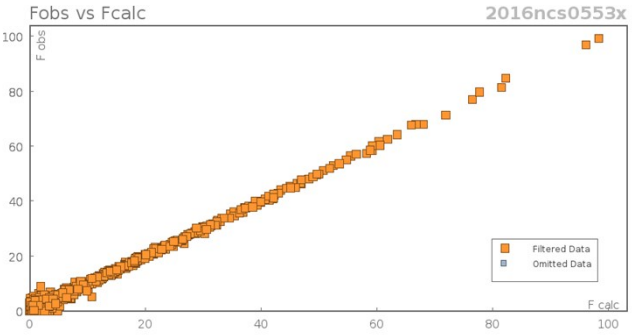


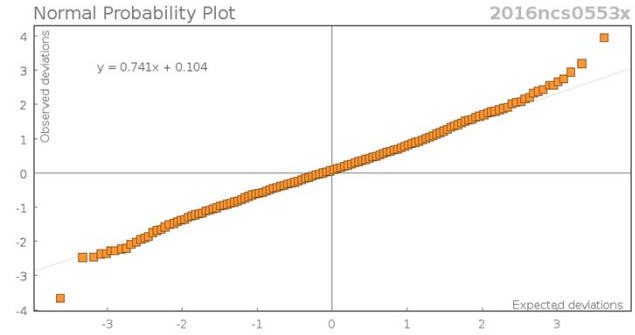






Data Plots: Refinement and Data





Reflection Statistics

Total reflections (after filtering)	28166	Unique reflections	3452
Completeness	1.0	Mean I/σ	17.55
hkl_{max} collected	(9, 17, 34)	hkl_{min} collected	(-9, -17, -38)
hkl_{max} used	(9, 17, 38)	hkl_{min} used	(0, 0, 0)
Lim d_{max} collected	100.0	Lim d_{min} collected	0.36
d_{max} used	10.06	d_{min} used	0.77
Friedel pairs	6225	Friedel pairs merged	1
Inconsistent equivalents	0	R_{int}	0.076
R_{sigma}	0.0432	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	0
Multiplicity	(11990, 6055, 1170, 119, 16)	Maximum multiplicity	21
Removed systematic absences	2376	Filtered off (Shel/OMIT)	0

Table 1: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **13**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
I1	3951.7(3)	3611.6(2)	6357.8(2)	19.76(7)
O1	5239(4)	1846.4(17)	7406.1(8)	33.7(6)
O2	3883(4)	3301.7(17)	7497.5(8)	29.2(6)
N1	3450(4)	920.1(18)	8663.3(8)	16.7(6)
C1	2000(5)	392(2)	8681.5(10)	17.1(7)
C2	1421(4)	243(2)	9162.0(10)	15.4(7)
C3	2906(4)	759(2)	9411.8(10)	12.9(6)
C4	3217(4)	895(2)	9863.6(10)	17.0(7)
C5	4699(5)	1458(2)	9992.4(11)	21.7(7)
C6	5825(4)	1878(2)	9674.2(12)	21.9(8)
C7	5533(4)	1743(2)	9221.3(11)	19.1(7)
C8	4077(4)	1180.9(19)	9104.7(10)	15.6(7)
C9	1032(5)	11(2)	8287.0(11)	28.8(8)
C10	-396(5)	774(2)	9229.2(11)	23.4(8)
C11	1242(4)	-856(2)	9272.8(10)	19.0(7)
C12	4418(5)	1201(2)	8253.2(11)	23.4(8)
C13	3999(5)	2260(2)	8121.4(10)	21.4(7)
C14	4453(5)	2431(2)	7638.6(11)	23.4(8)

Table 2: Anisotropic Displacement Parameters (×10^4) **13**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + \ldots + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I1	23.45(12)	20.94(11)	14.87(11)	-0.33(9)	-0.55(10)	-4.27(10)
O1	54.2(18)	24.8(13)	22.2(13)	0.4(11)	15.0(13)	4.7(13)
O2	49.4(17)	23.1(12)	15.0(12)	4.2(10)	3.7(13)	6.4(11)
N1	23.3(15)	13.4(12)	13.4(13)	2.1(11)	3.4(12)	1.9(11)
C1	21.1(18)	12.6(14)	17.5(17)	1.4(13)	1.7(15)	2.7(13)
C2	14.5(18)	18.2(16)	13.5(16)	1.1(13)	1.5(13)	-2.1(13)
C3	14.5(17)	9.0(14)	15.3(16)	0.0(12)	2.0(13)	4.4(12)
C4	18.8(17)	14.8(15)	17.4(17)	0.7(13)	4.8(14)	4.2(14)
C5	24.0(18)	20.5(17)	20.7(17)	-5.9(15)	-6.0(15)	8.3(15)
C6	16.9(19)	12.5(15)	36(2)	-4.6(14)	-8.7(16)	2.9(14)
C7	14.5(18)	13.1(15)	30(2)	3.2(14)	2.7(14)	0.4(13)
C8	19.0(17)	11.8(15)	16.0(16)	-0.4(12)	1.3(15)	2.9(13)
C9	42(2)	25.0(18)	19.8(18)	2.7(15)	-9.0(18)	-5.3(18)
C10	22.9(19)	21.3(18)	26.0(19)	2.7(15)	1.8(15)	0.1(15)
C11	23.1(19)	15.8(15)	18.1(16)	3.6(13)	1.6(15)	-3.8(14)
C12	32(2)	21.1(18)	17.3(18)	2.3(14)	10.9(15)	2.5(14)
C13	30(2)	17.0(16)	17.0(17)	2.7(13)	3.3(16)	0.4(16)
C14	32(2)	18.9(17)	19.7(19)	-1.2(15)	2.5(16)	-3.7(15)

Table 3: Bond Lengths in Å for **13**.

Atom	Atom	Length/Å
O1	C14	1.206(4)
O2	C14	1.328(4)
N1	C1	1.293(4)
N1	C8	1.440(4)
N1	C12	1.468(4)
C1	C2	1.509(4)
C1	C9	1.472(4)
C2	C3	1.503(4)
C2	C10	1.540(4)
C2	C11	1.541(4)
C3	C4	1.379(4)
C3	C8	1.385(4)
C4	C5	1.393(5)
C5	C6	1.387(5)
C6	C7	1.380(5)
C7	C8	1.368(4)
C12	C13	1.529(4)
C13	C14	1.496(4)

Table 4: Bond Angles in ° for **13**.

Atom	Atom	Atom	Angle/°
C1	N1	C8	111.5(3)
C1	N1	C12	125.8(3)
C8	N1	C12	122.7(3)
N1	C1	C2	110.5(3)
N1	C1	C9	124.5(3)
C9	C1	C2	124.9(3)
C1	C2	C10	107.9(3)
C1	C2	C11	111.0(2)
C3	C2	C1	101.5(2)
C3	C2	C10	110.7(2)
C3	C2	C11	114.4(3)
C10	C2	C11	110.8(3)
C4	C3	C2	132.0(3)
C4	C3	C8	119.1(3)
C8	C3	C2	108.9(3)
C3	C4	C5	118.4(3)
C6	C5	C4	120.8(3)
C7	C6	C5	121.4(3)
C8	C7	C6	116.5(3)
C3	C8	N1	107.5(3)
C7	C8	N1	128.6(3)
C7	C8	C3	123.9(3)
N1	C12	C13	111.2(3)
C14	C13	C12	110.4(3)
O1	C14	O2	124.2(3)
O1	C14	C13	123.9(3)
O2	C14	C13	111.9(3)

Table 5: Torsion Angles in ° for **13**.

Atom	Atom	Atom	Atom	Angle/°
N1	C1	C2	C3	-2.6(3)
N1	C1	C2	C10	113.8(3)
N1	C1	C2	C11	-124.6(3)
N1	C12	C13	C14	-160.8(3)
C1	N1	C8	C3	0.8(3)
C1	N1	C8	C7	-178.7(3)
C1	N1	C12	C13	102.0(3)
C1	C2	C3	C4	-179.5(3)
C1	C2	C3	C8	3.1(3)
C2	C3	C4	C5	-177.0(3)
C2	C3	C8	N1	-2.5(3)
C2	C3	C8	C7	177.0(3)
C3	C4	C5	C6	0.6(5)
C4	C3	C8	N1	179.6(3)
C4	C3	C8	C7	-0.9(5)
C4	C5	C6	C7	-0.9(5)
C5	C6	C7	C8	0.3(4)
C6	C7	C8	N1	179.9(3)
C6	C7	C8	C3	0.5(5)
C8	N1	C1	C2	1.3(3)
C8	N1	C1	C9	179.9(3)
C8	N1	C12	C13	-80.6(4)
C8	C3	C4	C5	0.3(4)
C9	C1	C2	C3	178.7(3)
C9	C1	C2	C10	-64.9(4)
C9	C1	C2	C11	56.7(4)

Atom	Atom	Atom	Atom	Angle/°
C10	C2	C3	C4	66.1(4)
C10	C2	C3	C8	-111.3(3)
C11	C2	C3	C4	-59.9(4)
C11	C2	C3	C8	122.7(3)
C12	N1	C1	C2	178.9(3)
C12	N1	C1	C9	-2.4(5)
C12	N1	C8	C3	-176.9(3)
C12	N1	C8	C7	3.6(5)
C12	C13	C14	O1	-8.3(5)
C12	C13	C14	O2	171.6(3)

Table 6: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **13**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H2	3900(50)	3310(30)	7211(13)	44
H4	2438.66	612.42	10081.48	20
H5	4941.66	1555.25	10302.15	26
H6	6818.16	2266.69	9770	26
H7	6304.27	2026.37	9001.86	23
H9A	713.33	556.27	8087.99	43
H9B	-70.78	-324.53	8384.48	43
H9C	1810.11	-451.67	8125.94	43
H10A	-712.2	772.42	9548.43	35
H10B	-1340.44	436.24	9058.38	35
H10C	-291.61	1452.48	9123.65	35
H11A	2362.75	-1195.38	9191.09	28
H11B	232	-1135.98	9103.02	28
H11C	1018.65	-936.92	9594.66	28
H12A	4062.95	757.08	8005.63	28
H12B	5734.91	1128.01	8301.83	28
H13A	2700.54	2396.1	8171.89	26
H13B	4709.12	2713.22	8311.69	26

Citations

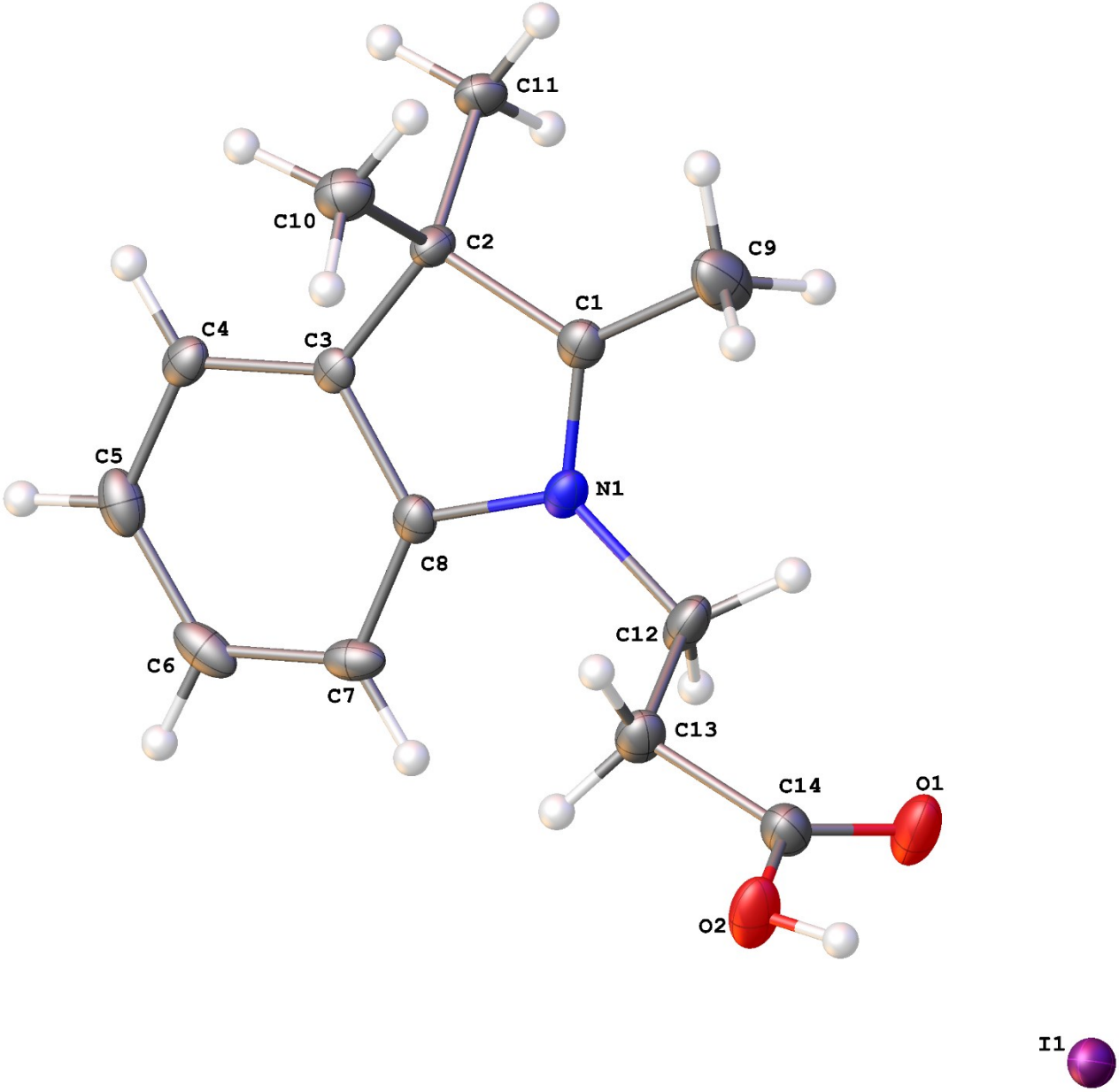
CrysAlisPro Software System, Rigaku Oxford Diffraction, (2019).

CrystalClear, Rigaku Corporation, The Woodlands, Texas, U.S.A., (2008-2014).

O.V. Dolomanov and L.J. Bourhis and R.J. Gildea and J.A.K. Howard and H. Puschmann, Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.*, (2009), **42**, 339-341.

Sheldrick, G.M., Crystal structure refinement with ShelXL, *Acta Cryst.*, (2015), **C27**, 3-8.

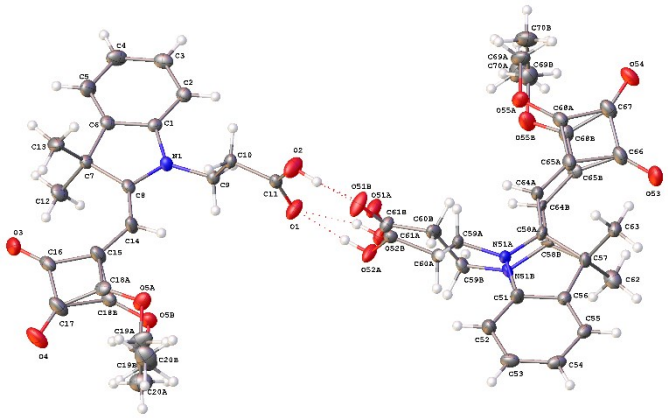
Sheldrick, G.M., ShelXT-Integrated space-group and crystal-structure determination, *Acta Cryst.*, (2015), **A71**, 3-8.


C11
C10
C2
C9
C1
C4
C3
C5
N1
C8
C12
C6
C7
C13
C14
O1
O2
I1

14

Submitted by: **Peter J. Holliman**
Swansea University
Solved by: **Graham J. Tizzard**
Sample ID: **15CK-05-62**

Crystal Data and Experimental



Experimental. Single brown block-shaped crystals of **14** were supplied. A suitable crystal 0.04×0.03×0.01 mm^3 was selected and mounted on a MITIGEN holder in perfluoroether oil on a Rigaku FRE+ equipped with VHF Varimax confocal mirrors and an AFC12 goniometer and HyPix 6000 detector. The crystal was kept at a steady T = 100(2) K during data collection. The structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program using the Intrinsic Phasing solution method and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The model was refined with version 2018/3 of **ShelXL** (Sheldrick, 2015) using Least Squares minimisation.

Crystal Data. $C_{20}H_{21}NO_5$, M_r = 355.38, orthorhombic, $Pca2_1$ (No. 29), a = 12.5207(3) Å, b = 10.7016(2) Å, c = 26.8410(5) Å, $\alpha = \beta = \gamma = 90^\circ$, V = 3596.47(13) Å^3, T = 100(2) K, Z = 8, Z' = 2, μ(MoK$_\alpha$) = 0.095 mm^{-1}, 39507 reflections measured, 8244 unique (R_{int} = 0.0257) which were used in all calculations. The final wR_2 was 0.0887 (all data) and R_1 was 0.0344 (I > 2(I)).

Compound	**14**
CCDC	1908060
Formula	$C_{20}H_{21}NO_5$
$D_{calc.}$/ g cm^{-3}	1.313
μ/mm^{-1}	0.095
Formula Weight	355.38
Colour	brown
Shape	block
Size/mm^3	0.04×0.03×0.01
T/K	100(2)
Crystal System	orthorhombic
Flack Parameter	0.1(2)
Hooft Parameter	0.20(18)
Space Group	$Pca2_1$
a/Å	12.5207(3)
b/Å	10.7016(2)
c/Å	26.8410(5)
α/°	90
β/°	90
γ/°	90
V/Å^3	3596.47(13)
Z	8
Z'	2
Wavelength/Å	0.71075
Radiation type	MoK$_\alpha$
Θ_{min}/°	1.903
Θ_{max}/°	27.485
Measured Refl.	39507
Independent Refl.	8244
Reflections with I > 2(I)	7642
R_{int}	0.0257
Parameters	635
Restraints	1355
Largest Peak	0.457
Deepest Hole	-0.189
GooF	1.041
wR_2 (all data)	0.0887
wR_2	0.0865
R_1 (all data)	0.0382
R_1	0.0344

Structure Quality Indicators

Reflections:		I/σ 45.3	Rint 2.57%		
Refinement:	Shift 0.000	Max Peak 0.5	Min Peak -0.2	GooF 1.041	Flack .1(2)

A brown block-shaped crystal with dimensions 0.04×0.03×0.01 mm^3 was mounted on a MITIGEN holder in perfluoroether oil. X-ray diffraction data were collected using a Rigaku FRE+ equipped with VHF Varimax confocal mirrors and an AFC12 goniometer and HyPix 6000 detector equipped with an Oxford Cryosystems low-temperature device, operating at T = 100(2) K.

Data were measured using profile data from ω-scans of 0.5 ° per frame for 5.0 s using MoK_α radiation (Rotating Anode, 45.0 kV, 55.0 mA). The total number of runs and images was based on the strategy calculation from the program **CrysAlisPro** (Rigaku, V1.171.39.31c, 2017).The maximum resolution achieved was Θ = 27.485°.

Cell parameters were retrieved using the **CrysAlisPro** (Rigaku, V1.171.39.31c, 2017) software and refined using **CrysAlisPro** (Rigaku, V1.171.39.31c, 2017) on 16643 reflections, 42 % of the observed reflections. Data reduction was performed using the **CrysAlisPro** (Rigaku, V1.171.39.31c, 2017) software which corrects for Lorentz polarisation. The final completeness is 100.00 % out to 27.485° in Θ.

A multi-scan absorption correction was performed using CrysAlisPro 1.171.39.31c (Rigaku Oxford Diffraction, 2017) using spherical harmonics as implemented in SCALE3 ABSPACK. The absorption coefficient μ of this material is 0.095 mm^{-1} at this wavelength (λ = 0.71075Å) and the minimum and maximum transmissions are 0.648 and 1.000.

The structure was solved in the space group $Pca2_1$ (# 29) by Intrinsic Phasing using the **ShelXT** (Sheldrick, 2015) structure solution program and refined by Least Squares using version 2018/3 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

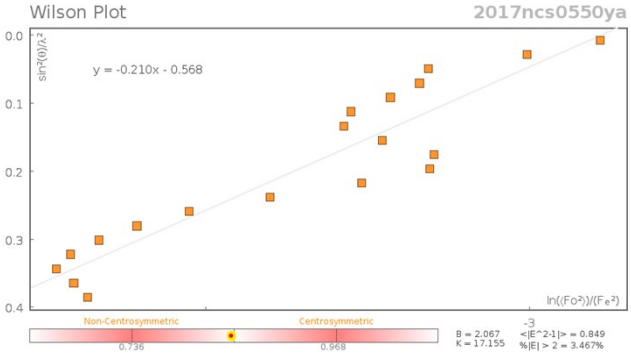
_refine_special_details: First molecule of asymmetric unit exhibits disorder in squaraine and ethoxy moiety (approx. 50:50). Second molecule exhibits disorder in indole, linker, squaraine, ethoxy and acid moieties (approx 82:18). RIGU and SIMU restraints applied throughout

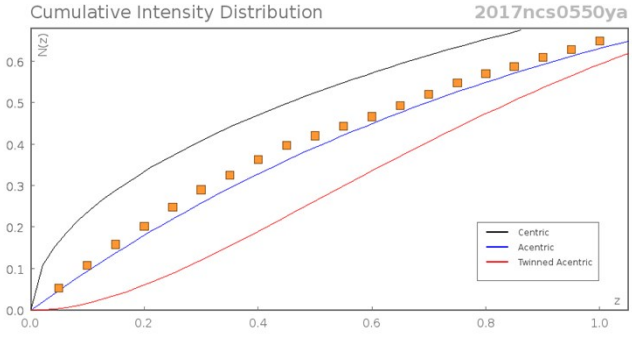
_exptl_absorpt_process_details: CrysAlisPro 1.171.39.31c (Rigaku Oxford Diffraction, 2017) using spherical harmonics as implemented in SCALE3 ABSPACK.

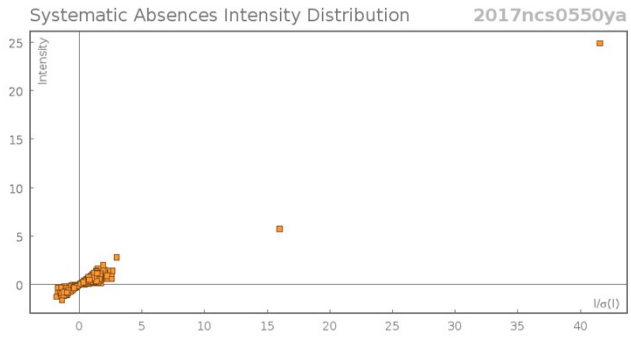
The value of Z' is 2. This means that there are two independent molecules in the asymmetric unit.

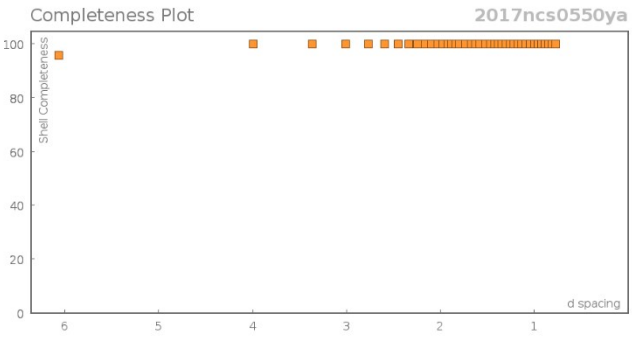
The Flack parameter was refined to 0.1(2). Determination of absolute structure using Bayesian statistics on Bijvoet differences using the Olex2 results in 0.20(18). Note: The Flack parameter is used to determine chirality of the crystal studied, the value should be near 0, a value of 1 means that the stereochemistry is wrong and the model should be inverted. A value of 0.5 means that the crystal consists of a racemic mixture of the two enantiomers.

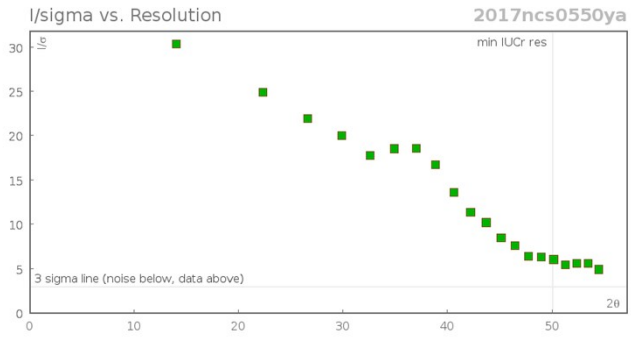
Data Plots: Diffraction Data



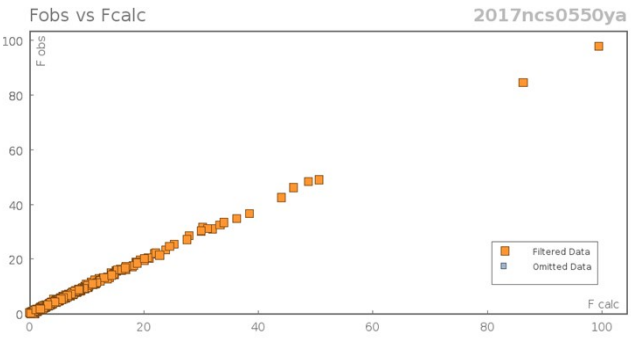


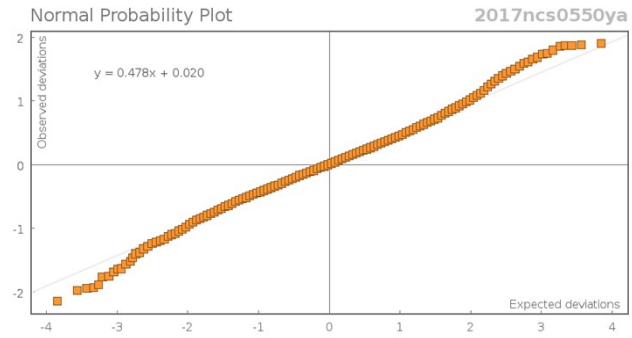






Data Plots: Refinement and Data





Reflection Statistics

Total reflections (after filtering)	41876	Unique reflections	8244

Completeness	0.998	Mean I/σ	31.07
hkl_{max} collected	(16, 13, 34)	hkl_{min} collected	(-13, -9, -34)
hkl_{max} used	(16, 13, 34)	hkl_{min} used	(0, 0, -34)
Lim d_{max} collected	100.0	Lim d_{min} collected	0.36
d_{max} used	11.35	d_{min} used	0.77
Friedel pairs	7202	Friedel pairs merged	0
Inconsistent equivalents	2	R_{int}	0.0257
R_{sigma}	0.0221	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	0
Multiplicity	(9473, 9271, 4237, 285, 2)	Maximum multiplicity	15
Removed systematic absences	2369	Filtered off (Shel/OMIT)	0

Table 1: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **14**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
O1	2722.2(13)	6616.6(17)	4812.5(6)	31.5(4)
O2	4036.9(13)	6377.3(19)	4270.7(6)	37.1(4)
O3	211.7(17)	12642.5(15)	3261.9(6)	39.1(4)
O4	1721.1(16)	14317.1(15)	3984.5(8)	43.0(5)
O5A	2803(3)	11709(3)	4359.1(14)	30.9(12)
O5B	2250(3)	11698(3)	4644.4(14)	28.8(12)
N1	599.5(13)	7872.6(15)	3731.6(6)	19.1(3)
C1	-97.4(15)	7181.4(18)	3422.8(7)	17.7(4)
C2	-290.9(16)	5911.8(19)	3426.8(8)	21.3(4)
C3	-1066.7(17)	5477(2)	3098.7(8)	25.0(4)
C4	-1594.7(18)	6272(2)	2779.5(9)	30.5(5)
C5	-1369.0(17)	7549(2)	2773.9(9)	28.9(5)
C6	-615.6(16)	8003.4(19)	3102.8(8)	20.4(4)
C7	-234.7(15)	9322.8(18)	3201.4(7)	19.3(4)
C8	566.0(15)	9118.8(18)	3623.9(7)	18.4(4)
C9	1235.1(16)	7303.5(18)	4123.9(7)	18.9(4)
C10	2377.7(16)	7053.6(18)	3958.7(7)	18.5(4)
C11	3060.5(16)	6651.4(18)	4387.2(8)	19.5(4)
C12	-1172.5(18)	10131(2)	3380.7(9)	29.1(5)
C13	304(2)	9894(2)	2741.7(8)	28.6(5)
C14	1177.1(18)	9967(2)	3878.4(9)	25.6(4)
C15	1249.1(18)	11276(2)	3847.6(9)	28.2(5)
C16	841.1(19)	12416(2)	3585.5(8)	25.6(4)
C17	1552(2)	13212(2)	3920.0(11)	36.3(6)
C18A	2024(5)	12062(5)	4054(2)	21.9(12)
C18B	1741(5)	12021(5)	4231(3)	22.2(12)
C19A	3420(6)	12709(7)	4589(2)	41.5(16)
C19B	2746(6)	12697(6)	4915(3)	34.4(15)
C20A	2847(6)	13201(8)	5010(3)	43.0(16)
C20B	3805(6)	12993(6)	4697(3)	40.5(15)
O51A	5111(2)	5697(3)	5089.2(12)	29.1(7)
O51B	5501(8)	6117(11)	4878(4)	35(3)
O52A	3779(2)	6102(2)	5615.2(8)	29.6(5)
O52B	4303(13)	5749(14)	5486(6)	23(3)
O53	7176.0(16)	-431.0(15)	6750.2(7)	37.4(4)
O54	6009.3(14)	-2075.8(14)	5895.9(7)	34.0(4)
O55A	5377.4(18)	560.3(18)	5309.4(8)	30.1(5)
O55B	4742(8)	555(9)	5635(4)	36(3)
N51A	7028(2)	4343(2)	6252.0(10)	20.6(5)
N51B	6653(10)	4395(10)	6439(5)	19(2)
C51	7704.7(19)	5022(2)	6574.5(8)	27.2(5)
C52	7912(2)	6293(2)	6577.1(9)	29.2(5)
C53	8687.0(18)	6711(2)	6904.6(8)	26.1(4)
C54	9221.5(17)	5895(2)	7215.4(8)	24.9(4)
C55	8985.4(16)	4619(2)	7212.5(8)	21.6(4)
C56	8209.9(16)	4189.3(19)	6890.6(7)	20.0(4)
C57	7793.7(16)	2879.0(19)	6800.3(8)	21.1(4)

Atom	x	y	z	U_{eq}
C58A	7046(4)	3097(5)	6344.0(14)	21.8(9)
C58B	6890(20)	3090(20)	6500(6)	20(4)
C59A	6478(2)	4923(2)	5836.1(10)	19.6(5)
C59B	5806(10)	4987(10)	6161(5)	21(2)
C60A	5318(2)	5185(2)	5954.2(9)	20.6(6)
C60B	6108(11)	5150(12)	5614(6)	26(3)
C61A	4743(4)	5692(4)	5508.8(17)	19.3(8)
C61B	5264(15)	5756(14)	5303(8)	21(3)
C62	7203.4(19)	2394(2)	7261.2(9)	30.0(5)
C63	8714.6(18)	2017(2)	6647.2(8)	24.3(4)
C64A	6479(3)	2272(3)	6059.8(14)	23.3(7)
C64B	6185(14)	2297(14)	6247(6)	20(3)
C65A	6404(4)	969(4)	6067.2(16)	23.4(9)
C65B	6178(16)	919(19)	6219(7)	17(3)
C66	6686.3(19)	-185(2)	6374.8(9)	27.4(5)
C67	6127.2(18)	-965(2)	5978.2(10)	30.3(5)
C68A	5882(3)	214(3)	5718.8(12)	23.4(6)
C68B	5540(12)	193(13)	5929(6)	26(3)
C69A	4753(4)	-418(4)	5063.0(17)	34.4(9)
C69B	4250(17)	-469(16)	5344(7)	37(4)
C70A	3681(4)	-539(4)	5302.4(15)	42.1(9)
C70B	4935(18)	-823(19)	4924(8)	42(4)

Table 2: Anisotropic Displacement Parameters (×10^4) **14**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + \ldots + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	29.0(8)	46.6(10)	18.7(7)	5.6(7)	-4.2(6)	1.5(7)
O2	24.0(8)	60.3(12)	27.1(8)	-2.1(8)	-5.2(7)	14.8(8)
O3	66.0(12)	20.7(8)	30.7(9)	4.9(7)	-9.9(8)	5.2(8)
O4	45.8(11)	16.4(8)	66.8(13)	-5.4(8)	-3.0(9)	-0.2(7)
O5A	37(2)	27.5(17)	29(2)	4.1(13)	-8.0(17)	-12.4(14)
O5B	36(2)	20.6(16)	30(2)	-2.1(12)	-7.4(17)	-3.7(13)
N1	19.0(8)	15.7(8)	22.6(8)	0.5(6)	-4.6(7)	-0.5(6)
C1	13.3(8)	20.9(9)	18.8(9)	-2.0(7)	-1.0(7)	0.7(7)
C2	21.4(10)	20.2(9)	22.1(9)	0.5(8)	1.3(8)	-0.8(7)
C3	23.7(10)	23.9(10)	27.4(10)	-4.4(8)	6.1(8)	-7.2(8)
C4	21.0(10)	34.2(12)	36.2(12)	-11.4(10)	-6.5(9)	-2.7(9)
C5	23.8(11)	29.6(11)	33.2(12)	-3.1(9)	-9.4(9)	6.5(9)
C6	16.7(9)	20.8(10)	23.7(9)	-2.7(8)	0.4(8)	3.9(7)
C7	18.5(9)	18.4(9)	21.0(9)	-1.1(7)	-2.0(8)	4.7(7)
C8	16.2(9)	16.6(9)	22.5(9)	-0.1(7)	0.6(8)	3.8(7)
C9	19.7(9)	16.5(9)	20.5(9)	1.0(7)	-3.4(7)	0.3(7)
C10	21.1(9)	16.7(9)	17.7(9)	2.6(7)	-3.3(7)	-1.3(7)
C11	21.9(10)	14.2(9)	22.2(10)	0.2(7)	-5.7(8)	-0.5(7)
C12	21.8(10)	29.0(11)	36.6(12)	-4.4(9)	-2.7(9)	10.0(8)
C13	41.8(13)	24.2(11)	19.8(10)	-2.0(8)	2.2(9)	3.1(9)
C14	25.8(11)	16.6(10)	34.3(11)	0.3(8)	-12.4(9)	3.4(8)
C15	26.0(11)	17.4(10)	41.2(13)	-3.4(9)	-8.7(9)	3.7(8)
C16	31.7(11)	16.5(9)	28.4(11)	-0.7(8)	6.1(9)	3.0(8)
C17	35.4(13)	17.6(11)	55.7(16)	-5.0(10)	-4.0(11)	2.6(9)
C18A	28(3)	22(2)	16(3)	2(2)	6(2)	-4.9(19)
C18B	28(3)	15(2)	23(3)	1(2)	2(2)	-3(2)
C19A	44(4)	48(4)	32(3)	2(2)	-4(3)	-33(3)
C19B	43(3)	29(3)	31(3)	-8(2)	-5(2)	-8(3)
C20A	48(4)	42(4)	39(4)	-7(3)	2(3)	-6(3)
C20B	32(4)	31(3)	58(4)	-2(3)	-3(3)	-10(2)
O51A	24.3(13)	45.0(14)	18.0(13)	2.6(12)	-1.9(12)	11.6(11)
O51B	19(5)	63(7)	22(5)	18(5)	0(4)	-5(4)
O52A	25.5(13)	47.2(14)	16.0(9)	2.0(8)	-2.7(8)	14.0(10)
O52B	18(7)	28(6)	22(6)	4(4)	-5(6)	-3(6)
O53	51.7(11)	21.8(8)	38.8(9)	8.4(7)	-10.7(8)	0.2(7)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O54	36.7(9)	15.8(7)	49.4(10)	-3.0(7)	-1.4(8)	0.3(6)
O55A	40.9(12)	21.9(9)	27.6(10)	-0.3(8)	-10.9(9)	-6.5(8)
O55B	35(5)	24(5)	48(6)	-2(4)	-17(4)	0(4)
N51A	27.4(15)	14.8(10)	19.7(13)	-1.3(10)	-9.7(10)	3.4(10)
N51B	25(5)	10(4)	21(6)	0(4)	-5(4)	3(4)
C51	33.8(12)	19.9(10)	27.9(11)	-1.3(8)	-15.4(9)	0.5(9)
C52	41.8(13)	18.1(10)	27.7(11)	-0.3(8)	-11.0(10)	1.0(9)
C53	29.0(11)	22.8(10)	26.6(10)	-7.2(8)	1.3(9)	-5.4(8)
C54	18.8(10)	33.0(12)	23.0(10)	-9.3(8)	-2.1(8)	-1.9(8)
C55	19.5(10)	27.7(11)	17.7(9)	-3.1(8)	-3.0(8)	4.4(8)
C56	22.3(10)	19.9(9)	17.8(9)	-1.4(7)	-1.8(8)	2.6(8)
C57	23.1(10)	17.8(9)	22.6(10)	2.3(7)	-7.4(8)	2.4(7)
C58A	30.2(19)	18.9(14)	16(2)	2.7(17)	-8.0(17)	4.4(12)
C58B	43(8)	5(4)	12(8)	-4(6)	-2(7)	-3(5)
C59A	25.1(13)	15.5(11)	18.3(12)	-0.2(9)	-8.8(11)	3.0(10)
C59B	15(5)	17(5)	31(6)	1(4)	-3(5)	4(4)
C60A	27.0(14)	17.5(12)	17.3(12)	-0.1(9)	-4.3(11)	2.9(10)
C60B	24(6)	24(6)	30(6)	-6(5)	-13(5)	4(5)
C61A	21(2)	16.6(13)	20.7(17)	-3.3(10)	-4(2)	-0.2(18)
C61B	21(8)	26(6)	17(7)	3(6)	-2(6)	0(5)
C62	29.0(12)	25.7(11)	35.4(12)	2.1(9)	5.6(10)	2.1(9)
C63	30.4(11)	22.2(10)	20.4(10)	1.5(8)	-2.9(8)	5.0(8)
C64A	32.8(19)	16.4(13)	20.8(18)	0.1(13)	-9.9(14)	2.8(12)
C64B	30(8)	19(5)	12(7)	1(5)	-11(5)	7(5)
C65A	27(2)	19.2(14)	25(2)	4.5(16)	-1.1(16)	1.6(14)
C65B	18(8)	15(5)	19(8)	2(6)	2(6)	-8(4)
C66	28.3(11)	16.8(9)	37.1(12)	3.2(8)	-2.9(9)	0.9(8)
C67	29.2(12)	18.3(10)	43.6(14)	0.3(9)	-3.4(10)	0.6(9)
C68A	27.3(16)	17.0(12)	25.9(15)	0.8(11)	0.7(12)	-1.0(11)
C68B	26(6)	22(5)	31(7)	2(5)	-8(5)	-2(5)
C69A	52(2)	23(2)	29(2)	-5.4(14)	-8.0(17)	-9.7(17)
C69B	32(9)	36(8)	41(9)	-1(6)	-10(7)	0(7)
C70A	51(2)	35.8(19)	39.7(18)	10.8(14)	-9.4(19)	-15.8(18)
C70B	55(10)	30(10)	40(10)	-13(7)	-9(7)	-7(8)

Table 3: Bond Lengths in Å for **14**.

Atom	Atom	Length/Å
O1	C11	1.218(3)
O2	C11	1.296(3)
O3	C16	1.197(3)
O4	C17	1.213(3)
O5A	C18A	1.328(7)
O5A	C19A	1.457(7)
O5B	C18B	1.326(7)
O5B	C19B	1.434(7)
N1	C1	1.413(2)
N1	C8	1.365(2)
N1	C9	1.454(3)
C1	C2	1.380(3)
C1	C6	1.390(3)
C2	C3	1.391(3)
C3	C4	1.376(3)
C4	C5	1.397(3)
C5	C6	1.380(3)
C6	C7	1.514(3)
C7	C8	1.529(3)
C7	C12	1.536(3)
C7	C13	1.533(3)
C8	C14	1.369(3)
C9	C10	1.521(3)
C10	C11	1.496(3)
C14	C15	1.406(3)
C15	C16	1.498(3)
C15	C18A	1.399(6)
C15	C18B	1.440(6)
C16	C17	1.525(3)
C17	C18A	1.412(6)
C17	C18B	1.543(6)
C19A	C20A	1.437(10)
C19B	C20B	1.484(10)
O51A	C61A	1.217(5)
O51B	C61B	1.24(2)
O52A	C61A	1.315(5)
O52B	C61B	1.30(2)
O53	C66	1.208(3)
O54	C67	1.218(3)
O55A	C68A	1.321(4)
O55A	C69A	1.464(4)
O55B	C68B	1.330(17)
O55B	C69B	1.48(2)
N51A	C51	1.413(3)
N51A	C58A	1.356(6)
N51A	C59A	1.451(4)
N51B	C51	1.523(12)
N51B	C58B	1.43(2)

Atom	Atom	Length/Å
N51B	C59B	1.443(18)
C51	C52	1.384(3)
C51	C56	1.383(3)
C52	C53	1.384(3)
C53	C54	1.381(3)
C54	C55	1.398(3)
C55	C56	1.379(3)
C56	C57	1.515(3)
C57	C58A	1.559(4)
C57	C58B	1.41(2)
C57	C62	1.532(3)
C57	C63	1.533(3)
C58A	C64A	1.366(6)
C58B	C64B	1.40(3)
C59A	C60A	1.514(4)
C59B	C60B	1.53(2)
C60A	C61A	1.497(5)
C60B	C61B	1.50(2)
C64A	C65A	1.398(6)
C64B	C65B	1.48(2)
C65A	C66	1.527(5)
C65A	C68A	1.398(6)
C65B	C66	1.41(2)
C65B	C68B	1.36(2)
C66	C67	1.523(3)
C67	C68A	1.474(4)
C67	C68B	1.448(14)
C69A	C70A	1.494(6)
C69B	C70B	1.47(3)

Table 4: Bond Angles in ° for **14**.

Atom	Atom	Atom	Angle/°
C18A	O5A	C19A	116.2(5)
C18B	O5B	C19B	116.0(4)
C1	N1	C9	122.94(16)
C8	N1	C1	111.61(16)
C8	N1	C9	125.41(16)
C2	C1	N1	128.27(18)
C2	C1	C6	123.08(18)
C6	C1	N1	108.63(17)
C1	C2	C3	116.54(19)
C4	C3	C2	121.5(2)
C3	C4	C5	120.9(2)
C6	C5	C4	118.4(2)
C1	C6	C7	109.58(17)
C5	C6	C1	119.44(19)
C5	C6	C7	130.96(19)
C6	C7	C8	101.72(15)
C6	C7	C12	109.84(17)
C6	C7	C13	111.69(17)
C8	C7	C12	110.44(16)
C8	C7	C13	111.43(17)
C13	C7	C12	111.34(17)
N1	C8	C7	108.45(16)
N1	C8	C14	121.63(18)
C14	C8	C7	129.91(18)
N1	C9	C10	112.17(16)
C11	C10	C9	111.33(16)
O1	C11	O2	123.19(19)
O1	C11	C10	122.04(19)
O2	C11	C10	114.75(18)
C8	C14	C15	131.8(2)
C14	C15	C16	144.8(2)
C14	C15	C18B	122.5(3)
C18A	C15	C14	128.4(3)
C18A	C15	C16	86.1(3)
C18B	C15	C16	91.8(3)
O3	C16	C15	136.9(2)
O3	C16	C17	134.3(2)
C15	C16	C17	88.83(18)
O4	C17	C16	136.9(2)
O4	C17	C18A	137.7(3)
O4	C17	C18B	134.6(3)
C16	C17	C18B	86.9(3)
C18A	C17	C16	84.7(3)
O5A	C18A	C15	125.6(5)
O5A	C18A	C17	135.5(5)
C15	C18A	C17	97.6(4)
O5B	C18B	C15	131.3(4)
O5B	C18B	C17	137.9(5)
C15	C18B	C17	90.3(4)
C20A	C19A	O5A	109.7(6)
O5B	C19B	C20B	110.3(6)
C68A	O55A	C69A	115.5(2)
C68B	O55B	C69B	114.2(11)
C51	N51A	C59A	122.4(2)
C58A	N51A	C51	112.6(3)
C58A	N51A	C59A	124.6(3)
C58B	N51B	C51	102.9(12)
C58B	N51B	C59B	129.6(13)
C59B	N51B	C51	124.5(9)
C52	C51	N51A	128.4(2)
C52	C51	N51B	126.6(4)
C56	C51	N51A	108.57(19)
C56	C51	N51B	105.0(4)
C56	C51	C52	123.0(2)
C53	C52	C51	116.9(2)
C54	C53	C52	121.2(2)
C53	C54	C55	120.82(19)
C56	C55	C54	118.57(19)
C51	C56	C57	109.94(18)
C55	C56	C51	119.4(2)
C55	C56	C57	130.60(19)
C56	C57	C58A	101.2(2)
C56	C57	C62	110.51(17)
C56	C57	C63	109.94(17)
C58B	C57	C56	102.5(9)
C58B	C57	C62	97.4(8)
C58B	C57	C63	123.4(8)
C62	C57	C58A	113.3(2)
C62	C57	C63	112.07(17)
C63	C57	C58A	109.3(2)
N51A	C58A	C57	107.5(4)
N51A	C58A	C64A	121.7(3)
C64A	C58A	C57	130.9(4)
C57	C58B	N51B	113.0(16)

Atom	Atom	Atom	Angle/°
C64B	C58B	N51B	114.0(18)
C64B	C58B	C57	133.0(18)
N51A	C59A	C60A	111.9(2)
N51B	C59B	C60B	111.4(11)
C61A	C60A	C59A	111.2(3)
C61B	C60B	C59B	114.3(13)
O51A	C61A	O52A	123.2(4)
O51A	C61A	C60A	123.9(5)
O52A	C61A	C60A	112.9(4)
O51B	C61B	O52B	124.8(15)
O51B	C61B	C60B	118.7(17)
O52B	C61B	C60B	116.1(17)
C58A	C64A	C65A	132.2(4)
C58B	C64B	C65B	129.6(16)
C64A	C65A	C66	143.1(4)
C68A	C65A	C64A	126.7(4)
C68A	C65A	C66	90.2(3)
C66	C65B	C64B	145.3(17)
C68B	C65B	C64B	127.1(17)

Atom	Atom	Atom	Angle/°
C68B	C65B	C66	87.5(13)
O53	C66	C65A	138.1(3)
O53	C66	C65B	131.3(9)
O53	C66	C67	134.1(2)
C65B	C66	C67	92.6(9)
C67	C66	C65A	87.7(2)
O54	C67	C66	135.8(2)
O54	C67	C68A	136.5(2)
O54	C67	C68B	139.3(6)
C68A	C67	C66	87.50(19)
C68B	C67	C66	80.1(6)
O55A	C68A	C65A	128.2(3)
O55A	C68A	C67	137.1(3)
C65A	C68A	C67	94.7(3)
O55B	C68B	C65B	128.0(15)
O55B	C68B	C67	133.2(12)
C65B	C68B	C67	97.9(12)
O55A	C69A	C70A	110.3(4)
C70B	C69B	O55B	110.7(17)

Table 5: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **14**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H2	4377.52	6230.12	4524.94	56
H2A	78.25	5374.68	3637.8	26
H3	-1232.47	4630.21	3095.08	30
H4	-2109.28	5952.72	2564.34	37
H5	-1718.02	8082.01	2553.79	35
H9A	905.88	6522.09	4223.63	23
H9B	1243.26	7852.49	4411.47	23
H10A	2379.32	6406.47	3705.69	22
H10B	2673.96	7806.52	3812.45	22
H12A	-1456.23	9788.77	3683.65	44
H12B	-1719.9	10142.14	3130.35	44
H12C	-927.43	10967.98	3440.28	44
H13A	521.53	10733.88	2815.01	43
H13B	-191.45	9899.93	2468.66	43
H13C	918.12	9404.64	2653.68	43
H14	1626.91	9611.6	4115.03	31
H19A	4106.56	12388.52	4697.41	50
H19B	3545.33	13368.19	4348.57	50
H19C	2831.68	12456.26	5261.28	41
H19D	2293.62	13432.03	4903.33	41
H20A	2201.36	13593.96	4896.85	65
H20B	3283.09	13803.75	5178.82	65
H20C	2672.33	12532.51	5234.13	65
H20D	3717.07	13249.69	4356.92	61
H20E	4252.39	12265.36	4710.11	61
H20F	4131.7	13657.04	4883.55	61
H52A	3474.36	6307.94	5357.59	44
H52B	3871.51	5898.94	5263.66	34
H52	7547.55	6839.49	6368.33	35
H53	8850.92	7558.58	6915.57	31
H54	9745.04	6198.54	7429.36	30
H55	9343.78	4070.69	7423.14	26
H59A	6519.37	4376.07	5548.48	24
H59B	6833.24	5700.38	5751.74	24
H59C	5652.54	5797.93	6305.1	25
H59D	5163.77	4482.36	6183.72	25
H60A	4973.88	4420.08	6062.72	25

Atom	x	y	z	U_{eq}
H60B	5275.06	5784.68	6224.61	25
H60C	6753.09	5649.79	5595.12	31
H60D	6268.71	4335.54	5474.34	31
H62A	7683.49	2378.35	7539.99	45
H62B	6944.51	1564.65	7197.87	45
H62C	6612.3	2934.83	7334.52	45
H63A	9014.93	2304.57	6338.67	36
H63B	8451.15	1181.23	6605.82	36
H63C	9254.51	2026.22	6901.09	36
H64A	6063.99	2649.18	5814.82	28
H64B	5643.66	2693.73	6071	24
H69A	5130.16	-1207.68	5085.18	41
H69B	4666.15	-213	4713.28	41
H69C	4139.41	-1187.91	5557.64	44
H69D	3559.47	-201.38	5219.49	44
H70A	3270.14	-1160.1	5129.24	63
H70B	3316.15	248.8	5287.74	63
H70C	3767.34	-785.04	5644	63
H70D	5042.27	-111.97	4711.69	62
H70E	4599.19	-1480.5	4737.79	62
H70F	5611.93	-1108.17	5047.48	62

Table 6: Atomic Occupancies for all atoms that are not fully occupied in **14**.

Atom	Occupancy
O5A	0.504(7)
O5B	0.496(7)
C18A	0.504(7)
C18B	0.496(7)
C19A	0.504(7)
H19A	0.504(7)
H19B	0.504(7)
C19B	0.496(7)
H19C	0.496(7)
H19D	0.496(7)
C20A	0.504(7)
H20A	0.504(7)
H20B	0.504(7)
H20C	0.504(7)
C20B	0.496(7)
H20D	0.496(7)
H20E	0.496(7)
H20F	0.496(7)
O51A	0.819(4)
O51B	0.181(4)
O52A	0.819(4)
H52A	0.819(4)
O52B	0.181(4)
H52B	0.181(4)
O55A	0.819(4)
O55B	0.181(4)
N51A	0.819(4)
N51B	0.181(4)
C58A	0.819(4)
C58B	0.181(4)
C59A	0.819(4)
H59A	0.819(4)
H59B	0.819(4)
C59B	0.181(4)
H59C	0.181(4)
H59D	0.181(4)
C60A	0.819(4)
H60A	0.819(4)
H60B	0.819(4)
C60B	0.181(4)
H60C	0.181(4)
H60D	0.181(4)
C61A	0.819(4)
C61B	0.181(4)
C64A	0.819(4)
H64A	0.819(4)
C64B	0.181(4)
H64B	0.181(4)
C65A	0.819(4)
C65B	0.181(4)
C68A	0.819(4)
C68B	0.181(4)
C69A	0.819(4)
H69A	0.819(4)
H69B	0.819(4)
C69B	0.181(4)
H69C	0.181(4)
H69D	0.181(4)
C70A	0.819(4)
H70A	0.819(4)
H70B	0.819(4)
H70C	0.819(4)
C70B	0.181(4)
H70D	0.181(4)
H70E	0.181(4)
H70F	0.181(4)

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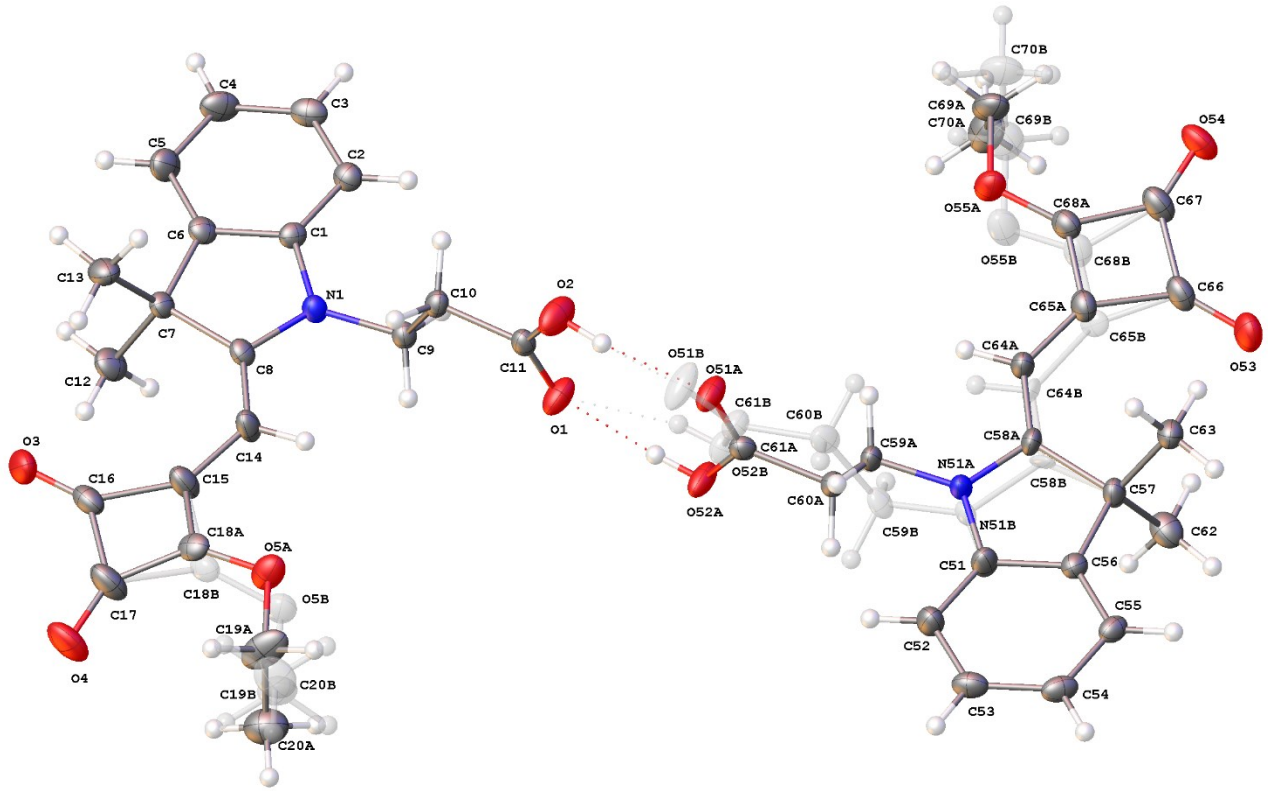
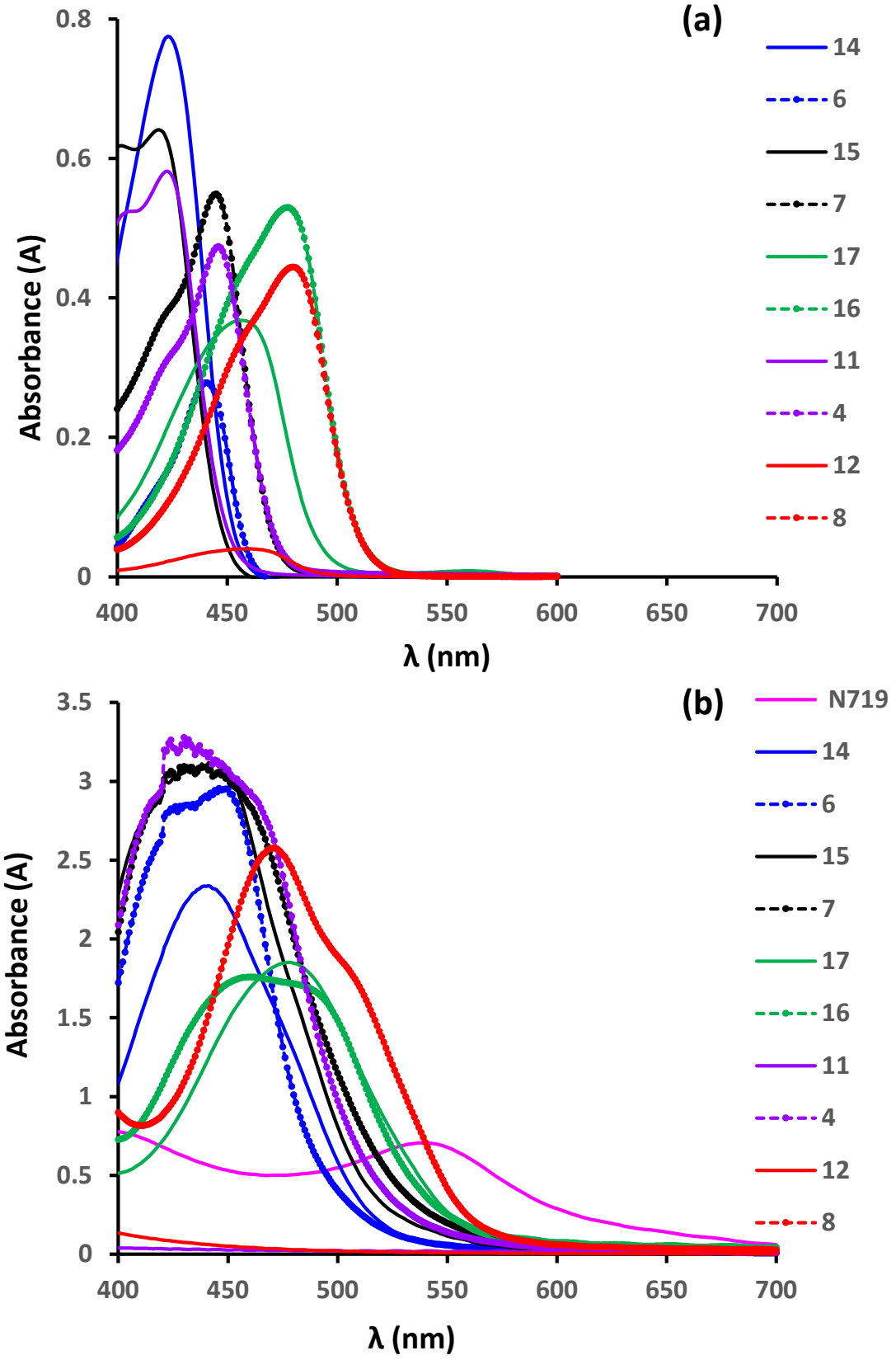
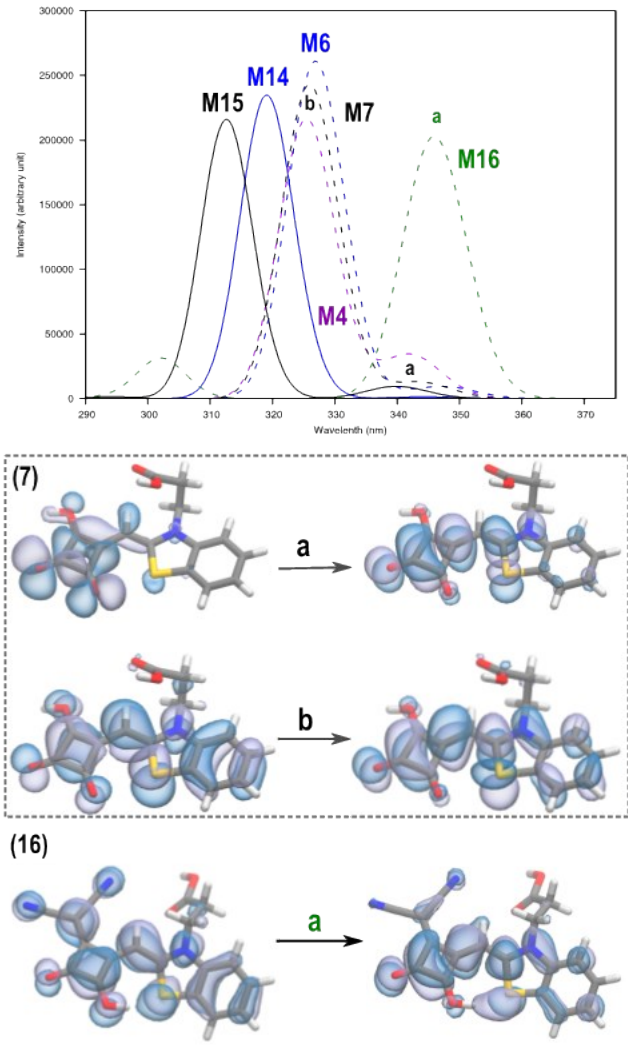


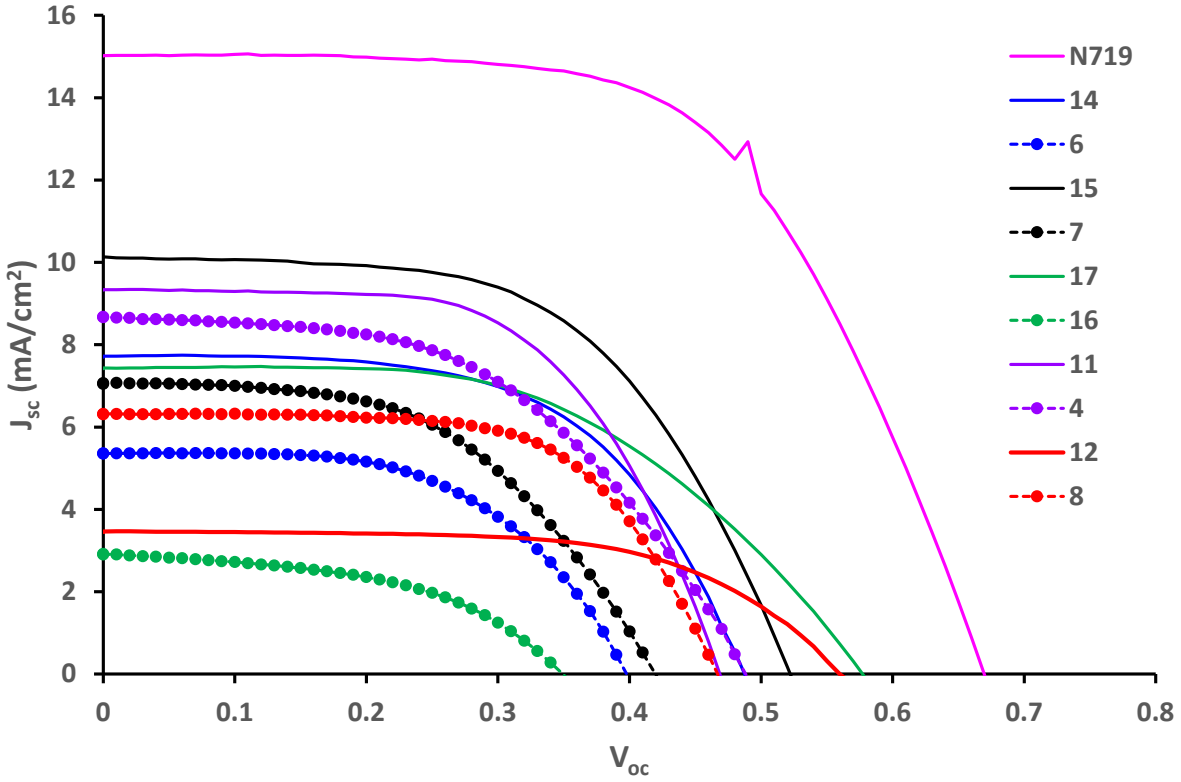
Disorder components are shown ‘ghosted’



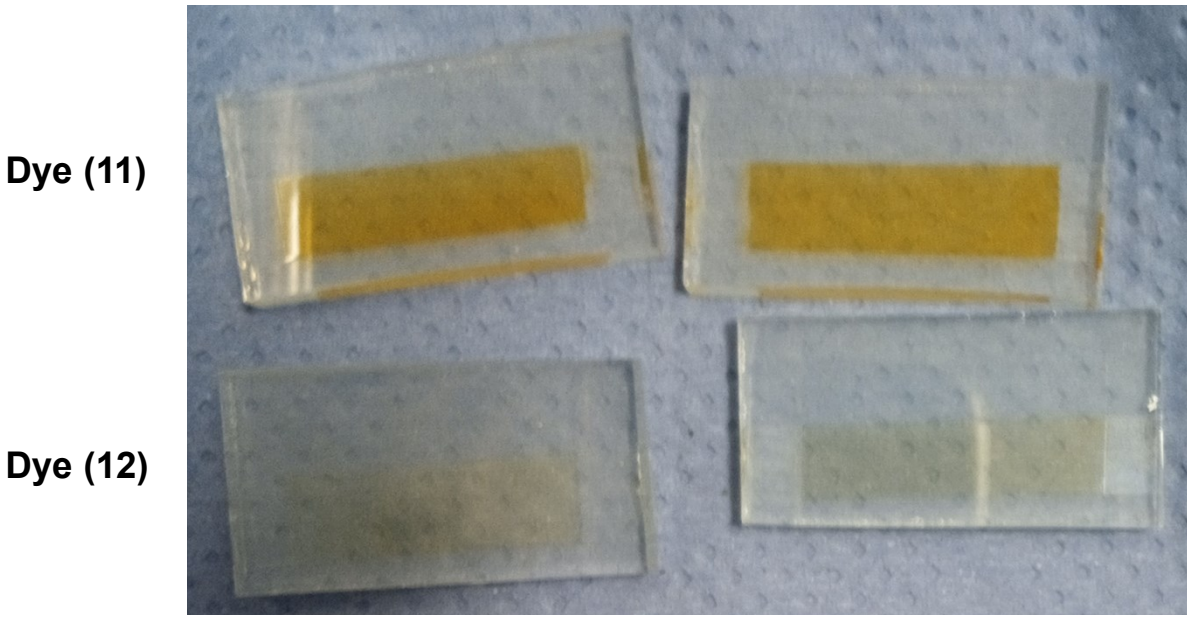
ESI Figure 10 UV-Vis spectra of (a) HfSQ dyes in solution and (b) dyes adsorbed onto a transparent TiO_2 surface. For clarity, structurally related dyes have same colour and $C(CH_3)_2$ dyes have solid lines, whilst S dyes have dashed lines with circle markers.



ESI Figure 11 (Top) Simulated UV-visible spectra for dyes **(4)**, **(6)**, **(7)**, **(14)**, **(15)** and **(16)** and (bottom) typical n-π* transition orbital (a) is shown for **(7)** along with the high intensity π-π* band (b). For **(16)** the π-π* transition orbitals (a) are also provided.



ESI Figure 12 I-V graphs for DSC devices made using the different dyes



ESI Figure 13 Images of replicate TiO_2 electrodes which have been dyed with **(11)** or **(12)** and then washed with ethanol. The image shows that **(11)** remains adsorbed to the TiO_2 while **(12)** desorbs.

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