Electronic Supplementary Material (ESI) for CrystEngComm.
This journal is © The Royal Society of Chemistry 2015

Vapochromism associated with the changes in the molecular arrangement of organic crystals

Shinji Yamada,* Ayaka Katsuki, Yuka Nojiri and Yoko Tokugawa

†Department of Chemistry, Faculty of Science, Ochanomizu University, Bunkyo-ku Tokyo 112-8610, Japan

yamada.shinji@ocha.ac.jp

Supporting Information

1. General experimental procedures

X-Ray measurements at 298K and 123 K were made on a Rigaku RAXIS RAPID II imaging plate area detector with graphite monochromated Cu-Kα radiation. All calculations were performed using the CrystalStructure crystallographic software package except for refinement, which was performed using SHELXL-97. All structures were solved by a combination of direct methods and difference Fourier syntheses, and refined by full-matrix leastsquares on F_2, by using the SHELXTL software package. Powder X-ray diffraction profiles were recorded using a Regaku Ultima IV with monochromated Cu-Kα radiation (λ = 1.54184 A, 50 kV, 40 mA, scan speed 2.0°/min, scan range 4 - 60°) equipped with a cross-beam optics system consisting of a PSA100U parallel slip analyzer. Thermogravimetric analyses were carried out using a TG-DTA2000SA instrument manufactured by Bruker. Three to five milligrams of the crystal samples were heated from 25°C to 150°C in aluminum pans with 5 mm in diameter. A ramping rate of 5 °C/min was used with a nitrogen purge rate of 150 mL/min. DSC measurements were carried out using a Burker DSC3100SA. In all the experiments the samples were examined in a sealed pan under nitrogen atmosphere. UV-vis reflection spectra were measured using a JASCO V-650.

2. General procedure for X-ray structural analyses

Data Collection for **1b**·HCl

A yellow prism crystal of $C_{16}H_{16}ClNO_2$ having approximate dimensions of 0.300 x 0.200 x 0.200 mm was mounted on a CryoLoop. All measurements were made on a Rigaku R-AXIS RAPID diffractometer using graphite monochromated Cu-Kα radiation.

The data were collected at a temperature of -150 ± 1°C to a maximum 2θ value of 136.5°. A total of 60 oscillation images were collected. A sweep of data was done using ω scans from 80.0 to 260.0° in 15.0° step, at χ=54.0° and ϕ = 0.0°. The exposure rate was 20.0 [sec./°]. A second sweep was performed using w scans from 80.0 to 260.0° in 15.0° step, at χ=54.0° and ϕ = 90.0°. The exposure rate was 20.0 [sec./°]. Another sweep was performed using ω scans from 80.0 to 260.0° in 15.0° step, at χ = 54.0° and ϕ = 180.0°. The exposure rate was 20.0 [sec./°]. Another sweep was performed using w scans from 80.0 to 260.0° in 30.0° step, at χ = 54.0° and ϕ = 270.0°. The exposure rate was 20.0 [sec./°]. Another sweep was performed using ω scans from 80.0 to 260.0° in 15.0° step, at χ = 0.0° and ϕ = 0.0°. The exposure rate was 20.0 [sec./°]. The crystal-to-detector distance was 127.40 mm. Readout was performed in the 0.100 mm pixel mode.

Data Reduction

Of the 15692 reflections that were collected, 2621 were unique (R_{int} = 0.0445).

The linear absorption coefficient, m, for Cu-Kα radiation is 23.786 cm^{-1}. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods[1] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement[2] on F^2 was based on 2621 observed reflections and 182 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma \, ||Fo| - |Fc|| \, / \, \Sigma \, |Fo| = 0.0370$$

$$wR2 = [\, \Sigma \, (\, \omega \, (Fo^2 - Fc^2)^2 \,) / \, \Sigma \, \omega (Fo^2)^2]^{1/2} = 0.1004$$

The standard deviation of an observation of unit weight[3] was 1.07. Unit weights were

used. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.29 and -0.19 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[5]. Anomalous dispersion effects were included in Fcalc[6]; the values for Δf' and Δf'' were those of Creagh and McAuley.[7] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[8] All calculations were performed using the CrystalStructure[9] crystallographic software package except for refinement, which was performed using SHELXL-97.[10] Crystal data, data collection parameters, and results of the analyses are listed in Tables S1-S3.

References

(1) SIR92: Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M., Polidori, G., and Camalli, M. (1994) J. Appl. Cryst., 27, 435.

(2) Least Squares function minimized: (SHELXL97)

$\Sigma w(F_o^2-F_c^2)^2$ where w = Least Squares weights.

(3) Standard deviation of an observation of unit weight:

$[\Sigma w(F_o^2-F_c^2)^2/(N_o-N_v)]^{1/2}$

where: N_o = number of observations

N_v = number of variables

(4) Flack, H. D. (1983), Acta Cryst. A39, 876-881.

(5) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(6) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).

(7) Creagh, D. C. & McAuley, W.J .; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(8) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(9) CrystalStructure 4.0: Crystal Structure Analysis Package, Rigaku Corporation (2000-2010). Tokyo 196-8666, Japan.

(10) SHELX97: Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

2-1. X-ray structural analysis of **1a**·HCl·H_2O

A. Crystal Data

Empirical Formula	$C_{15}H_{16}O_3NCl$
Formula Weight	293.75
Crystal Color, Habit	red, block
Crystal Dimensions	0.80 X 0.20 X 0.15 mm
Crystal System	monoclinic
Lattice Type	Primitive
Indexing Images	3 oscillations @ 180.0 seconds
Detector Position	127.40 mm
Pixel Size	0.100 mm
Lattice Parameters	a = 5.19126(15) Å b = 33.4280(10) Å c = 9.2170(3) Å b = 112.0213(14) ^{o} V = 1482.77(8) $Å^3$
Space Group	$P2_1/n$ (#14)
Z value	4
D_{calc}	1.316 g/cm^3
F_{000}	616.00
m(CuKα)	23.440 cm^{-1}
Diffractometer	Rigaku RAXIS-RAPID
Radiation	CuKα (λ = 1.54187 Å) graphite monochromated
$2\theta_{max}$	136.5^o
No. of Reflections Measured	Total: 23293 Unique: 2669 (R_{int} = 0.074)
Corrections	Lorentz-polarization Secondary Extinction (coefficient: 3.55000e-003)

B. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\Sigma\ w\ (Fo^2 - Fc^2)^2$
Least Squares Weights	$w = 1/[\ \sigma^2(Fo^2) + (0.0775 \cdot P)^2 + 0.2230 \cdot P\ ]$ where $P = (Max(Fo^2,0) + 2Fc^2)/3$
$2\theta_{max}$ cutoff	136.5^o
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	2669
No. Variables	191
Reflection/Parameter Ratio	13.97
Residuals: R1 (I>2.00s(I))	0.0500
Residuals: R (All reflections)	0.0600
Residuals: wR2 (All reflections)	0.1510
Goodness of Fit Indicator	1.113
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	$0.32\ e^-/Å^3$
Minimum peak in Final Diff. Map	$-0.25\ e^-/Å^3$

2-2. X-ray structural analysis of **1b**·HCl

A. Crystal Data

Empirical Formula	$C_{16}H_{16}ClNO_2$
Formula Weight	289.76
Crystal Color, Habit	yellow, prism
Crystal Dimensions	0.300 X 0.200 X 0.200 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 7.1274(2) Å b = 12.8781(3) Å c = 15.9623(5) Å b = 103.450(2) ^{o} V = 1424.95(6) Å^3
Space Group	$P2_1/c$ (#14)
Z value	4
D_{calc}	1.351 g/cm^3
F_{000}	608.00
m(CuKα)	23.786 cm^{-1}
Diffractometer	R-AXIS RAPID
Radiation	CuKα (λ = 1.54187 Å) graphite monochromated
Voltage, Current	50kV, 100mA
Temperature	-150.0^{o}C
$2\theta_{max}$	136.4^o
No. of Reflections Measured	Total: 15692 Unique: 2621 (R_{int} = 0.0445)
Corrections	Lorentz-polarization

B. Structure Solution and Refinement

Structure Solution	Direct Methods (SHELX97)
Refinement	Full-matrix least-squares on F^2
Function Minimized	Σ w $(Fo^2 - Fc^2)^2$
Least Squares Weights	$w = 1/ [\sigma^2(Fo^2) + (0.0495 \cdot P)^2 + 0.5911 \cdot P]$ where $P = (Max(Fo^2,0) + 2Fc^2)/3$
$2\theta_{max}$ cutoff	136.4^o
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	2621
No. Variables	182
Reflection/Parameter Ratio	14.40
Residuals: R1 (I>2.00s(I))	0.0370
Residuals: R (All reflections)	0.0432
Residuals: wR2 (All reflections)	0.1004
Goodness of Fit Indicator	1.073
Max Shift/Error in Final Cycle	0.001
Maximum peak in Final Diff. Map	0.29 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.19 $e^-/Å^3$

2-3. X-ray structural analysis of **1b**·HCl·H_2O

A. Crystal Data

Empirical Formula	$C_{16}H_{18}ClNO_3$
Formula Weight	307.78
Crystal Color, Habit	unknown, platelet
Crystal Dimensions	0.500 X 0.200 X 0.050 mm
Crystal System	triclinic
Lattice Type	Primitive
Lattice Parameters	a = 4.88516(18) Å b = 8.6653(3) Å c = 18.6176(7) Å a = 86.980(3) ° b = 85.549(3) ° g = 80.147(2) ° V = 773.52(5) Å^3
Space Group	P-1 (#2)
Z value	2
D_{calc}	1.321 g/cm^3
F_{000}	324.00
m(CuKα)	22.702 cm^{-1}
Diffractometer	R-AXIS RAPID
Radiation	CuKα (λ = 1.54187 Å) graphite monochromated
Voltage, Current	50kV, 100mA
Temperature	-150.0°C
$2\theta_{max}$	136.4°
No. of Reflections Measured	Total: 8223 Unique: 2764 (R_{int} = 0.0865)
Corrections	Lorentz-polarization

B. Structure Solution and Refinement

Structure Solution	Direct Methods (SHELX97)
Refinement	Full-matrix least-squares on F^2
Function Minimized	Σ w $(Fo^2 - Fc^2)^2$
Least Squares Weights	$w = 1/ [\sigma^2(Fo^2) + (0.0514 \cdot P)^2 + 0.0000 \cdot P]$ where $P = (Max(Fo^2,0) + 2Fc^2)/3$
$2\theta_{max}$ cutoff	136.4^o
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	2764
No. Variables	198
Reflection/Parameter Ratio	13.96
Residuals: R1 (I>2.00s(I))	0.0549
Residuals: R (All reflections)	0.0777
Residuals: wR2 (All reflections)	0.1249
Goodness of Fit Indicator	0.923
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.43 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.29 $e^-/Å^3$

3. TG-DTA measurements of 1a·HCl after exposure to H_2O vapor

TG-DTA measurements of compound **1a**·HCl after exposure to water vapor were carried out in the temperature interval 25°C – 150°C at a heating rate of 5 °C/min. After exposure for 7 days, a peak at 85°C was observed with a 2.67 wt% loss, which is corresponding to a loss of 0.5 water molecule. After exposure for 10 days, a peak at 85°C was observed with a 5.40 wt% loss, which is corresponding to a loss of 1.0 water molecule.

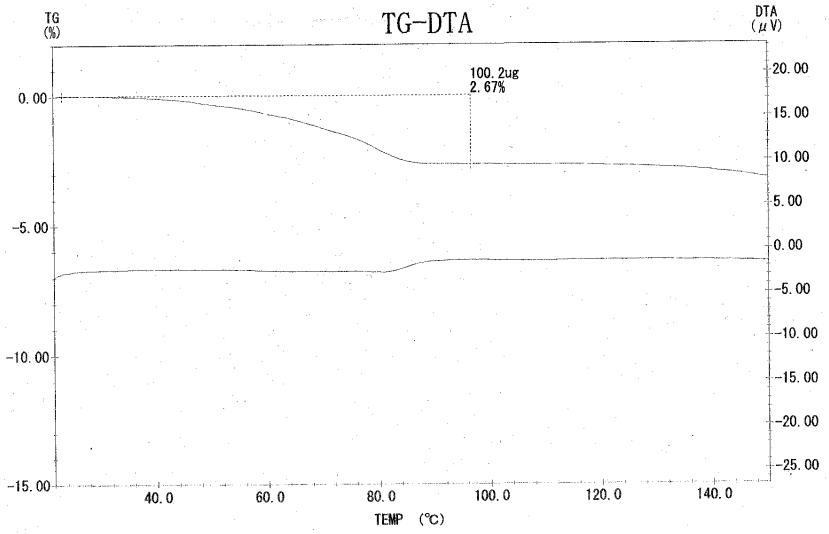

Figure S1. TG-DTA data for **1a**·HCl after exposure to water vapor for 7 days.

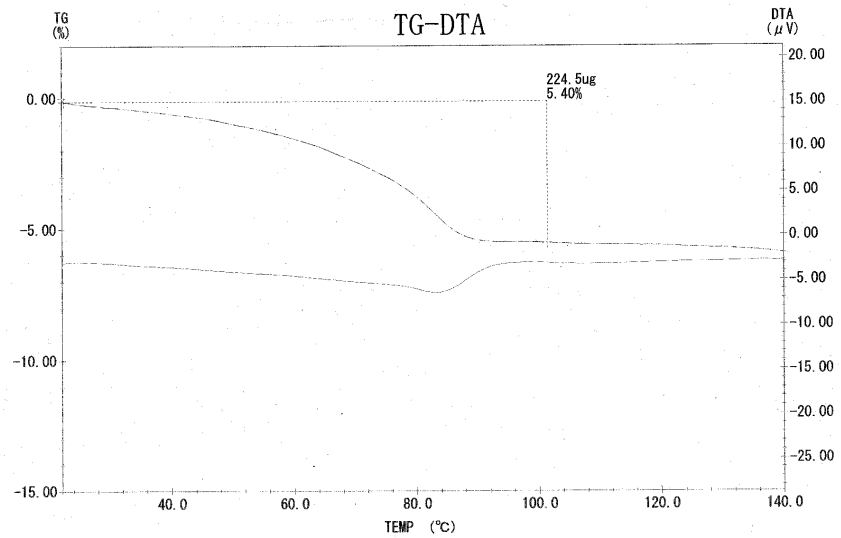

Figure S2. TG-DTA data for **1a**·HCl after exposure to water vapor for 10 days.

4. PXRD patterns of 1b·HCl·H_2O after heating and 1b·HCl after exposure to H_2O vapor

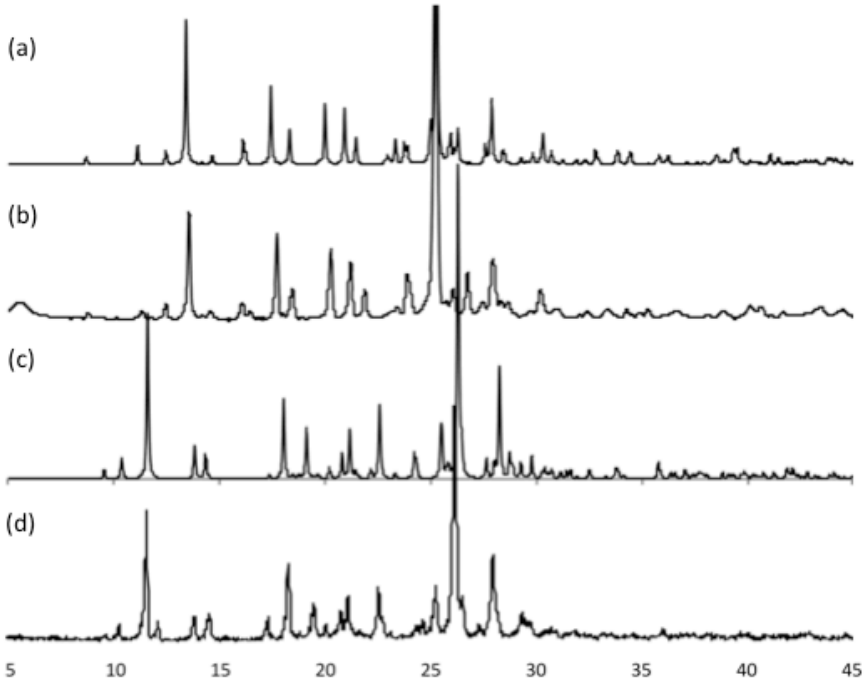

Figure S3. Simulated PXRD patterns for (a) **1b**·HCl and (c) **1b**·HCl·H_2O, and PXRD patterns for (b) **1b**·HCl·H_2O after heating at 80°C for 5h, and the dehydrate **1b**·HCl after exposure to H_2O vapor for (d) 2 days.