Supporting Information: Solid state transformations in stoichiometric hydrogen bonded molecular salts: ionic interconversion and dehydration processes.

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Table S1. Hydrogen bonding geometries in the crystal structures of the molecular salts **A_1B_1**, **A_1B_2•H_2O** and **A_1B_2**.

2. CheckCIF/PLATON

1. Experimental Details

Commercial HPLC-grade solvents were used without further purification. All the reagents were commercially available and used without *any* further purification.

X-Ray powder diffraction (XRPD) patterns were recorded on a Bruker D8 diffractometer (reflection mode; at 40 kV, 100 mA for a Cu-target tube (λ = 1.5406 Å) and a graphite monochromator; 2θ range 5º – 40º; step size 0.02º; total data collection time 10 min.

TGA measurements were carried out in a **DTG**-60H/DSC-**60,** SHIMADZU, Japan instrument. The heating rate was 10 °C/min and the measurement was from RT to 700 °C.

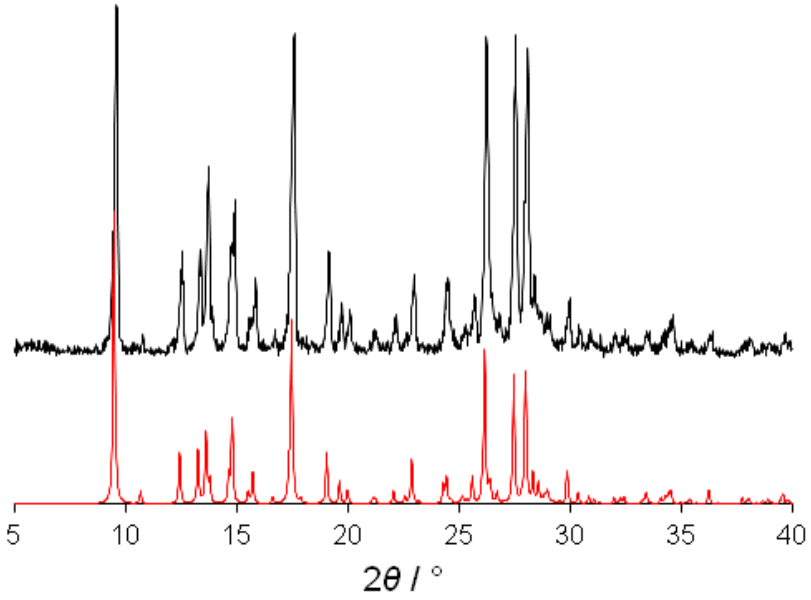

Figure S1. Comparison of XRPD patterns between bulk sample (black) of $\mathbf{A_1B_1}$ and its simulated XRPD from single crystal (red).

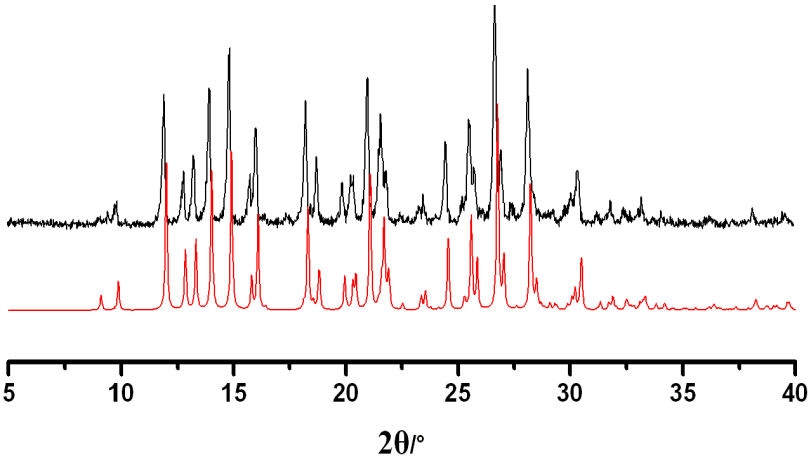

Figure S2. Comparison of XRPD patterns between bulk sample (black) of $\mathbf{A_1B_2{\bullet}H_2O}$ and its simulated XRPD from single crystal (red).

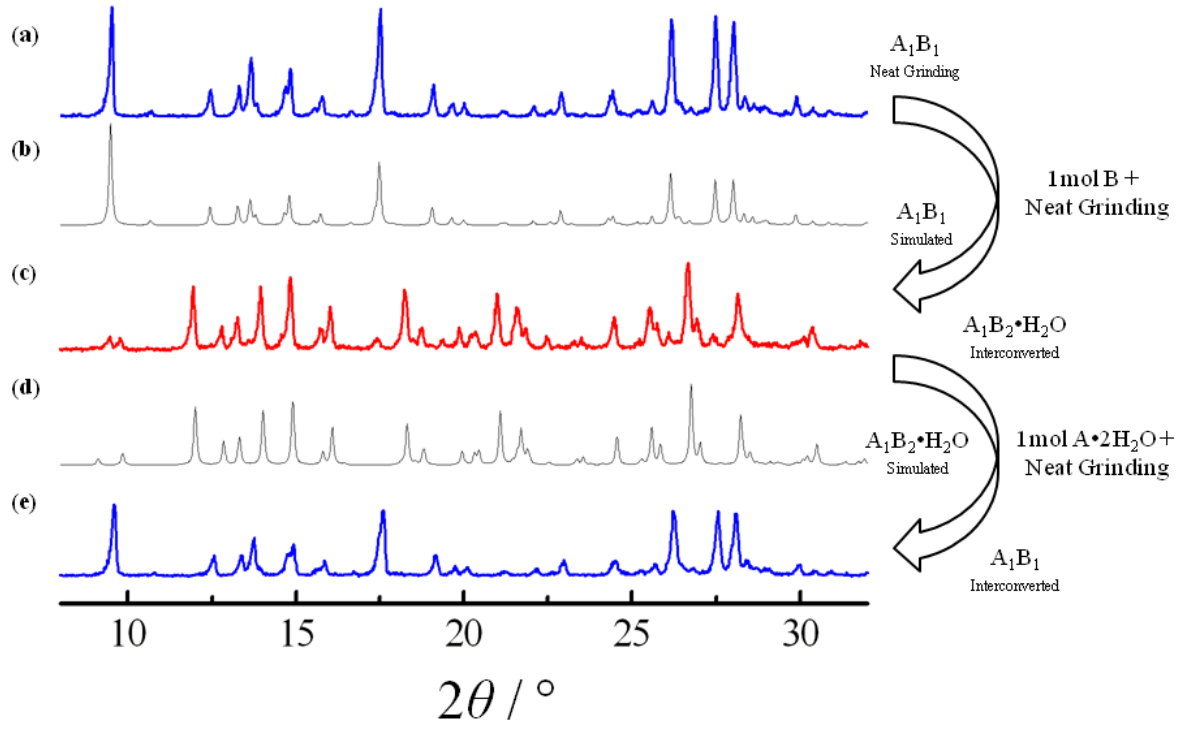

Figure S3. (a) Experimental XRPD pattern of $\mathbf{A_1B_1}$ obtained after grinding $\mathbf{A{\bullet}2H_2O}$ and **B** (1:1); (b) $\mathbf{A_1B_1}$ simulated XRPD from single crystal; (c) experimental XRPD after adding 1 mol of **B** to $\mathbf{A_1B_1}$ and subsequent grinding; (d) $\mathbf{A_1B_2{\bullet}H_2O}$ simulated XRPD from single crystal; and (e) experimental XRPD after adding and grinding one mol of $\mathbf{A{\bullet}2H_2O}$ to $\mathbf{A_1B_2{\bullet}H_2O}$. We note that there is a small amount of unreacted $\mathbf{A_1B_1}$ in interconverted $\mathbf{A_1B_2{\bullet}H_2O}$.

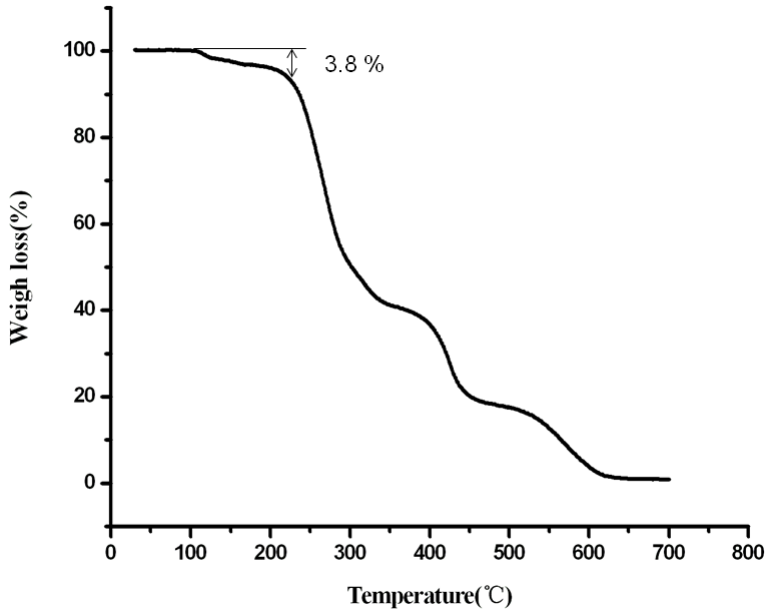

Figure S4. TG plot corresponding to $\mathbf{A_1B_2{\bullet}H_2O}$.

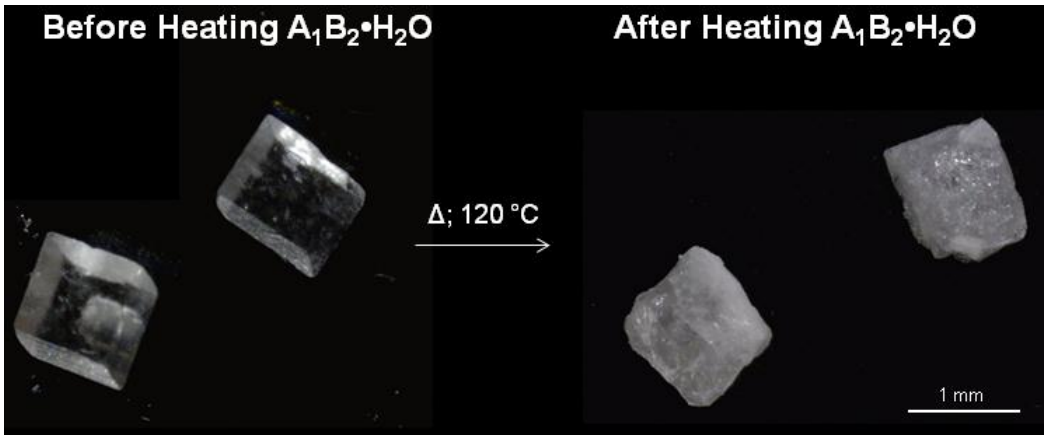

Figure S5. Photographs of **$A_1B_2•H_2O$** taken before and after heating to 120 °C in a furnace for *ca*. 24 mins. The clear change in the transparency indicates that a major structural transformation due to the release of water has taken place. This is corroborated by single crystal X-ray diffraction analysis.

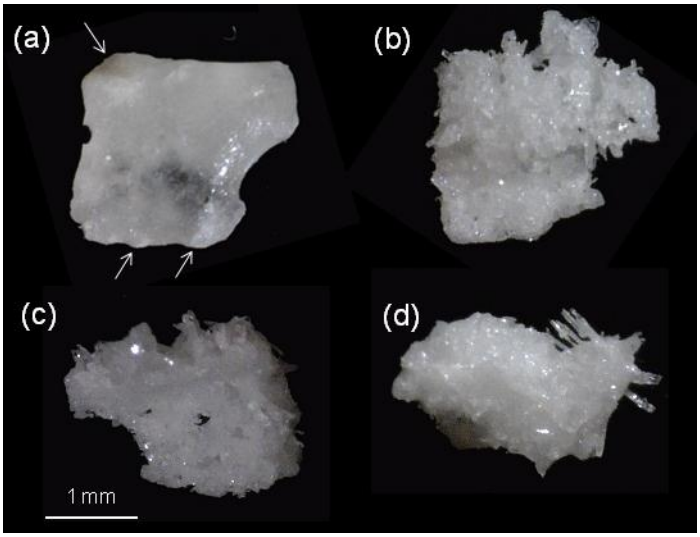

Figure S6. (a) Photograph of **$A_1B_2•H_2O$** taken after heating to 120 °C *ca*. 20 mins. The white areas (arrows) indicate that release of water occurred and a microcrystalline solid has formed. Note that the central part is more transparent, thus denoting that still there is parent crystal **$A_1B_2•H_2O$**. (b) The same crystal after being covered by a small amount of methanol (*i.e.*; 100 μl dropped onto the crystals) and left it overnight. (c) The same crystal viewed from the bottom. (d) A second crystal also after being heated and exposed to methanol shows the growth of larger needles of anhydrous crystal **A_1B_2**.

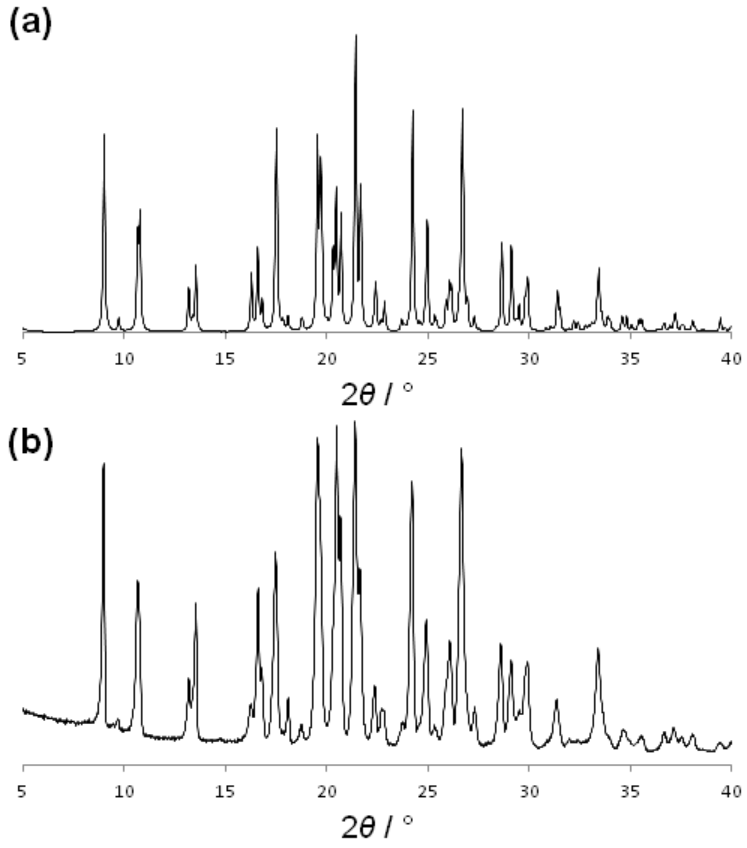

Figure S7. Simulated vs experimental XRPD patterns of $\mathbf{A_1B_2}$.

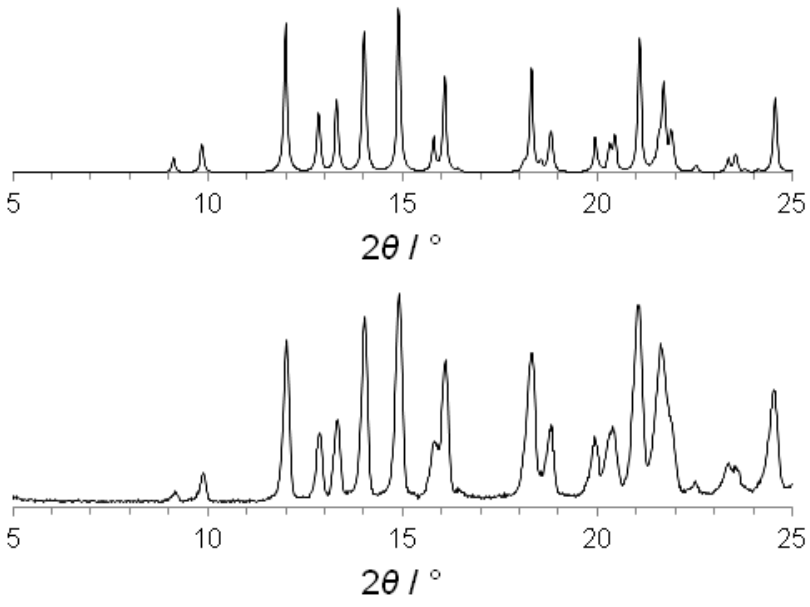

Figure S8. At top, simulated from single crystal data powder diffraction pattern of $\mathbf{A_1B_2{\bullet}H_2O}$. Bottom, powder diffraction pattern of $\mathbf{A_1B_2}$ after exposing it to vapors of H_2O for two days. Clearly, in $\mathbf{A_1B_2}$ adsorbtion of H_2O takes place as shown by the good match between both diffraction patterns.

Table S1. Hydrogen bonding geometries in the crystal structures of the molecular salts **A_1B_1**, **A_1B_2•H_2O** and **A_1B_2**.

	D···A(Å)	H···A (Å)	D–H···A (°)	Symmetry Code
A_1B_1				
i. N1–H1A···O3	2.889	2.122	148.2	x,y,z
ii. N2–H2A···O2	2.954	2.110	166.8	x,y,z
iii. O5–H2···O2	2.738	1.860	176.4	-1-x,-1/2+y,1/2-z
iv. O6–H3···O1	2.849	2.259	121.4	-1-x,-1-y,1-z
A_1B_2•H_2O				
i. N3–H3N···O3	2.737	1.940	153.6	x-1,1+y,z
ii. N4–H4N···O5	2.673	1.820	171.5	x,y,z
iii. O1w–H2w···O5	2.672	1.805	175.8	x,y,z
iv. N1–H1···O1w	2.627	1.778	169.3	1-x, 2-y,-z
v. O1w–H1w···O1	2.756	1.994	166.4	1-x,1-y,-z
vi. N2–H2N···O2	2.706	1.887	158.9	x-1,1+y,z
A_1B_2				
i. N2–H2···O3	2.733	1.895	164.4	x, y, z
ii. N1–H1···O5	2.692	1.874	158.2	1-x,y-1/2,1/2-z
iii. N3–H3···O6	2.667	1.699	170.1	1-x,1-y,1-z
iv. N4–H4···O2	2.716	1.864	170.8	x, y, z

2. CheckCIF/PLATON

checkCIF/PLATON (standard)

Structure factors have been supplied for datablock(s) 1

No syntax errors found. CIF dictionary
Please wait while processing .... Interpreting this report

Datablock: A1B1

Bond precision: C-C = 0.0028 A Wavelength=0.71073

Cell: a=7.8714(5) b=16.5514(11) c=13.6543(7)

alpha=90 beta=124.464(3) gamma=90

Temperature: 293 K

	Calculated	Reported
Volume	1466.69(16)	1466.69(15)
Space group	P 21/c	P21/c
Hall group	-P 2ybc	?
Moiety formula	C7 H5 O6 S, C7 H7 N2	?
Sum formula	C14 H12 N2 O6 S	C14 H12 N2 O6 S
Mr	336.33	336.33
Dx,g cm-3	1.523	1.523
Z	4	4
Mu (mm-1)	0.255	0.255
F000	696.0	696.0
F000'	696.88	
h,k,lmax	10,21,17	10,21,17
Nref	3354	3345
Tmin,Tmax	0.950,0.950	

```
Tmin'               0.950

Correction method= Not given

Data completeness= 0.997        Theta(max)= 27.460

R(reflections)= 0.0416( 3020)      wR2(reflections)= 0.1048( 3345)

S = 1.014              Npar= 208
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT052_ALERT_1_B Info on Absorption Correction Method Missing ...
?

Alert level C

PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor ....
2.4
PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Resd. #
1
C7 H5 O6 S

Alert level G

PLAT005_ALERT_5_G No _iucr_refine_instructions_details in the CIF
?
PLAT007_ALERT_5_G Note: Number of Unrefined D-H Atoms .....
4
PLAT093_ALERT_1_G No su's on H-positions, refinement reported as .
mixed
PLAT194_ALERT_1_G Missing _cell_measurement_reflns_used datum
.... ?
PLAT195_ALERT_1_G Missing _cell_measurement_theta_max datum
.... ?
PLAT196_ALERT_1_G Missing _cell_measurement_theta_min datum
.... ?
PLAT199_ALERT_1_G Check the Reported
_cell_measurement_temperature 293 K
PLAT200_ALERT_1_G Check the Reported
_diffrn_ambient_temperature 293 K
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd. #
2
C7 H7 N2

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0 **ALERT level A** = Most likely a serious problem - resolve or explain
1 **ALERT level B** = A potentially serious problem, consider carefully
2 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
9 **ALERT level G** = General information/check it is not something unexpected

7 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
1 ALERT type 2 Indicator that the structure model may be wrong or deficient
0 ALERT type 3 Indicator that the structure quality may be low
2 ALERT type 4 Improvement, methodology, query or suggestion

2 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

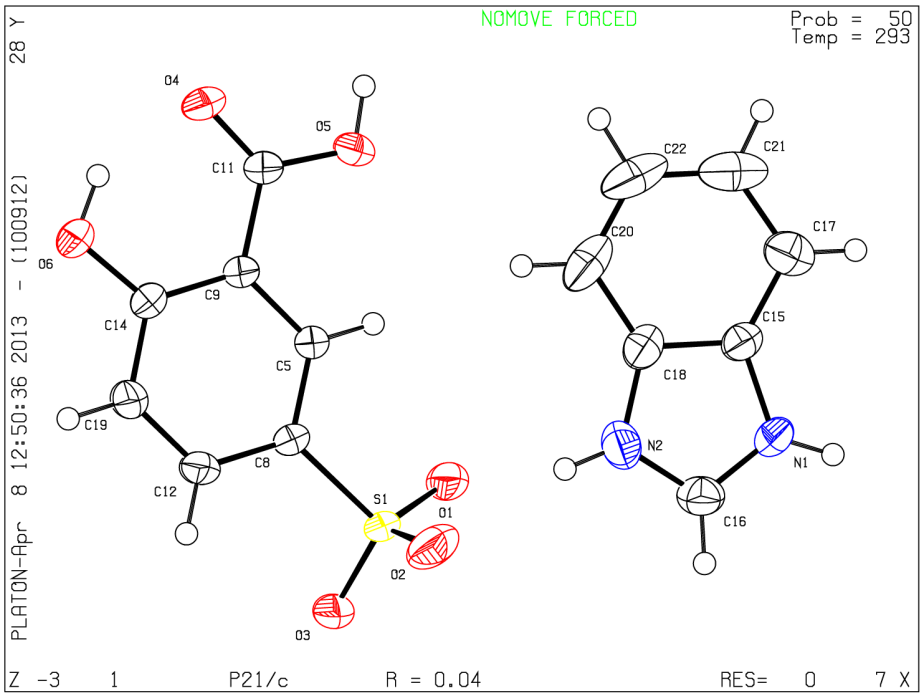
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 05/11/2012; check.def file version of 05/11/2012

Datablock A1B1 - ellipsoid plot



Download CIF editor (publCIF) from the IUCr
Download CIF editor (enCIFer) from the CCDC
Test a new CIF entry

checkCIF/PLATON (standard)

Structure factors have been supplied for datablock(s) shelx

No syntax errors found. CIF dictionary
Please wait while processing .... Interpreting this report

Datablock: A1B2.H2O

Bond precision: C-C = 0.0040 A Wavelength=0.71073

Cell: a=9.924(8) b=9.781(6) c=22.976(16)

alpha=90 beta=102.64(3) gamma=90

Temperature: 293 K

	Calculated	Reported
Volume	2176(3)	2176(3)
Space group	P 21/c	P21/c
Hall group	-P 2ybc	?
Moiety formula	C7 H4 O6 S, 2(C7 H7 N2), H2 O	?
Sum formula	C21 H20 N4 O7 S	C21 H20 N4 O7 S
Mr	472.48	472.48
Dx,g cm-3	1.442	1.442
Z	4	4
Mu (mm-1)	0.201	0.201
F000	984.0	984.0
F000'	985.00	
h,k,lmax	13,12,30	13,12,30
Nref	5240	5195
Tmin,Tmax	0.961,0.961	
Tmin'	0.961	

Correction method= Not given

Data completeness= 0.991 Theta(max)= 28.010

R(reflections)= 0.0510(2742) wR2(reflections)= 0.1574(5195)

S = 0.965 Npar= 310

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT052_ALERT_1_B Info on Absorption Correction Method Missing ...
?

Alert level C

PLAT241_ALERT_2_C Check High Ueq as Compared to Neighbors for C12
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for S1
PLAT245_ALERT_2_C U(iso) H2W Smaller than U(eq) O1W by ... 0.022 AngSq

PLAT355_ALERT_3_C Long O-H Bond (0.82A) O4 - H4 ...
1.01 Ang.
PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Resd. #
1
C7 H4 O6 S

Alert level G

PLAT005_ALERT_5_G No _iucr_refine_instructions_details in the CIF
?
PLAT007_ALERT_5_G Note: Number of Unrefined D-H Atoms .....
4
PLAT194_ALERT_1_G Missing _cell_measurement_reflns_used datum
.... ?
PLAT195_ALERT_1_G Missing _cell_measurement_theta_max datum
.... ?
PLAT196_ALERT_1_G Missing _cell_measurement_theta_min datum
.... ?
PLAT199_ALERT_1_G Check the Reported
_cell_measurement_temperature 293 K
PLAT200_ALERT_1_G Check the Reported
_diffrn_ambient_temperature 293 K
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd. #
2
C7 H7 N2

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6 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
3 ALERT type 2 Indicator that the structure model may be wrong or deficient
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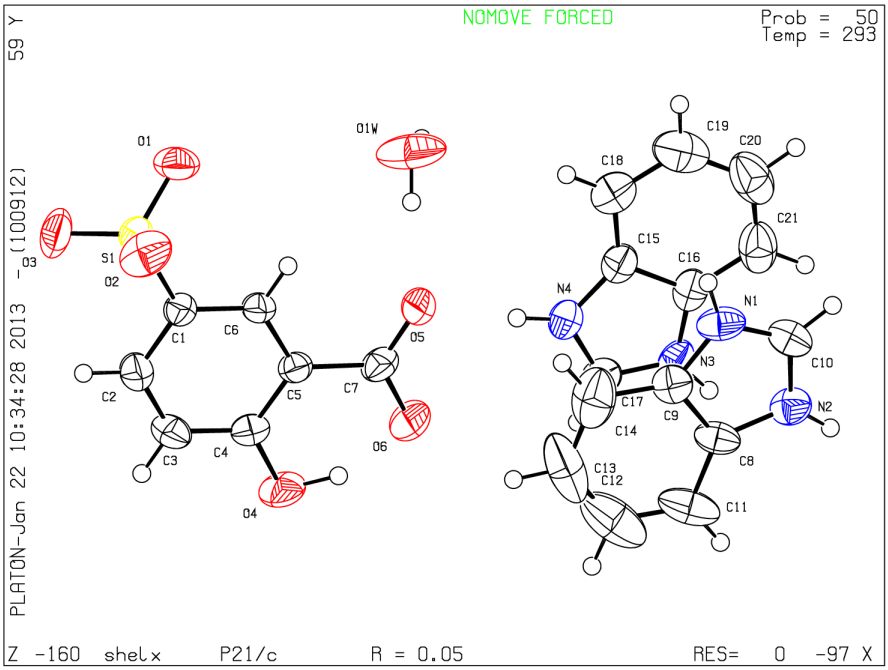
PLATON version of 05/11/2012; check.def file version of 05/11/2012

Datablock shelx - ellipsoid plot



checkCIF/PLATON (standard)

Structure factors have been supplied for datablock(s) mono_2

No syntax errors found. CIF dictionary
Please wait while processing .... Interpreting this report

Datablock: A1B2

Bond precision: C-C = 0.0061 A Wavelength=1.54178

Cell: a=21.4632(18) b=5.7527(5) c=18.1385(15)

alpha=90 beta=114.205(6) gamma=90

Temperature: 298 K

	Calculated	Reported

Volume	2042.7(3)	2042.7(3)
Space group	P 21/c	P21/c
Hall group	-P 2ybc	?
Moiety formula	C7 H4 O6 S, 2(C7 H7 N2)	?
Sum formula	C21 H18 N4 O6 S	C21 H18 N4 O6 S
Mr	454.46	454.45
Dx,g cm-3	1.478	1.478
Z	4	4
Mu (mm-1)	1.838	1.838
F000	944.0	944.0
F000'	948.37	
h,k,lmax	25,6,21	25,6,20
Nref	3607	3397
Tmin,Tmax	0.863,0.929	0.861,0.933
Tmin'	0.863	

Correction method= MULTI-SCAN

Data completeness= 0.942 Theta(max)= 66.610

R(reflections)= 0.0576(1715) wR2(reflections)= 0.1629(3397)

S = 1.003 Npar= 296

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT029_ALERT_3_B _diffrn_measured_fraction_theta_full Low
..... 0.942
PLAT230_ALERT_2_B Hirshfeld Test Diff for S1 -- O1 ..
7.5 su

Alert level C

ABSTY02_ALERT_1_C An _exptl_absorpt_correction_type has been
given without
a literature citation. This should be contained in the
_exptl_absorpt_process_details field.
Absorption correction given as multi-scan
REFLT03_ALERT_3_C Reflection count < 95% complete

From the CIF: _diffrn_reflns_theta_max 66.61
From the CIF: _diffrn_reflns_theta_full 66.61
From the CIF: _reflns_number_total 3397
TEST2: Reflns within _diffrn_reflns_theta_max
Count of symmetry unique reflns 3607
Completeness (_total/calc) 94.18%
PLAT340_ALERT_3_C Low Bond Precision on C-C Bonds .....
0.0061 Ang

Alert level G

PLAT005_ALERT_5_G No _iucr_refine_instructions_details in the CIF
?
PLAT007_ALERT_5_G Note: Number of Unrefined D-H Atoms
..... 3
PLAT194_ALERT_1_G Missing _cell_measurement_reflns_used
datum .... ?
PLAT195_ALERT_1_G Missing _cell_measurement_theta_max
datum .... ?
PLAT196_ALERT_1_G Missing _cell_measurement_theta_min
datum .... ?

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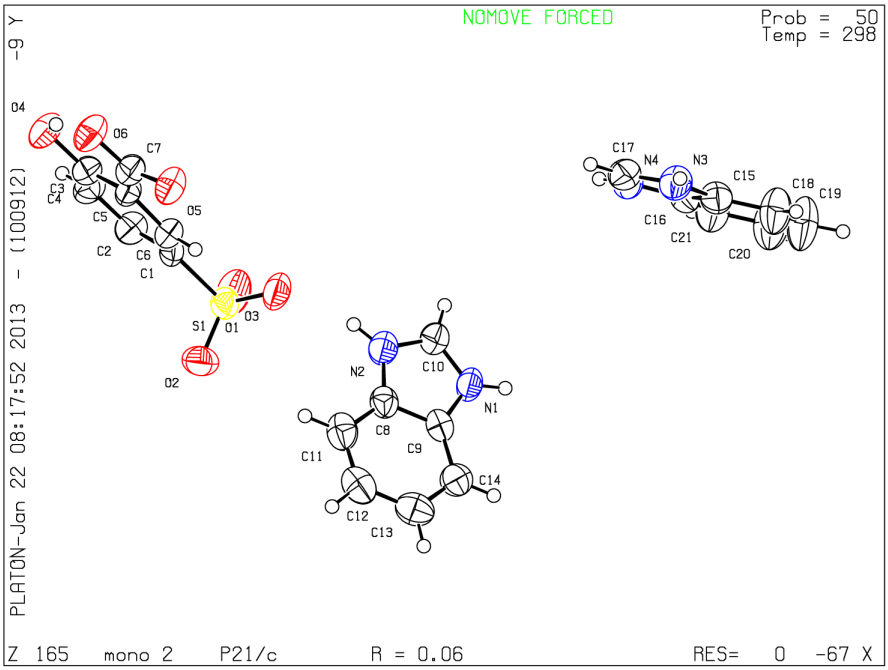
Datablock A1B2 - ellipsoid plot



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