Electronic Supplementary Material (ESI) for Dalton Transactions.

Sulfonamide-Substituted Iron Phthalocyanine: Design, Solubility Range, Stability and Oxidation of Olefins

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Content

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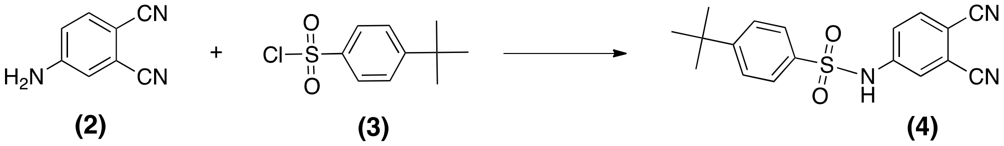
1. Synthesis

1.1. General

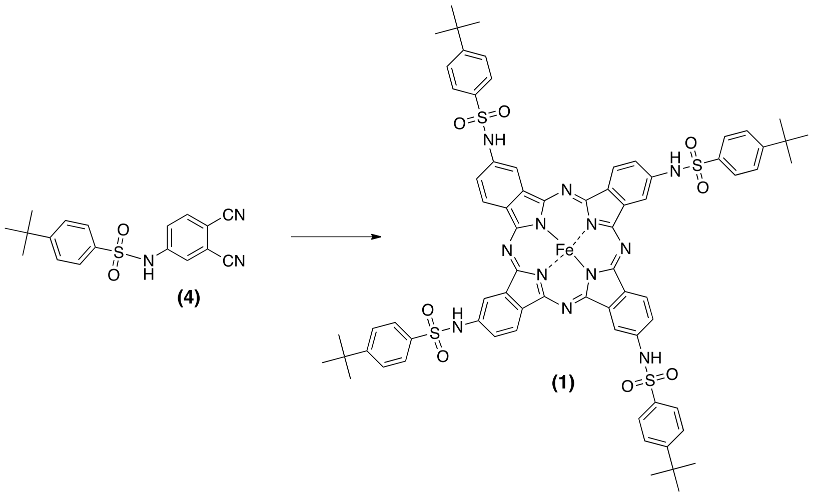
All solvents were dried before use as described.[1] Infrared spectra (IR) were recorded on a Bio-Rad FTS 175C FTIR spectrophotometer. UV-visible absorption spectra were obtained using a Shimadzu 2001 UV Pc spectrophotometer. The mass spectra were recorded on a LCQ-ion trap (Thermo Finnigan, an Jose, CA, USA), equipped with an ES (Electrospray) source and MALDI (Matrix Assisted Laser Desorption Ionization) BRUKER Microflex LT using 2,5-dihydroxybenzoic acid as matrix. ^{1}H and ^{13}C NMR spectra were recorded in deuterated chloroform (DMSO-d_6) on a Varian 500 MHz spectrometer.

1.2. Preparation of 4-*tert*-butylbenzenesulfonylaminophthalonitrile (4)



To a solution of 4-aminophthalonitrile (2.05 g, 14.32 mmol) in pyridine (10 mL) cooled at 0^{o}C was slowly added 4-tertbutylbenzene sulfonyl chloride (5 g, 21.48 mmol) in pyridine (10 mL). The reaction mixture was allowed to slowly reach room temperature and was stirred under argon for 24h. Then the mixture was poured into water (400 mL) and stirred for 1 hour. The resulting solid was collected by filtration and washed with HCl solution (5 %) then with water. The crude product was recrystallized from ethanol. White solid. Yield: 50% (2.45 g), mp 201^{o}C. MW: 339.41. Anal. calcd. for $C_{18}H_{17}N_3O_2S$: C, 63.70; H, 5.05; N, 12.38 %. Found: C, 63.76; H, 5.15; N, 12.30 %. ^{1}H NMR (500 MHz, DMSO- d_6): δ, ppm 1.2 (s, 9H), 7.5 (d, 1H), 7.6 (d, 3H), 7.8 (d, 2H), 8.0 (d, 1H). ^{13}C NMR (500 MHz, DMSO- d_6): δ, ppm 31.08, 35.40, 108.49, 115.96, 116.30, 116.47, 122.05, 122.20 127.03, 127.09, 135.99, 136.44, 143.22, 157.33. IR (KBr): ν, cm^{-1} 3232, 2967, 2231, 1600, 1477, 1394, 1343, 1161, 1084, 967, 856, 838, 646, 623. ESI-MS: m/z 338.19 $[MH]^+$

1.3. Preparation of sulfonamide-substituted iron phthalocyanine (1)



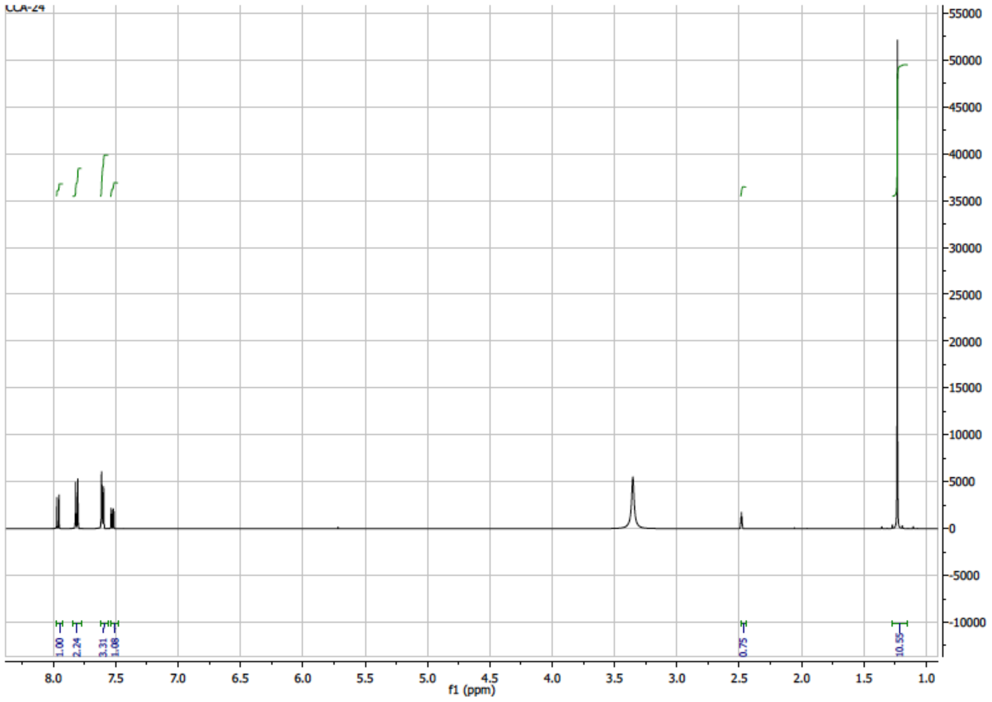
(4)

(1)

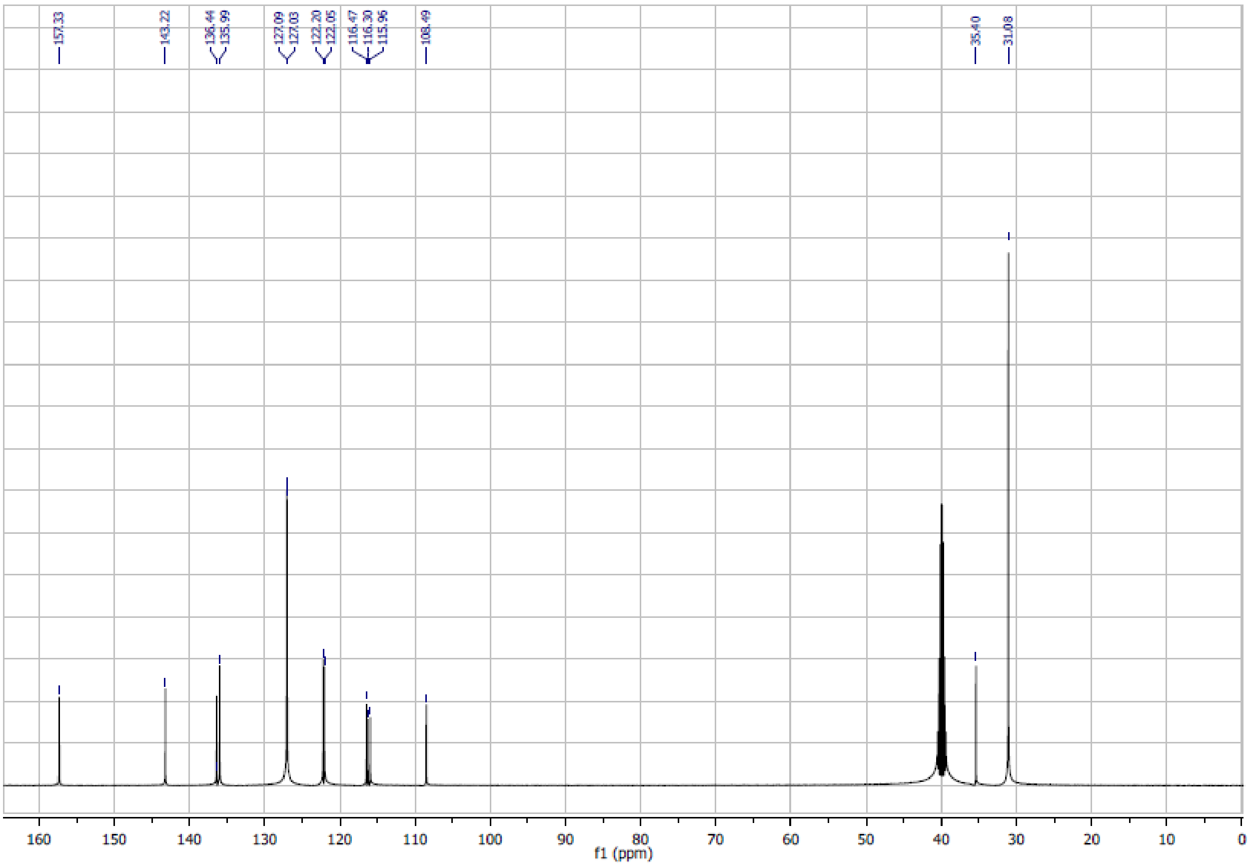
Phthalonitrile **4** (250 mg, 0.73 mmol) was dissolved in ethylene glycol (1 mL) and $FeCl_2$ (0.4 mmol) was added to the reaction mixture. The reaction was kept at 180-190 °C for 5 h. The mixture was cooled to room temperature and ethanol (10 mL) was added. The resulting precipitate was collected by centrifugation. The green-blue phthalocyanine **1** was isolated by chromatography on silica gel using a mixture of CH_2Cl_2-EtOH (50:1). Dark blue solid. Yield: 32% (85 mg). MALDI-MS: m/z 1413.6 $[M]^+$. IR (KBr): νmax, cm^{-1} 3435 (N-H), 1373 and 1159 ($-SO_2$). UV-vis λ nm (log ε) acetonitrile 654 (4.54)

2. Characterizations

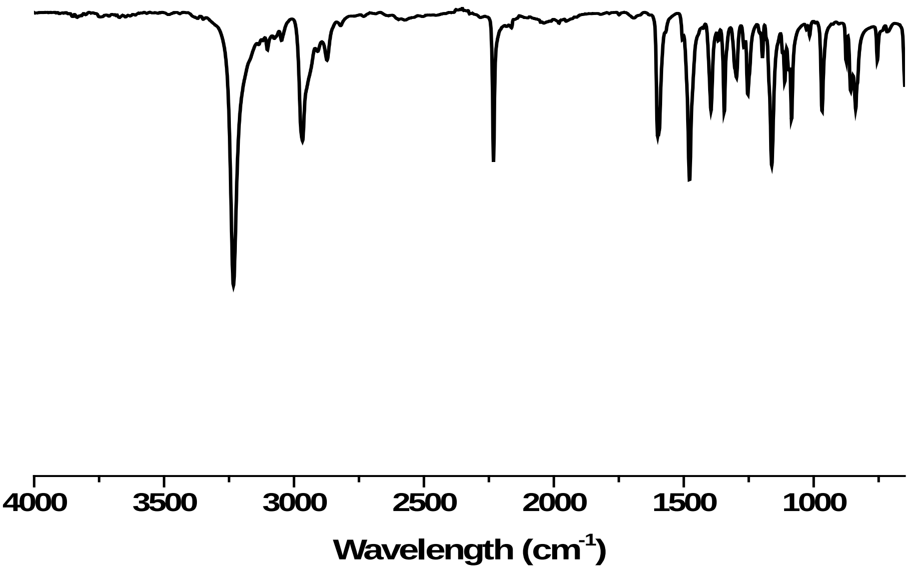
2.1. ^{1}H spectrum of phthalonitrile (4)



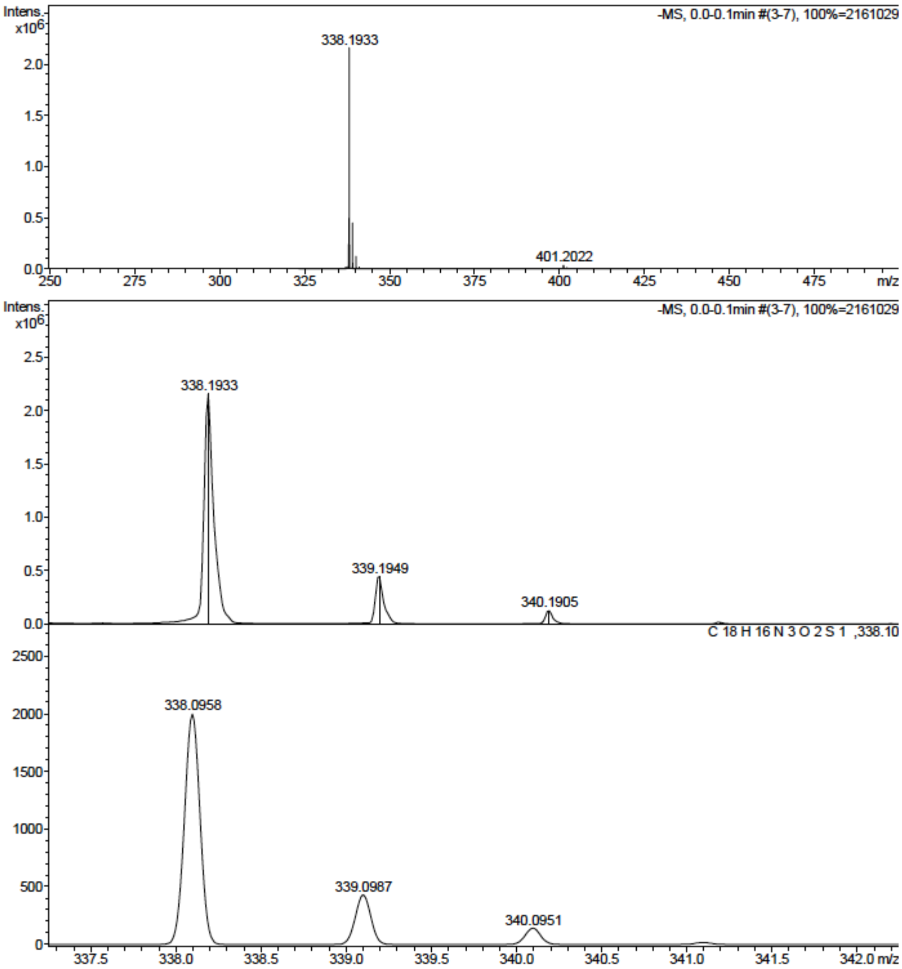
2.2. ^{13}C spectrum of phthalonitrile (4)



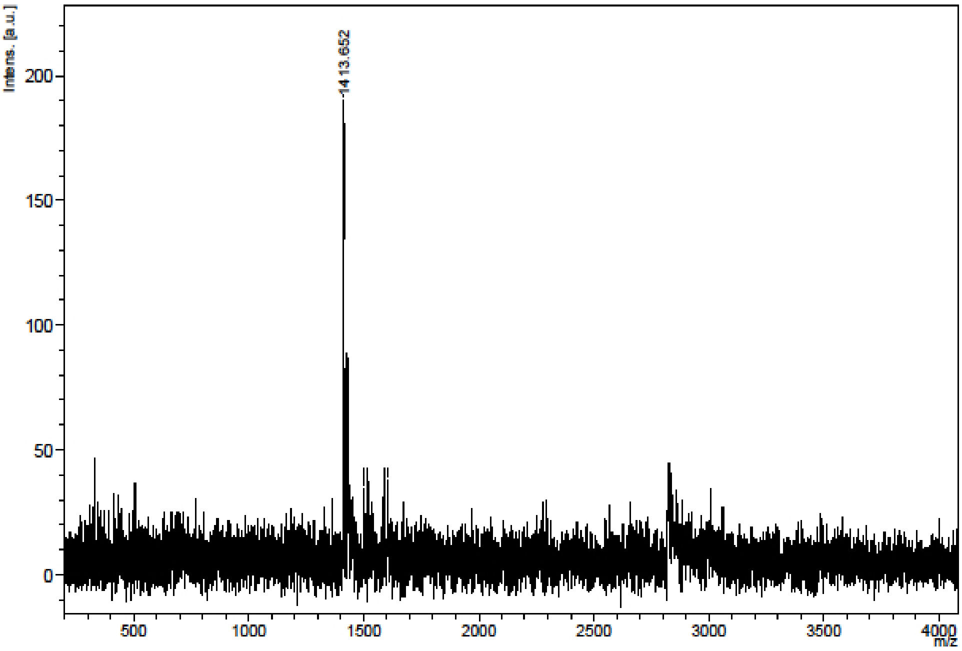
2.3. FT-IR spectrum of phthalonitrile (4)



2.4. ESI-MS spectrum of phthalonitrile (4)



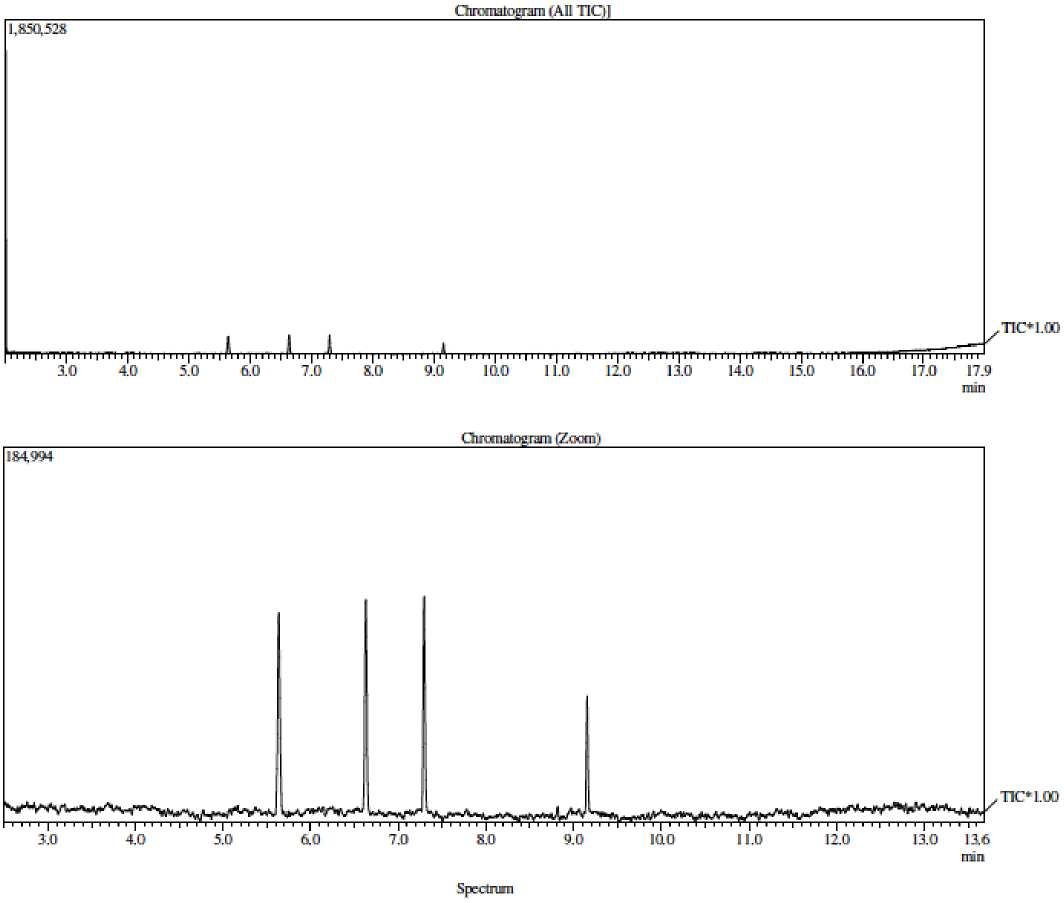
2.5. MALDI-TOF Spectrum of (1)



3. Catalytic oxidations

Oxidation reactions were carried out in a two-necked flask at 25°C using 1:200:400 molar ratio between catalyst, substrate and oxidant. In a typical procedure a catalyst sample (10^{-6} mol) was added to cyclohexene or styrene (0.1 M); then, H_2O_2 (%30 vol.) (0.2 M) was added and the reaction mixture was stirred at 25 °C and analyzed in a Agilent 5975C GC/MSD gas chromatograph. Chlorobenzene or bromobenzene was used as internal standard.

Th GC-MS spectra of styrene oxidaton experiments is provided below.



4. X-ray data collection and structure refinement

Unit cell measurements and intensity data collection was performed on an Bruker APEX II QUAZAR three-circle diffractometer using monochromatized Mo Kα X–radiation (λ = 0.71073 Å) using φ and ω technique. Indexing was performed using APEX2.[2] Data integration and reduction were carried out with SAINT V8.27B.[3] Absorption correction was performed by multi-scan method implemented in SADABS V2012/1.[4] The structure was solved using the direct methods procedure in SHELXS-97 [5] and then refined by full-matrix least-squares refinements on F^2 using the SHELXL-97.[5] All non-hydrogen atoms were refined anisotropically using all reflections with $I > 2\sigma(I)$. C-bound H atoms were positioned geometrically and refined using a riding mode. For compound **4**, N-bound H atom was located from the difference Fourier map and and restrained to be 0.89 Å from N atom using DFIX and their position were constrained to refine on their parent N atoms with Uiso(H) = 1.2Ueq(N). Crystallographic data and refinement details of the data collection for **4** is given in Table 1. The final geometrical calculations and the molecular drawings were carried out with Platon v1.16[6] and Mercury CSD 3.1[7] program.

Table S1. Crystal data and refinement parameters for (**4**)

Crystal parameters	**4**
CCDC	925679
Empirical Formula	$C_{18}H_{17}N_3O_2S$
Formula weight (g. mol^{-1})	339.41
Temperature (K)	130(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	$Pca2_1$
***a* (Å)**	8.5105(6)
***b* (Å)**	8.8219(6)
***c* (Å)**	21.8277(14)
α(°)	90
β(°)	90
γ(°)	90
Crystal size (mm)	0.07 x 0.13 x 0.18
***V* (Å^3)**	1638.80(19)
Z	4

ρ_{calcd} (g. cm^{-3})	1.376
μ (mm^{-1})	0.213
***F*(000)**	712
θ range for data collection (°)	2.97 - 25.00
h*/*k*/*l	-10/8, -10/10, -25/25
Reflections collected	11431
Independent reflections	2837 [R(int) = 0.0402]
Absorption correction	Multi-scan
T_{max} and T_{min}	0.9856 and 0.9618
Data/restraints/parameters	2837 / 2 / 223
Goodness-of-fit on F^2 (*S*)	1.060
***R* indices [$I > 2\sigma(I)$]**	R_1= 0.0295, wR_2= 0.0724
***R* indices (all data)**	R_1= 0.0319, wR_2= 0.0742
Largest diff. peak and hole (e.Å^{-3})	0.206 and -0.288

CCDC-925679 (for **4**), contain the supplementary crystallographic data for this paper. This data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223-336033; email: deposit@ccdc.cam.ac.uk]. The checkcif file is available at the end of this document.

6. References

1 D. D. Perrin and W. L. F. Armarego, Purification of Laboratory Chemicals, Pergamon Press, Oxford, 2nd edn, 1989.

2 Bruker (2012) APEX2, version 2012.10-0, Bruker AXS Inc., Madison, Wisconsin, USA

3 Bruker (2012) SAINT, version V8.27B, Bruker AXS Inc., Madison, Wisconsin, USA.

4 Bruker (2012) SADABS, version 2012/1, Bruker AXS Inc., Madison, Wisconsin, USA.

5 G. M. Sheldrick, *Acta Cryst.* 2008, **A64**, 112.

6 A. L. Spek, *Acta Cryst*. 2009, **D65**, 148.

7 C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler, J. van de Streek, *J. Appl. Cryst*., 2006, **39**, 453.

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found.   CIF dictionary   Interpreting this report

Datablock: I

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Bond precision:  C-C = 0.0030 A            Wavelength=0.71073

Cell:             a=8.5105(6)     b=8.8219(6)     c=21.8277(14)
                  alpha=90        beta=90         gamma=90
Temperature:      130 K

                Calculated                Reported
Volume          1638.80(19)               1638.80(19)
Space group     P c a 21                  P c a 21
Hall group      P 2c -2ac                 P 2c -2ac
Moiety formula  C18 H17 N3 O2 S           C18 H17 N3 O2 S
Sum formula     C18 H17 N3 O2 S           C18 H17 N3 O2 S
Mr              339.42                    339.41
Dx,g cm-3       1.376                     1.376
Z               4                         4
Mu (mm-1)       0.213                     0.213
F000            712.0                     712.0
F000'           712.76
h,k,lmax        10,10,25                  10,10,25
Nref            2879[ 1484]               2837
Tmin,Tmax       0.967,0.985               0.760,0.990
Tmin'           0.962

Correction method= MULTI-SCAN

Data completeness= 1.91/0.99      Theta(max)= 25.000

R(reflections)= 0.0295( 2713)     wR2(reflections)= 0.0742( 2837)

S = 1.060                  Npar= 223
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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 C

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PLAT089_ALERT_3_C Poor Data / Parameter Ratio (Zmax < 18) ........       6.65
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Alert level G

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PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite          2 Note
PLAT005_ALERT_5_G No _iucr_refine_instructions_details  in the CIF     Please Do !
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... #          1 Do !
            N2  -C2  -C3  -C4    -14.00  4.00   1.555   1.555   1.555   1.555
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... #          2 Do !
            N2  -C2  -C3  -C8    164.00  4.00   1.555   1.555   1.555   1.555
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... #         16 Do !
            N1  -C1  -C8  -C7     41.00  5.00   1.555   1.555   1.555   1.555
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... #         17 Do !
            N1  -C1  -C8  -C3   -138.00  5.00   1.555   1.555   1.555   1.555
PLAT860_ALERT_3_G Number of Least-Squares Restraints ............           2 Note
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   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   1 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   7 ALERT level G = General information/check it is not something unexpected

   0 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
   2 ALERT type 3 Indicator that the structure quality may be low
   4 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check
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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 18/09/2013; check.def file version of 12/09/2013

Datablock I - ellipsoid plot