

Diacenaphtho[1,2-c:1',2'-e]-1,2-dithiin: synthesis, structure and reactivity

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Abstract

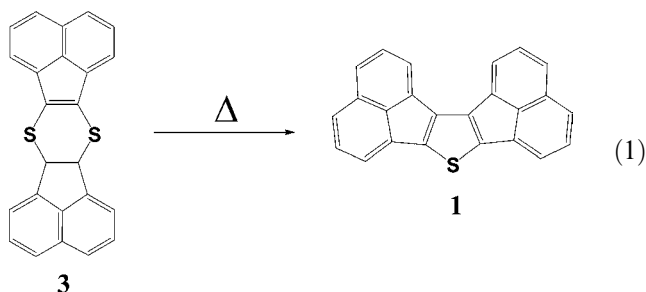
Diacenaphtho[1,2-c:1',2'-e]-1,2-dithiin **2** was synthesized in 23% yield by the reaction of acenaphthylene with elemental sulfur at 120 °C. This reaction also afforded either diacenaphtho[1,2-b:1',2'-d]thiophene **1** or diacenaphtho[1,2-b:1',2'-e]-dihydro[e]-1,4-dithiin **3** depending on the reaction time. Compound **2** was desulfurized and converted to **1** under UV-vis irradiation in a benzene solution. Reaction of **2** with Pt(COD)₂ yielded the complex Pt(COD)(C₂₄H₁₂S₂) **4** (COD = 1,5-cyclooctadiene) by insertion of a Pt(COD) group into the S–S bond of **2**. When heated, **4** was desulfurized and converted to **1** by elimination of a (COD)PtS grouping. Compounds **1–4** were characterized crystallographically.

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1. Introduction

Diacenaphtho[1,2-b:1',2'-d]thiophene, C₂₄H₁₂S, **1** was first isolated a century ago as a bi-product in the synthesis of decacyclene (C₃₆H₁₈) [1]. It is obtained in combination with diacenaphtho[1,2-b:1',2'-e]-dihydro[e]-1,4-dithiin **3** by treatment of acenaphthylene with sulfur [1,2]. Compound **3** is transformed into **1** by loss of H₂S when heated,



We have now reinvestigated the reaction of acenaphthylene with sulfur. At 120 °C, we have obtained

and isolated the new 1,2-dithiin, diacenaphtho[1,2-c:1',2'-e]-1,2-dithiin, **2** which we have fully characterized and investigated its reactivity and its relationship to compound **1**. 1,2-Dithiins have attracted considerable attention because of their chemical and biological properties [3]. 1,2-Dithiins such as the thiarubrines can be found in plants and show extensive biological activity [4]. These compounds are also of interest to theoretical chemists because they adopt a non-planar twisted geometry and are antiaromatic [5–7]. Their high reactivity and structural instability have limited the synthesis and characterization of derivatives of these naturally occurring molecules [8,9].

It is known that metal-containing groups can insert into the sulfur–sulfur bond of organic disulfides [10]. Reactions of mononuclear metal phosphine complexes with Fe₂(CO)₆(μ-S₂) result in mixed metal compounds containing two sulfido ligands [11]. Previously our group has demonstrated the ability of transition metal groups to insert into the sulfur–sulfur bond of Mn₂(CO)₇(μ-S₂) [12]. We have found that Pt(COD)₂, (COD = 1,5-cyclooctadiene) reacts with **2** to form Pt(COD)(C₂₄H₁₂S₂) **4** by insertion of a Pt(COD) group into the sulfur–sulfur bond. The results of this reaction along with the crystal structures of **1–4** are reported herein.

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2. Results and discussion

The reaction of acenaphthylene with elemental sulfur in DMF at 120 °C for 5 h affords thiophene **1** and the 1,2-dithiin **2** in 20% and 23% yields, respectively. The formation of **1** proceeds through the intermediate 1,4-dithiin **3** which was isolated in 11% yield by quenching the reaction after 1.5 h. As reported previously, **3** can be converted to **1** by heating in the absence of solvent [2]. Compounds **1** and **3** were characterized by comparison of previously reported spectral data and by single crystal X-ray diffraction analyses reported for the first time herein. Crystallographic data are presented in Table 1. ORTEP diagrams of **1** and **3** are shown in Figs. 1(a) and (b), respectively. Selected bond distances and angles for **1** and **3** are given in Table 2. Compound **1** consists of a thiophene with each double bond annulated by an acenaphthylene molecule. The three carbon–carbon bond distances in the thiophene ring are not significantly different ($C(1)–C(2) = 1.404(5)$ Å, $C(2)–C(3) = 1.404(5)$ Å, and $C(3)–C(4) = 1.392(5)$ Å), which suggests that the 6π electrons are fully delocalized. Compound **3** is a 2,3-dihydro-1,4-dithiin also annulated by two acenaphthylene molecules and the two hydrogen atoms are *cis* to each other. Both sets of rings are bent to the same side resulting in a butterfly structure.

Compound **2** was characterized by NMR, mass spectra, and single crystal X-ray diffraction analysis. As

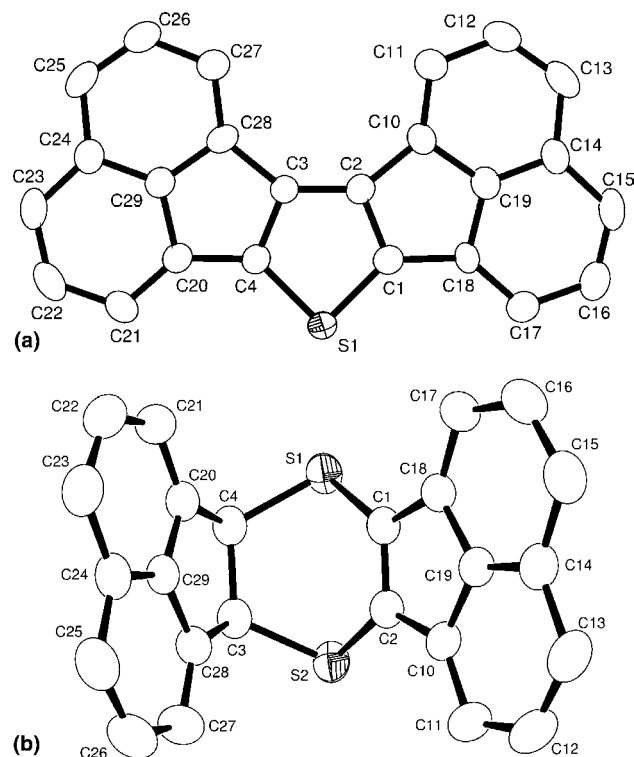


Fig. 1. ORTEP diagrams of the molecular structures of (a), diacenaphtho[1,2-b:1',2'-d]thiophene (**1**) and (b), diacenaphtho[1,2-b:1',2'-e]-dihydro[e]-1,4-dithiin (**3**) showing 50% thermal ellipsoid probabilities.

Table 1
Crystallographic data for compounds 1–4

Compound	1	2	3	4
Empirical formula	C ₂₄ H ₁₂ S	C ₂₄ H ₁₂ S ₂	C ₂₄ H ₁₄ S ₂	C ₃₂ H ₂₄ PtS ₂
Formula weight	332.4	728.91	366.47	667.72
Crystal system	monoclinic	monoclinic	monoclinic	tetragonal
Lattice parameters				
<i>a</i> (Å)	15.110(3)	21.0230(13)	9.1846(6)	23.6311(6)
<i>b</i> (Å)	3.9080(7)	7.4767(5)	18.6521(12)	23.6311(6)
<i>c</i> (Å)	26.068(4)	21.5930(12)	11.0654(7)	8.7066(4)
β (deg)	98.511(4)	98.478(2)	113.749(1)	90
<i>V</i> (Å ³)	1522.4(5)	3357.0(4)	1735.11(19)	4862.0(3)
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -421 <i>c</i>
<i>Z</i> -value	4	8	4	8
ρ_{calc} (g cm ⁻³)	1.450	1.442	1.403	1.824
μ (Mo K α) (mm ⁻¹)	0.214	0.321	0.311	5.964
Temperature (K)	296	296	296	296
2 θ_{max} (deg)	50.04	56.62	56.62	50.06
No. of observations	2024	3897	3714	3763
No. of parameters	226	565	291	316
Goodness of fit (GOF)	1.139	1.023	1.039	1.178
Max. shift in final cycle	0.000	0.005	0.001	0.001
Residuals ^a : <i>R</i> ₁ ; <i>wR</i> ₂ (<i>I</i> > 2 σ (<i>I</i>))	0.0801; 0.1638	0.0886; 0.1694	0.0364; 0.0985	0.0525; 0.1030
Absorption correction	SADABS	SADABS	SADABS	SADABS
Max/min	1.00/0.760	1.00/0.855	1.00/0.892	1.00/0.756
Largest peak in final diff. map (e ⁻ Å ⁻³)	0.378	0.698	0.296	1.008

^a $R = \sum_{hkl} (||F_{\text{obs}}| - |F_{\text{calc}}||) / \sum_{hkl} |F_{\text{obs}}|$; $R_w = \left[\frac{\sum_{hkl} w (|F_{\text{obs}}| - |F_{\text{calc}}|)^2}{\sum_{hkl} w F_{\text{obs}}^2} \right]^{1/2}$; $w = 1/\sigma^2(F_{\text{obs}})$; $\text{GOF} = \left[\frac{\sum_{hkl} w (|F_{\text{obs}}| - |F_{\text{calc}}|)^2}{(n_{\text{data}} - n_{\text{vari}})} \right]^{1/2}$.

Table 2
Selected bond distances and angles for compounds 1–3^a

1		2		3	
Atoms	Distance (Å)	Atom	Distance (Å)	Atom	Distance (Å)
S(1)–C(1)	1.714(4)	S(1)–C(1)	1.750(4)	S(1)–C(1)	1.7398(13)
S(1)–C(4)	1.726(4)	S(1)–S(2)	2.090(2)	S(1)–C(4)	1.8445(14)
C(1)–C(2)	1.404(5)	S(2)–C(4)	1.758(5)	S(2)–C(2)	1.7386(14)
C(2)–C(3)	1.404(5)	C(1)–C(2)	1.381(5)	S(2)–C(3)	1.8291(14)
C(3)–C(4)	1.392(5)	C(2)–C(3)	1.454(6)	C(1)–C(2)	1.3645(19)
		C(3)–C(4)	1.384(6)	C(3)–C(4)	1.568(2)
Atoms	Angle (deg)	Atoms	Angle (deg)	Atoms	Angle (deg)
C(1)–S(1)–C(4)	90.5(2)	C(1)–S(1)–S(2)	97.72(16)	C(1)–S(1)–C(4)	99.66(6)
C(2)–C(1)–S(1)	113.1(3)	C(4)–S(2)–S(1)	98.66(16)	C(2)–S(2)–C(3)	98.60(6)
C(3)–C(2)–C(1)	111.4(4)	C(2)–C(1)–S(1)	123.2(3)	C(2)–C(1)–S(1)	122.15(10)
C(4)–C(3)–C(2)	112.2(3)	C(1)–C(2)–C(3)	123.2(4)	C(1)–C(2)–S(2)	122.12(10)
C(3)–C(4)–S(1)	112.8(3)	C(4)–C(3)–C(2)	122.5(4)	C(4)–C(3)–S(2)	117.05(10)
		C(3)–C(4)–S(2)	124.1(3)	C(3)–C(4)–S(1)	116.14(9)

^a Estimated standard deviation in the least significant figure is given in parentheses.

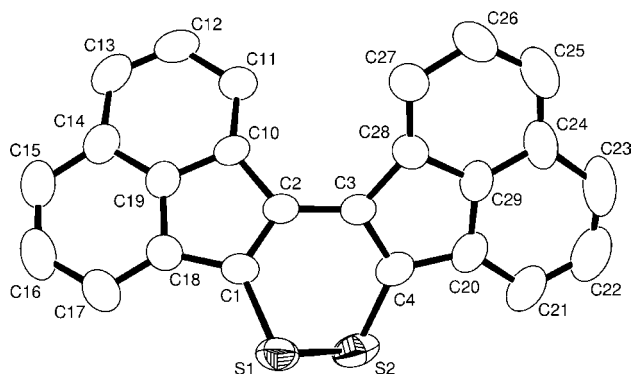
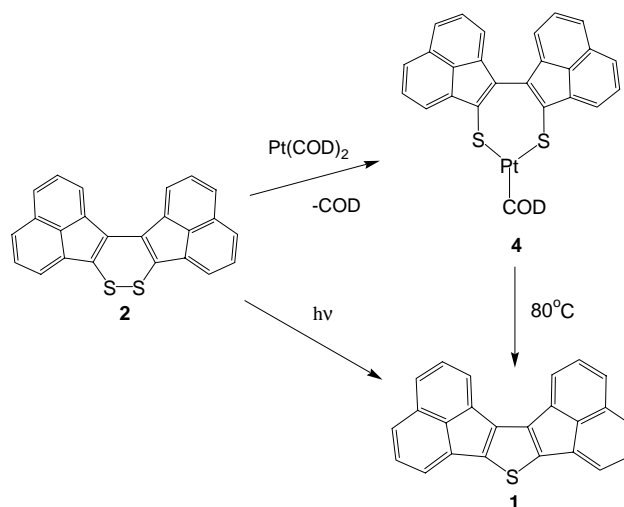


Fig. 2. An ORTEP diagram of the molecular structure of dicianaphtho[1,2-c:1',2'-e]-1,2-dithiin (**2**) showing 50% thermal ellipsoid probabilities.

shown in the ORTEP diagram of **2** in Fig. 2, the molecule adopts a twisted conformation with a C(1)–S(1)–S(2)–C(4) dihedral angle of 52.4°. The bond distances and angles correspond to those of other known 1,2-dithiins [13,14]. The S–S bond distance 2.090(2) Å is similar to that found in other cyclic disulfides, such as dithieno[3,2-c:2',3'-e]-1,2-dithiin (2.059(3) Å) [15] and dinaphtho[1,2-c:7,8-e]-1,2-dithiin (2.063(2) Å) [16]. 1,2-Dithiins contain an 8 π -electron heterocyclic ring which readily loses sulfur upon exposure to light or heat to form thiophenes [13,14]. Likewise, irradiation of **2** caused elimination of one sulfur atom to give **1** in high (91%) yield (Scheme 1).

It is well known that zero-valent platinum phosphine compounds insert into the S–S bond of organic disulfides to yield platinum dithiolate compounds [10]. Similarly, compound **2** reacts with Pt(COD)₂ in CH₂Cl₂ at room temperature by loss of COD and insertion into the S–S bond of **2** to give the new compound Pt(COD)(C₂₄H₁₂S₂) **4** in 14% yield. Compound **4** was characterized by NMR, elemental, and single crystal X-ray dif-



Scheme 1.

fraction analysis. An ORTEP diagram of **4** is shown in Fig. 3. Selected bond distances and angles are shown in Table 3. Compound **4** contains two Pt–S bonds, Pt(1)–S(1) = 2.285(4) Å and Pt(1)–S(2) = 2.321(4) Å. These distances are similar to those found in the compounds Pt(COD)(C₆H₄S₂) (Pt–S = 2.264(5) Å) [17] and Mn₂(CO)₇Pt(PPh₃)₂(μ_3 -S)₂ (Pt(1)–S(1) = 2.346(2) Å and Pt(1)–S(2) = 2.355(3) Å) [12a]. The two acenaphthyl groups are planar and the dihedral angle between them is 45.6°. Like binaphthyl groups, the biacenaphthyl grouping is chiral and appears to be sufficiently crowded sterically so that interconversion of the enantiomers will be slow. Suitably difunctionalized stable derivatives could be useful as ligands for metal complexes involved in asymmetric synthesis and asymmetric catalysis [18]. Unfortunately, the dithiolato ligand in **4** is not stable. When heated to 80 °C for 3 h, compound **4** decomposes by elimination of Pt(COD)S with formation of **1** in 50%

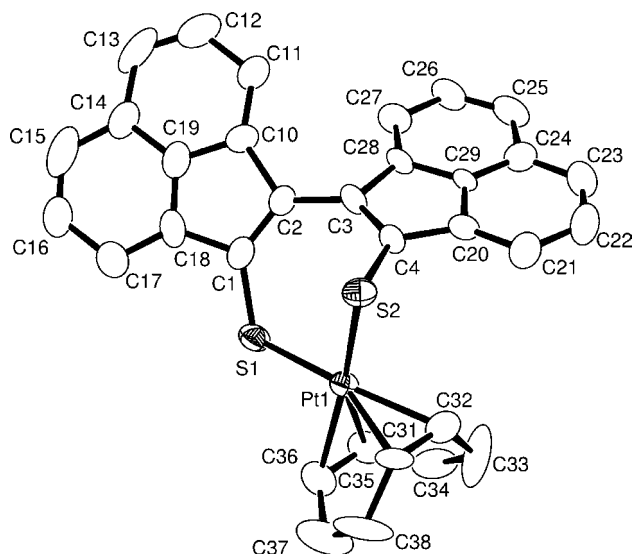


Fig. 3. An ORTEP diagram of the molecular structure of $\text{Pt}(\text{COD})(\text{C}_{24}\text{H}_{12}\text{S}_2)$ (**4**) showing 50% thermal ellipsoid probabilities.

yield. The fate of the $\text{Pt}(\text{COD})\text{S}$ grouping was not determined. Antebi et al. [19] have shown that cobalt carbonyl induces removal of one sulfur atom from benzyl disulfide to yield dibenzylsulfide when heated under a CO atmosphere. Bianchini [20] and Jones [21] have demonstrated the metal promoted desulfurization of dibenzothiophene which is a major contaminant of fossil fuels.

3. Summary

The new 1,2-dithiin **2** was obtained as a coproduct with the known thiophene **1** and 1,4-dithiin **3**, from the reaction of acenaphthylene with elemental sulfur. Compound **2** readily loses sulfur to form **1** by simple UV–vis irradiation and by a series of steps involving treatment with $\text{Pt}(\text{COD})_2$, see Scheme 1. In the latter reaction, the complex **4** formed by insertion of a metal into the S–S bond was obtained and structurally characterized.

4. Experimental

4.1. General data

All reactions were performed under a nitrogen atmosphere and in the absence of light. Reagent grade solvents were dried by the standard procedures and were freshly distilled prior to use. ^1H NMR spectra were recorded on a Varian Inova 300 spectrometer operating at 300.08 MHz. Mass spectra were recorded on a VG70SQ mass spectrometer. Elemental analyses were performed by Desert Analytics (Tucson, AZ). TLC was performed in air on Analtech 0.25 mm silica gel 60 ÅF^{254} glass plates. Acenaphthylene (75%) and elemental sulfur were purchased from Aldrich Chemical Company and used without further purification. $\text{Pt}(\text{COD})_2$ was prepared according to the published procedure [22].

4.2. Preparation of $\text{C}_{24}\text{H}_{12}\text{S}$ (**1**) and $\text{C}_{24}\text{H}_{12}\text{S}_2$ (**2**)

The reaction was carried out following previously reported procedures [2]. Acenaphthylene (150 mg, 0.74 mmol) and elemental sulfur (24 mg, 0.75 mmol) were dissolved in 25 mL DMF and placed in an oil bath maintained at 120 °C for 5 h. After cooling the solvent was removed in vacuo, and the products were isolated by column chromatography on silica gel using a hexane/ CH_2Cl_2 (3:1) solvent mixture. The second and third bands were collected to give 30.5 mg of green $\text{C}_{24}\text{H}_{12}\text{S}_2$, **2**, in 23% yield and 24.2 mg of red $\text{C}_{24}\text{H}_{12}\text{S}$, **1**, in 20% yield, respectively. Spectral data for **2**: ^1H NMR (C_6D_6): $\delta = 7.4\text{--}8.1$ (m, 12 H, Ph). MS (DEP) m/z 364 (M^+), 332 ($\text{M}^+ - \text{S}$).

4.3. Preparation of $\text{C}_{24}\text{H}_{14}\text{S}_2$ (**3**)

The reaction was carried out following the previously reported procedure [2]. Acenaphthylene (300 mg, 1.47 mmol) and elemental sulfur (48 mg, 1.50 mmol) were dissolved in 50 mL DMF and placed in an oil bath maintained at 120 °C for 1.5 h. After cooling the solvent was removed in vacuo and the products were isolated by column chromatography on silica gel using a hexane/

Table 3
Selected bond lengths and angles for $\text{Pt}(\text{COD})(\text{C}_{24}\text{H}_{12}\text{S}_2)$ **4**^a

Atoms	Distance (Å)	Atom	Angle (deg)
Pt(1)–S(1)	2.285(4)	S(1)–Pt(1)–S(2)	94.02(13)
Pt(1)–S(2)	2.321(4)	C(1)–S(1)–Pt(1)	117.5(5)
S(1)–C(1)	1.745(14)	C(4)–S(2)–Pt(1)	94.8(4)
S(2)–C(4)	1.764(13)	C(2)–C(1)–S(1)	132.6(11)
C(1)–C(2)	1.359(19)	C(1)–C(2)–C(3)	129.4(12)
C(2)–C(3)	1.448(18)	C(4)–C(3)–C(2)	125.4(12)
C(3)–C(4)	1.390(17)	C(3)–C(4)–S(2)	125.0(10)
S(1)⋯S(2)	3.369		

^a Estimated standard deviation in the least significant figure is given in parentheses.

CH₂Cl₂ (3:1) solvent mixture. The second and third bands were collected to give 26.1 mg of green C₂₄S₁₂S₂, **2**, in 10% yield and 29.7 mg of red C₂₄H₁₄S₂, **3**, in 11% yield, respectively.

4.4. Conversion of **2** to **1**

Compound **2** (43.5 mg, 0.120 mmol) was dissolved in 25 mL benzene and irradiated (medium pressure mercury lamp at 360 W). After 30 min, the color of the reaction mixture changed from green to red. After cooling, the solvent was removed in vacuo, and the product was isolated by column chromatography on silica gel using a hexane/CH₂Cl₂ (3:1) solvent mixture. The red band was collected to give 36.1 mg of C₂₄S₁₂S, **1**, in 91% yield.

4.5. Synthesis of Pt(COD)(C₂₄H₁₂S₂), (**4**)

Pt(COD)₂ (5.0 mg, 0.012 mmol) was added to a solution of **2** (4.5 mg, 0.012 mmol) in 10 mL CH₂Cl₂. After 30 min, the dark brown mixture was filtered through a short column of florisil and the solvent was removed by rotary evaporation. The product was separated by TLC using a 2:1 hexane/CH₂Cl₂ mixture. The brown band was collected to give 1.1 mg of Pt(COD)(C₂₄H₁₂S₂), **4**, in 14% yield. Spectral data for **4**: ¹H NMR (CDCl₃): δ = 7.87 (d, 2H, Ph), 7.83 (d, 2H, Ph), 7.76 (d, 2H, Ph), 7.74 (d, 2H, Ph), 7.62 (t, 2H, Ph), 7.5 (t, 2H, Ph), 5.50–5.55 (m, 4H, CH, COD), 2.46–2.52 (m, 8H, CH₂, COD). Anal. Found (Calc.): C, 56.90 (57.56); H, 3.08 (3.63)%. MS (DEP) *m/z* 668 (M⁺), 332 (M⁺ – Pt(COD)S).

4.6. Conversion of **4** to **1**

Compound **4** (12.2 mg, 0.018 mmol) was dissolved in benzene and heated to reflux. After 3 h, the mixture was filtered through a short column of florisil and the solvent was removed by rotary evaporation. The product was separated by TLC using a 2:1 hexane/CH₂Cl₂ mixture. The red band was collected to give 2.9 mg of **1** in 50% yield.

4.7. Crystallographic analysis

Red crystals of **1**, **2**, and **3** and brown crystals of **4** suitable for diffraction analysis were grown by slow evaporation of solvent from a hexane/methylene chloride solvent mixture at 5 °C. Each data crystal was glued onto the end of a thin glass fiber. X-ray intensity data were measured by using a Bruker SMART APEX CCD-based diffractometer using Mo K α radiation ($\lambda = 0.71073$ Å). The raw data frames were integrated with the SAINT+ program using a narrow-frame integration algorithm [23]. Corrections for the Lorentz and polarization effects were also applied by using the pro-

gram SAINT. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied by using the program SADABS. All structures were solved by a combination of direct methods and difference Fourier syntheses, and refined by full-matrix least squares on F^2 , by using the SHELXTL software package [24]. Crystal data, data collection parameters, and results of the analyses for compounds **1–4** are given in Table 1.

Compounds **1–3** crystallized in the monoclinic crystal system. For compounds **1** and **2**, the space group $P2_1/n$ was identified uniquely on the basis of the systematic absences in the intensity data. Compound **2** contains two symmetry independent molecules in the asymmetric crystal unit. Both molecules are structurally similar. For compound **3** an alternative monoclinic setting $P2_1/c$ of the same space group was used. Compound **4** crystallized in the tetragonal crystal system. The space group $P-42_1c$ was identified uniquely on the basis of the systematic absences in the intensity data. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms in compounds **1**, **3**, and **4** were placed in geometrically idealized positions and included as standard riding atoms. Hydrogen atoms in compound **2** were located and refined with an isotropic displacement parameter.

5. Supplementary material

CIF files for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre CCDC 218990–218993 for compounds for **1–4**, respectively.

Acknowledgements

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