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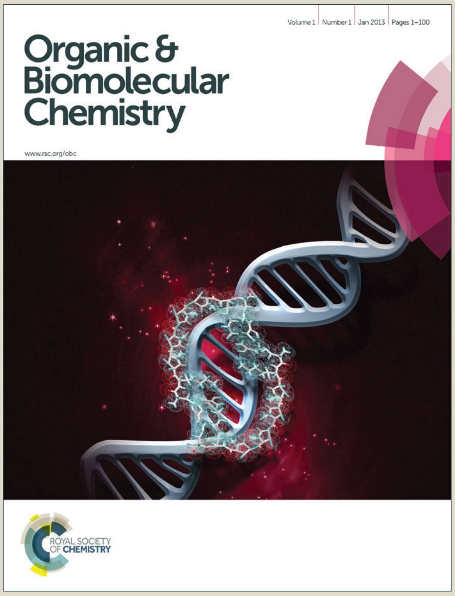

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ARTICLE

Multiple optical properties of naphthoquinone pigment: 2-methyl-3-(hydroxyphenylthio)-1,4-naphthalenedione

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Naphthoquinone pigments 2-methyl-3-(4- or 2-hydroxyphenylthio)-1,4-naphthalenedione show characteristic optical properties in solution and in the solid state. The position of the OH group in the pigment leads to varied optical properties, including a characteristic colour, in the solid state. The pigment with a 2-OH substituent displays solvatochromism in solution, and that with a 4-OH substituent displays optical chirality in the solid state.

Introduction

Organic dyes and pigments are among the most important and useful organic materials for molecular sensors and colorants used throughout the industry. In particular, functional organic dyes and pigments bearing various properties have received considerable attention because of the fundamental research interest in photochemistry and their application as photomaterials. Although numerous organic dyes and pigments have been developed, there are only a few reports of naphthoquinone derivatives utilized as colorant compounds.[1] We have previously focused on naphthoquinone derivatives as novel functional dyes and pigments.[2] Recently, we have reported naphthoquinone pigments containing an arylthio unit, such as 2-methyl-3-chlorophenylthio-1,4-naphthalenedione, which show unique colour properties in the solid state.[3] On the other hand, in solution, these naphthoquinone pigments show similar colour properties but no special characteristics such as solvatochromic property.[4]

Here, we studied alternative naphthoquinone pigments which may show characteristic multiple optical properties in solution and in the solid state. Two naphthoquinone compounds, 2-methyl-3-(4-hydroxyphenylthio)-1,4-naphthalenedione **1** and 2-methyl-3-(2-hydroxyphenylthio)-1,4-naphthalenedione **2**, which differ by the hydroxyl group position on the phenylthio ring, were used as target naphthoquinone pigments (Fig. 1), and their characteristic solution- and solid-state optical properties and molecular structures were investigated. Through this study, it was found that naphthoquinone pigments having a hydroxyphenylthio unit show characteristic multiple optical properties: solvatochromic properties in solution and characteristic colour in the solid state. Notably, chirality was observed in the solid state, although the pigment is achiral.

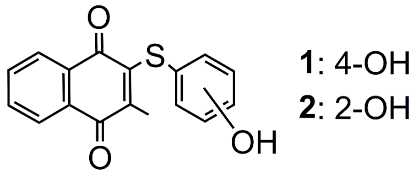
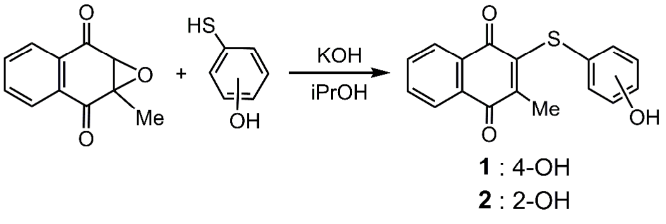


Fig. 1 Naphthoquinone pigments **1** and **2**.

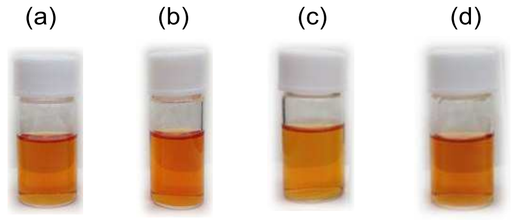
Results and discussion

Pigments **1**[5] and **2** were prepared in the same manner as previously reported for 2-methyl-3-(4-chlorophenylthio)-1,4-naphthalenedione.[3] The reaction of 2,3-epoxy-2-methyl-1,4-naphthoquinone with 4- or 2-mercaptophenol in a potassium hydroxide solution (0.15%) afforded **1** and **2** in 80% and 82% yields, respectively (Scheme 1).

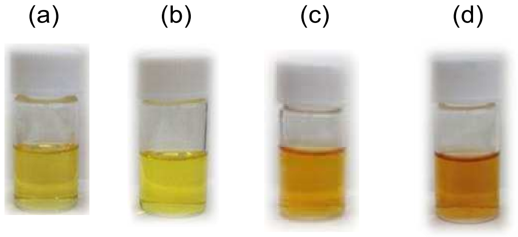


Scheme. 1 Syntheses of pigments **1** and **2**.

First, in order to investigate the colour of these pigments in the solution state, **1** and **2** were dissolved in four solvents of differing polarity: chloroform, dichloromethane, acetone, and methanol (Fig. 2). Interestingly, although pigment **1** showed a deep orange colour in all the solvents, the colour of **2** appeared to change with the solvent type, indicating a solvatochromic effect. When the polar solvents acetone and methanol were used, the colour of **2** in solution was deep orange (Figs. 2c and 2d, respectively), similar to that for **1**. However, when non- or low-polar solvents chloroform and dichloromethane were used, the colour of **2** in solution changed to yellow (Figs. 2a and 2b, respectively).



Pigment 1



Pigment 2

Fig. 2 Photographs of pigments **1** and **2** (1.0×10^{-2} M) in (a) chloroform, (b) dichloromethane, (c) acetone, and (d) methanol.

The UV-Vis absorption spectra of **1** and **2** in the four solvents used were measured (Fig. 3). As expected, the UV-Vis absorption spectra of **1** were similar (Fig. 3a) in all the solvents, but those of **2** were markedly different (Fig. 3b).

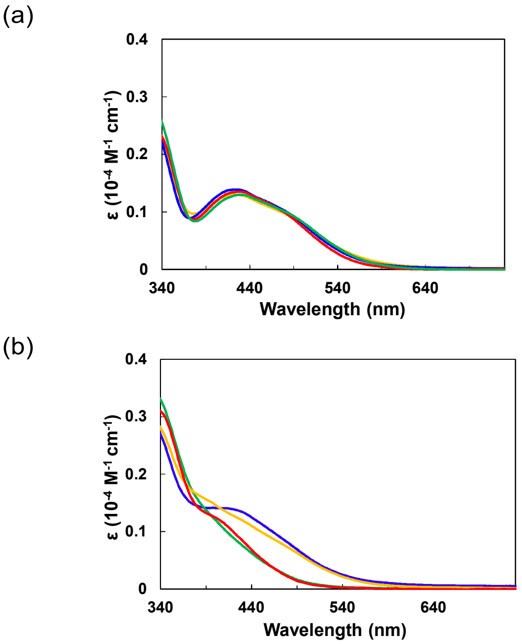


Fig. 3 UV-Vis absorption spectra of (a) **1** and (b) **2** (1.0×10^{-4} M) in chloroform (green), dichloromethane (red), acetone (blue), and methanol (orange).

In order to study the origin of this solvatochromic effect in solution for **2** and not **1**, ^{1}H-NMR analysis of **1** and **2** was performed in the corresponding deuterated solvents: chloroform-*d*, dichloromethane-d_2, acetone-d_6, and methanol-d_4 (Fig. 4).

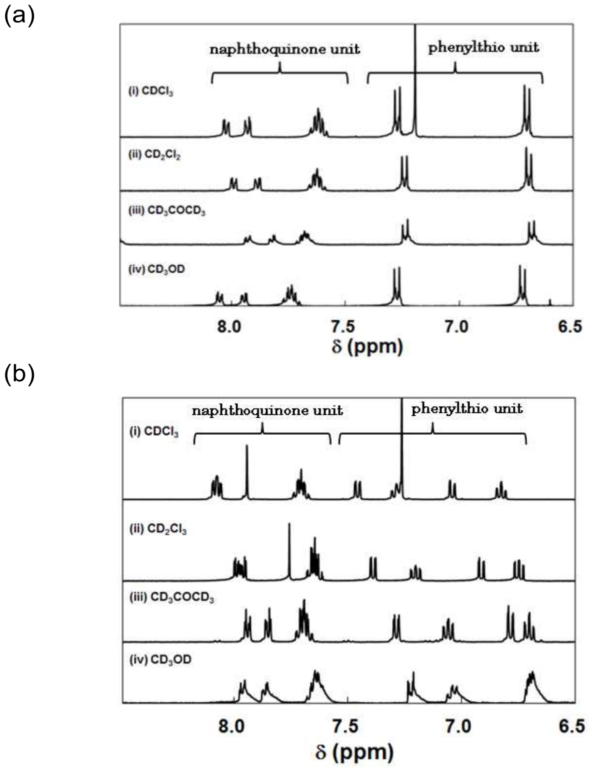


Fig. 4 ^{1}H-NMR spectra of (a) **1** and (b) **2** in (i) chloroform-*d* ($CDCl_3$), (ii) dichloromethane-d_2 (CD_2Cl_2), (iii) acetone-d_6 (CD_3COCD_3), and (iv) methanol-d_4 (CD_3OD).

As shown in Figs. 4a(i)–(iv), the ^{1}H-NMR spectra of **1** were similar in all the solvents. The ^{1}H-NMR spectra of **2** in chloroform-*d* (Fig. 4b(i)) and dichloromethane-d_2 (Fig. 4b(ii)) were also similar. However, the ^{1}H-NMR spectra of **2** in acetone-d_6 (Fig. 4b(iii)) and methanol-d_4 (Fig. 4b(iv)) were clearly different for both the naphthoquinone and phenylthio units.

The NMR data imply that the solvatochromic effect of **2** originates from solvent dependent molecular structure change. Theoretical calculations were carried out to investigate possible molecular structures of **2** (Fig. 5).[6,7]

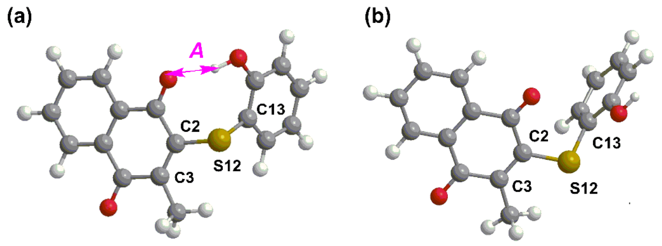


Fig. 5 Theoretical equilibrium structures of pigment **2** (a) with an intramolecular hydrogen bond (b) without it.

It was found that two conformers are possible for **2** in the absence of solvent molecules; one is with an intramolecular hydrogen bond between the OH of the phenylthio ring and a C=O group of the naphthoquinone ring (Fig.5a) and the other is without it (Fig.5b). The former conformer is more stable by 6.5 kcal/mol in the gas phase owing to the intramolecular interaction. Molecule **2** is likely to take hydrogen bonded conformer in non- or low-polar solvent chloroform or dichloromethane. The distance of intramolecular hydrogen bond (indicated by purple *A* arrow in Fig. 5a, O…O) is 2.72 Å (Fig. 5a). On the contrary, the intramolecular hydrogen bond is expected to be hindered by solvent molecules in polar solvent methanol or acetone. Thus, the solvatochromism of **2** is potentially related to the structural changes between these two types of conformers. In other words, the solvatochromism of **2** is potentially related to the formation of this intramolecular hydrogen bond. This supposition is further supported by the fact that **1** cannot form intramolecular hydrogen bonds and is not solvatochromic.

Next, in order to investigate the colour of these pigments in the solid state, **1** and **2** were crystallized from methanol. Methanolic solutions of **1** and **2** were allowed to stand at room temperature. After a few days, large amounts of coloured crystals of **1** and **2** were obtained from the solution. Crystals of both pigments were found to contain no additional molecules such as those of the crystallization solvent. Interestingly, the crystal colour was quite different for each pigment: deep red for **1** and yellow/orange for **2**, as shown in Fig. 6. This was most probably due to the differing position of the OH group on the phenylthio ring, although the colour of the supernatant was deep orange in both cases.

Fig. 6 Images of isolated crystals of pigments **1** and **2**.

Solid-state diffuse reflectance spectra (DRS) of **1** and **2** were measured (Fig. 7). As expected, the solid-state DRS of **1** and **2** were markedly different; the absorption edges were located at *ca*. 600 and 480 nm, respectively.

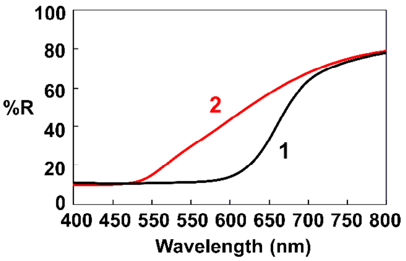


Fig. 7 Diffuse reflectance spectra (DRS) of pigments **1** (black) and **2** (red).

Consequently, to investigate the potential solid-state optical chirality of these achiral pigments, circular dichroism (CD) spectra of the obtained crystals were measured using KBr pellets. Pigment **2** showed no CD signal, while the achiral **1** showed a clear CD signal. The solid-state CD and absorption spectra of **1** are shown in Fig. 8.

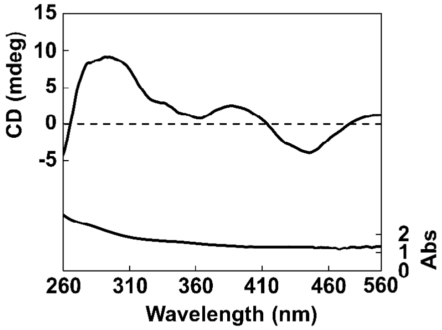


Fig. 8 Solid-state CD and absorption spectra of crystal **1** (KBr pellet).

Peaks originating from the naphthoquinone unit were observed in the CD spectrum, between 360 and 500 nm. The circular anisotropy ($|g_{CD} = \Delta OD/OD|$) factor of the first Cotton band (λ_{CD} = 446 nm) was ~9.1 × 10^{-5}. This result suggested that achiral pigment **1** induces chirality in the solid state.

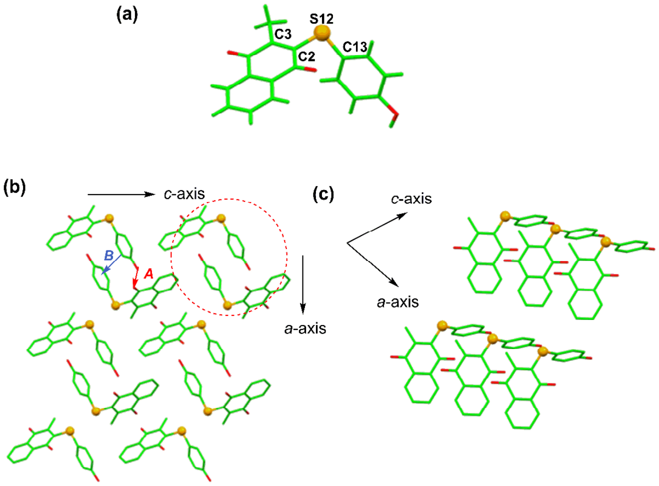


Fig. 9 Crystal structures of **1**. Oxygen and sulfur atoms are shown in red and orange, respectively. (a) Structure of extracted single molecule **1**. (b) Packing structure observed along the *b*-axis. (c) Stacking arrangement between naphthoquinone units. Red *A* and blue *B* arrows indicate hydrogen bond and benzene-benzene edge-to-face interaction, respectively. The red dotted circle shows a columnar unit.

Pigments **1** and **2** exhibit rather different optical properties in the solid state due to the position of the OH group on the phenylthio ring. In order to study the structures of these pigments, X-ray crystallographic analyses were performed. The structures of **1** are shown in Fig. 9. As expected, this crystal belongs to the chiral space group $P2_1$. The torsion angle is -133.0° (C(3)-C(2)-S(12)-C(13)), shifted from the vertical axis (Fig. 9a). In one crystal, all hydroxyphenylthio rings are inclined in the same direction with respect to the naphthalenedione ring. That is, only one handedness of **1** exists in one crystal, resulting in the achiral **1** displaying optical chirality in the solid state. A columnar unit is formed (indicated by the red dotted circle in Fig. 9b) along the *b*-axis through OH-O intermolecular hydrogen bonds between the OH group on the phenylthio ring and a C=O group on the naphthoquinone ring (indicated by the red *A* arrow in Fig. 9b, O…O; 2.76 Å), and benzene-benzene edge-to-face interaction between phenylthio rings (indicated by the blue *B* arrow in Fig. 9b, C…π; 3.63 Å).[8] This crystal is formed by the self-assembly of this columnar unit without major interactions.[8]

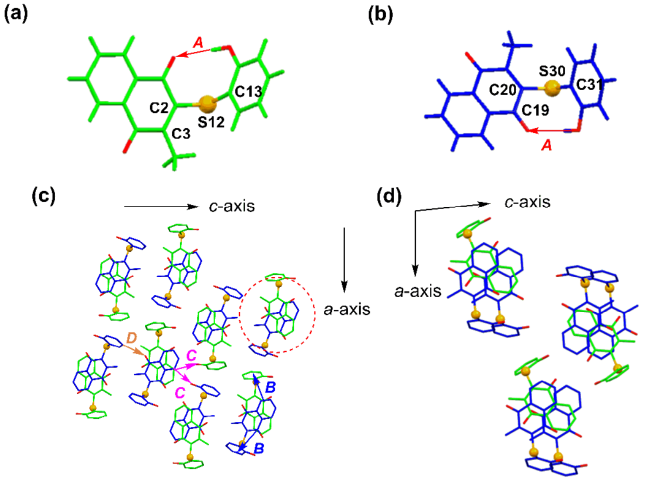


Fig. 10 Crystal structures of **2**. Oxygen and sulfur atoms are shown in red and orange, respectively. (a) Structure of extracted single molecule **2a**. (b) Structure of extracted single molecule **2b**. (c) Packing structure observed along the *b*-axis. Red *A*, purple *C*, and orange *D* arrows indicate hydrogen bonds. Blue *B* arrows indicate naphthoquinone-benzene edge-to-face interaction. (d) Stacking arrangement between naphthoquinone units. The red dotted circle shows a columnar unit.

The crystal structures of **2** are shown in Fig. 10. This crystal belongs to the achiral space group $P2_1/n$. A characteristic feature of the structure is the presence of two independent conformations, **2a** and **2b**, which have different torsion angles around the sulfur atom in an asymmetric unit (Figs. 10a and 10b, indicated in green for **2a** and blue for **2b**). The torsion angles of these molecules are ±110.9° for **2a** (C(3)-C(2)-S(12)-C(13)) and ±111.9° for **2b** (C(19)-C(20)-S(30)-C(31)). Both **2a** and **2b** have intramolecular hydrogen bonds (indicated by red *A* arrows in Figs. 10a and 10b, O…O; 2.77 and 2.82 Å, respectively,). A columnar unit is formed by **2a** and **2b** (indicated by the red dotted circle in Fig. 10c) along the *b*-axis through π-π interactions between naphthoquinone rings (3.47 Å, in Fig. 10c)[9] and naphthoquinone-benzene edge-to-face interactions between the hydrogen atom in the naphthoquinone ring and the benzene ring (C…π; 3.68 and 3.72 Å, indicated by blue *B* arrows in Fig. 10c).[8] This achiral crystal is formed by the self-assembly of this columnar unit *via* intercolumnar hydrogen bonds between a H atom on the naphthoquinone ring and the OH group on the phenylthio ring (indicated by purple *C* arrows in Fig. 10c, C…O; 3.35 and 3.38 Å) and between a H atom on the phenylthio ring and the C=O unit on the naphthoquinone ring (indicated by orange *D* arrows in Fig. 10c, C…O; 3.34 Å).[8]

Comparing the crystallographic analysis to the DRS, crystal **2** with a larger stacking area between the benzene and benzoquinone motifs in the naphthoquinone units was found to have shorter wavelength absorption edges (**2** (480 nm) < **1** (600 nm)) (Figs. 9c and 10d). The major difference in the crystal structures of **1** and **2** is the formation of the intramolecular hydrogen bond in the latter **2**, and this gives rise to the differing colour and solvatochromic effect.

Conclusions

Two distinct naphthoquinone pigments, 2-methyl-3-(4- or 2-hydroxyphenylthio)-1,4-naphthalenedione, were successfully prepared. The variation in the position of the OH group on the phenylthio ring gave rise to alternate optical properties, particularly due to different hydrogen bonding. The pigment possessing a 4-OH showed solvatochromism in solution, and that possessing a 2-OH showed optical chirality in the solid state. Notably, chirality was successfully detected in the solid state even though the pigment is achiral. The crystals of the 4-OH pigment were deep red in colour, and those of the 2-OH pigment were yellow/orange. We believe that the results of this study will be useful for the exploration and design of additional novel functional organic pigments that exhibit multiple optical properties.

Experimental section

General methods

The solvent used for measurement of optical properties was purchased from Wako Pure Chemical (Osaka, Japan). ^{1}H-NMR spectra were recorded with a *JEOL JNM-ECP700* spectrometer using tetramethylsilane as an internal standard (400 MHz). High resolution mass spectrum (HRMS) was measured by AXIMA Confidence (Shimadzu. Co).

Syntheses of 2-methyl-3-(4-hydroxyphenylthio)-1,4-naphthalenedione (1) and 2-methyl-3-(2-hydroxyphenylthio)-1,4-naphthalenedione 2

Pigments **1**[5] and **2** were prepared in the same manner as previously reported for 2-methyl-3-(4-chlorophenylthio)-1,4-naphthalenedione.[3] 2,3-Epoxy-2-methyl-1,4-naphthoquinone (103 mg, 0.55 mmol) and 4- or 2-mercaptophenol (69 mg, 0.55 mmol) were dissolved in isopropanol (40 mL). Then, potassium hydroxide (0.15%; 0.025 mL) solution was added to the isopropanol solution, and the reaction mixture was stirred at room temperature for 3 h. The solvent in the reaction mixture was evaporated under vacuum, and the residue was dissolved in diethyl ether (100 mL). The resultant solution was washed with brine, dried over $MgSO_4$, and evaporated under vacuum to give the crude naphthoquinone compound. Pigments **1** and **2** were purified by column chromatography (SiO_2, acetone/hexane, 1:3) in 80% and 82 % yields, respectively. ^{1}H-NMR data of **2**: δ_H (400 MHz, $CDCl_3$) 8.08 (m, 2H), 7.70 (m, 2H), 7.46 (dd, J = 1.4 Hz, 7.8 Hz, 1H), 7.29 (m, 1H), 7.04 (dd, J = 1.2, 8.3 Hz, 1H), 6.82 (m, 1H), 2.64 (s, 3H). ^{13}C-NMR data of **2**: δ_C (100 MHz, $CDCl_3$) 183.3, 181.8, 158.2, 151.7, 145.1, 136.9, 134.1, 133.9, 132.1, 132.0, 131.9, 127.4, 126.8, 120.9, 117.1, 117.0, 16.3. mp of **2** = 159.1–161.0 ºC (from MeOH). HRMS(MALDI-TOF) of **2**: calcd for $[M-H]^-$ 295.0429; found 295.0433.

Measurement of diffuse reflectance spectra (DRS) and UV-Vis absorption spectra

Diffuse reflectance spectra (DRS) and UV-Vis absorption spectra were measured with a *Jasco V-670 Spectrometer*.

X-ray crystallographic study of 1 and 2

X-ray diffraction data for a single crystal of **1** and **2** were collected using *RIGAKU SATURN 70R* and *BRUKER APEX* instruments, respectively. The crystal structures were solved by direct methods[10] and refined by full-matrix least-squares using *SHELXL97*.[10] The diagrams were prepared using *PLATON*.[11] Absorption corrections for **1** and **2** were performed using *multi-scan* and *SADABS*[12], respectively. Nonhydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were included in the models in their calculated positions in the riding model approximation. Crystallographic data for **1**: $C_{17}H_{12}O_3S$, M = 296.33, triclinic, space group $P2_1$, a = 10.900(3) Å, b = 5.5397(12) Å, c = 11.358(3) Å, β = 100.557(4) º, V = 674.2(3) Å^3, Z = 2, Dc = 1.460 g/cm^3, μ (Mo Kα) = 0.247 mm^{-1}, 5013 reflections measured, 2773 unique, final $R(F^2)$ = 0.0392, using 2672 reflections with $I > 2.0\ \sigma(I)$, R(all date) = 0.0406, T = 100(2) K, CCDC 1000472. Crystallographic data for **2**: $C_{17}H_{12}O_3S$, M = 296.33, Monoclinic, space group $P2_1/n$, a = 13.1132(16) Å, b = 7.6905(9) Å, c = 28.214(4) Å, β = 103.057(2) º, V = 2771.7(6) Å^3, Z = 8, Dc = 1.420 g/cm^3, μ (Mo Kα) = 0.240 mm^{-1}, 15993 reflections measured, 6023 unique, final $R(F^2)$ = 0.0624, using 5138 reflections with $I > 2.0\ \sigma(I)$, R(all date) = 0.0706, T = 93(2) K, CCDC 1000471. Crystallographic data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: +44 1223 336 033; deposit@ccdc.cam.ac.uk).

Theoretical calculations

The theoretical calculations were carried out with the GAUSSIAN 03 program.[6] The geometries of molecule **2** were optimized by hybrid density functional theory (B3LYP functional)[7] with the cc-pVDZ basis set[13].

Acknowledgements

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† Electronic Supplementary Information (ESI) available: CIF file of X-ray crystallographic analyses and ^{1}H- and ^{13}C-NMR spectra. See DOI: 10.1039/b000000x/

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