# 63. Conformation Analysis of the 8-Membered Ring of 12*H*-Dibenzo[*d,g*][1,3,2]dioxathiocines: Symmetric and Asymmetric Conformations

by **P. Hug, Sandra Kolly, Hansrudolf Meier*, Rita Pitteloud, Dieter Poppinger, Grety Rihs,** and **Günther Rist**
*Ciba-Geigy AG*, CH-1700 Fribourg

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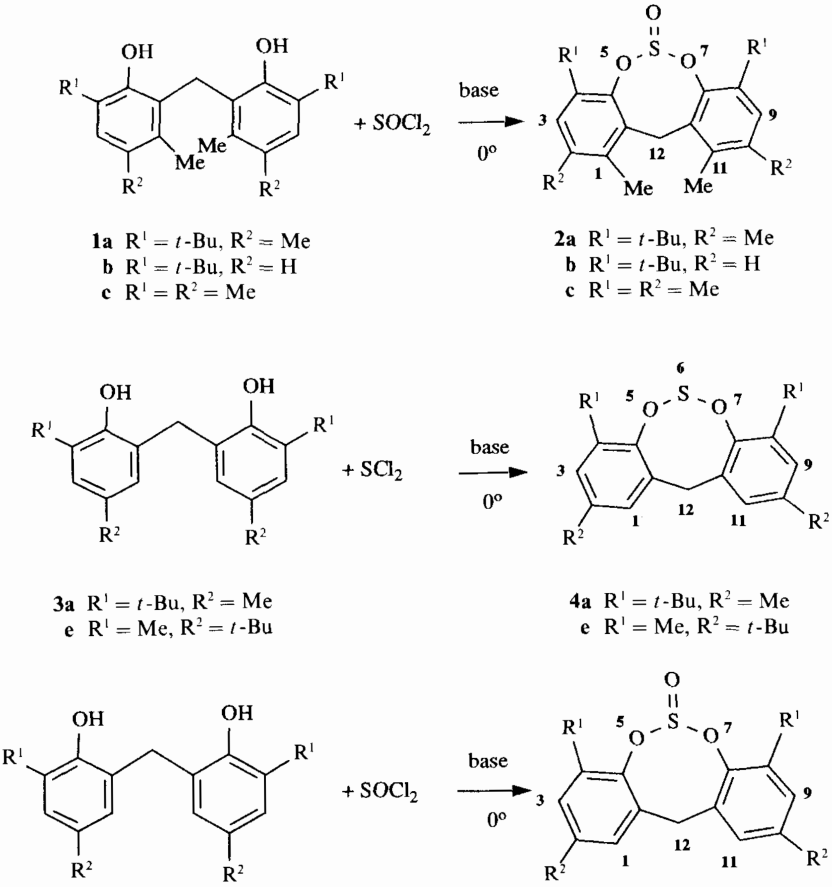
The 12*H*-dibenzo[*d,g*]dioxathiocines **2** and **4** are prepared by condensation of the corresponding bis[phenols] **1** and **3** with $SOCl_2$ and $SCl_2$, respectively. X-Ray analysis reveals the presence of the boat-chair (*BC*) form as the only conformer in the solid state of the cyclic thiodioxy derivative **4a**, whereas the sulfinyldioxy compound **2a** exists in the asymmetric axial boat (*B*) form, *i.e.* with *endo* (axial) orientation of the exocyclic O-atom. Conformational analysis using $^1$H-NMR spectroscopy indicates the presence of a boat form for compounds **2**, whereas compounds **4** again exist in the boat chair form. A comparison of $^1$H-NMR and thermodynamic parameters with those of the cyclic sulfinyldioxy compound **5** with an equilibrium between e-*BC* and a-*BC* form (*i.e. BC* form with equatorial and axial orientation of the exocyclic O-atom) is made.

**Introduction.** – In a search for novel antioxidants, a series of medium-ring heterocycles derived from sterically hindered phenols has been prepared and investigated [1]. In the course of this work, we prepared compounds **2** and **4** by condensation of the corresponding bis[phenols] **1** and **3** with $SOCl_2$ and $SCl_2$, respectively (*Scheme*, *cf.* [1g]). Recently, we also reported the unusual reaction of bis[phenol] **3b** with $S_2Cl_2$ leading to a tetracyclic ring system [2]. This report deals with the major conformations present in the 8-membered ring of compounds **2** and **4** in comparison with compounds **5**.

**Conformations in Solution.** – The conformational analysis of 8-membered heterocycles with two planar fragments has been subject of a large number of investigations. A detailed discussion of the conformations of 1,3,2-dioxaphosphocines which are closely related to the dioxathiocines described in this paper is given in [3]. A review of conformations of heterocyclic rings is given in [4a] and a discussion of 8-membered rings with planar fragments in [4b]. The presence of the two aromatic moieties annelated to the 8-membered ring reduces the number of possible conformers compared with saturated systems. According to [3] [4], molecular models, and our own force-field calculations [5], four different ring conformations have to be considered for the compounds discussed in this paper (*Fig. 1*). We adopt the nomenclature used by *Arshinova et al.* [3a]. There are two conformations with a vertical mirror plane (point group $C_s$), (*a*) the boat-chair conformation *BC* and (*b*) the boat-boat conformation *BB*.

Without this symmetry element, an infinite number of conformations is possible. The best way of characterising them is by the two C–O–S–O dihedral angles ($\vartheta_1$, $\vartheta_2$). The two extreme conformations are characterized by the following dihedral angles: (*c*) boat conformation *B* with $\vartheta_1 \approx 0°$ and $\vartheta_2 \approx 100°$ (no symmetry element) and (*d*) twist-boat conformation *TB* with $\vartheta_1 = \vartheta_2 = 60°$ (twofold axis).

*Scheme*



**1a** $R^1 = t\text{-Bu}, R^2 = Me$
**b** $R^1 = t\text{-Bu}, R^2 = H$
**c** $R^1 = R^2 = Me$

**2a** $R^1 = t\text{-Bu}, R^2 = Me$
**b** $R^1 = t\text{-Bu}, R^2 = H$
**c** $R^1 = R^2 = Me$

**3a** $R^1 = t\text{-Bu}, R^2 = Me$
**e** $R^1 = Me, R^2 = t\text{-Bu}$

**4a** $R^1 = t\text{-Bu}, R^2 = Me$
**e** $R^1 = Me, R^2 = t\text{-Bu}$

**3a** $R^1 = t\text{-Bu}, R^2 = Me$
**b** $R^1 = R^2 = t\text{-Bu}$
**c** $R^1 = t\text{-Bu}, R^2 = H$
**d** $R^1 = R^2 = Me$
**e** $R^1 = Me, R^2 = t\text{-Bu}$
**f** $R^1 = Me, R^2 = H$

**5a** $R^1 = t\text{-Bu}, R^2 = Me$
**b** $R^1 = R^2 = t\text{-Bu}$
**c** $R^1 = t\text{-Bu}, R^2 = H$
**d** $R^1 = R^2 = Me$
**e** $R^1 = Me, R^2 = t\text{-Bu}$
**f** $R^1 = Me, R^2 = H$

It is instructive to compare the conformations of compounds **2** and **4** with those of **5**, which has no Me substituents at C(1) and C(11).

The conformation of compound **5a** [1g] has been determined by X-ray analysis [6a] to be a *BC* spatial arrangement with equatorial orientation of the exocyclic O-atom (e-*BC*). The $^1$H-NMR spectra of all compounds **5** exhibit a main and a minor set of NMR transitions. In the time scale of the NMR experiment down to −90°, the two aromatic rings are equivalent, indicating either symmetric conformations or fast exchange between asymmetric ones. For compound **5a**, *Arbuzov et al.* [6b] have shown that there exists an equilibrium e-*BC* ⇄ a-*BC*, with e-*BC* being the main conformation. Some $^1$H-NMR

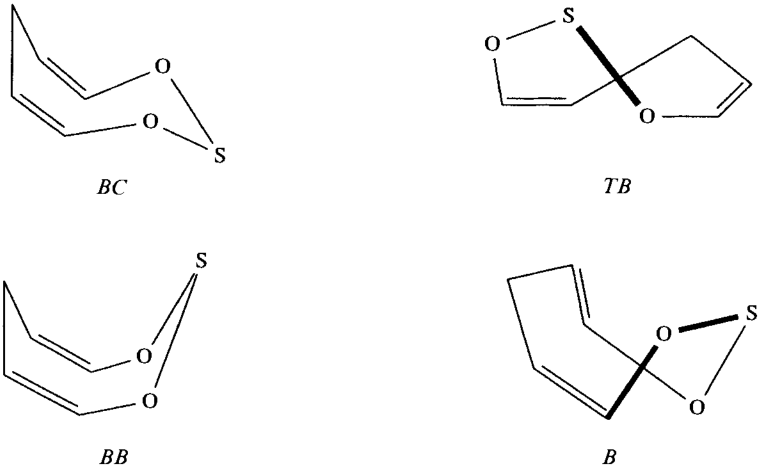


Fig. 1. *Conformations of the 8-membered ring. BC* = boat-chair, *BB* = boat-boat, *TB* = twist-boat, and *B* = boat conformation.

parameters for these compound are collected in *Table 1*. They are in good agreement with the exchange process corresponding to a complete ring inversion. The chemical-shift parameters of the two $CH_2$ protons almost exchange their values between major and minor conformation. *Table 2* lists some relevant thermodynamic parameters. They lead to the speculation that the bulkiness of substituent $R^1$ increases the energy barrier of the ring inversion.

Table 1. *$^1$H-NMR Parameters of the $CH_2$ Group in Compounds* **4** *and* **5**

| Compound | Conformation[a]) | Geminal coupling constant [Hz] | Chemical-shift value of $H^1$[b]) | Chemical-shift value of $H^2$[b]) | $\delta(H^1)$–$\delta(H^2)$ |
|---|---|---|---|---|---|
| **5a** | MA | 12.5 | 4.42 | 3.02 | 1.39 |
| | MI | 12.5 | 3.10 | 4.24 | −1.14 |
| **b** | MA | 12.6 | 4.53 | 3.09 | 1.44 |
| | MI | 12.5 | 3.20 | 4.33 | −1.33 |
| **c** | MA | 12.5 | 4.38 | 2.97 | 1.41 |
| | MI | 12.5 | 3.05 | 4.19 | −1.14 |
| **d** | MA | 12.3 | 4.38 | 3.04 | 1.34 |
| | MI | 12.3 | 2.91 | 4.42 | −1.51 |
| **e** | MA | 12.3 | 4.42 | 3.12 | 1.30 |
| | MI | 12.3 | 2.98 | 4.50 | −1.52 |
| **f** | MA | 12.5 | 4.27 | 2.98 | 1.29 |
| | MI | 12.7 | 2.89 | 4.34 | −1.45 |
| **4a** | | 12.6 | 4.49 | 3.19 | 1.30 |
| **e** | | 12.6 | 4.60 | 3.24 | 1.36 |

[a]) MA = major conformation, MI = minor conformation.

[b]) In ($D_8$)toluene; δ in ppm *vs.* TMS; slow-exchange limit; assignment of exchanging protons by comparing chemical-shift values of fast and slow-exchange limits.

Table 2. *Thermodynamic Parameters of Compounds* **5a–f**[a])

| Compound | Statistical weights of major and minor conformation | Free-energy difference between conformations | | Approximate temp. of coalescence of $CH_2$ *d*'s | $\Delta G^{\neq}$, estimated [kcal/mol] |
|---|---|---|---|---|---|
| | | [kcal/mol] | kJ/mol | [°] | |
| **5a** | 3:1 | 0.7 | 2.7 | *ca.* 20° | 13 |
| **b** | 7:1 | 1.2 | 4.8 | *ca.* 10° | |
| **c** | 2:1 | 0.4 | 1.7 | *ca.* 20° | |
| **d** | 10:1 | 1.4 | 5.7 | −15° | 12 |
| **e** | 8:1 | 1.3 | 5.2 | −20° | |
| **f** | 10:1 | 1.4 | 5.7 | −15° | |

[a]) Solvent: ($D_8$)toluene.

*Compounds* **2a–c.** As compared to **5**, the situation is altered significantly for compounds **2a–c** with Me groups at C(1) and C(11) which give rise to strong steric interaction. The $^1$H-NMR spectra of **2a–c** show only one set of $^1$H-NMR resonances. At room temperature, the $^1$H-NMR spectra are characteristic for a symmetric system. When the temperature is lowered, however, the two aromatic substituents lose their equivalence. This proves that due to the additional Me substituents, symmetric conformations *BC* or *BB* do not correspond any longer to the lowest energy, and so we have to distinguish between *TB* and *B* as spatial arrangements. As pointed out in [3], the geminal coupling constant $^2J(H^1,H^2)$ of the ring $CH_2$ group depends strongly on the orientation of the C–H bond relative to the $\pi$-orbitals of the two aromatic rings. This hyperconjugative $\alpha$-substitution effect is discussed in detail in [7]. The geminal coupling constant is negative. When the H–H axis of the $CH_2$ group is oriented perpendicular to the $\pi$-orbitals of the aromatic rings as in the *BC* and *BB* conformations, the contribution of the hyperconjugation to $^2J$ is slightly positive but extremely small, and $^2J$ reaches its minimal absolute value of *ca.* 12.5 Hz. This is approximately the same value as found for the coupling constant of methane. Larger absolute values are expected and measured for the conformations *B* ($^2J(H,H) \approx 15.5$ Hz) and *TB* ($^2J(H,H) \approx 19.0$ Hz) [3b]. The experimental geminal-coupling constants for **2a–c** is *ca.* 15.5 Hz, pointing to a boat conformation (*B*). The NMR experiments did not allow to determine the orientation of the exocyclic O-atom. The dynamic process is an exchange between the two inequivalent aromatic substituents. The coalescence temperature for this exchange process is *ca.* −40 to −30°, corresponding to a $\Delta G^{\neq}$ value of *ca.* 12 kcal/mol and nearly the same for all three compounds **2**. In contrast to the total ring inversion in the series of compounds **5**, the substituent $R^1$ does not influence the barrier of this exchange process.

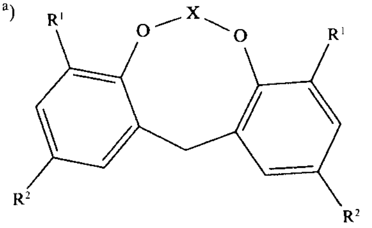
*Compounds* **4a** *and* **4e.** The $^1$H-NMR spectra of these two compounds show only one set of NMR resonances. In the time scale of the $^1$H-NMR experiment down to −90°, the two aromatic rings are again equivalent. *Table 1* shows a comparison of $^1$H-NMR parameters of **4a** and **4e** with those of **5a–f.** The $^1$H-NMR parameters for **4a** and **4e** are almost the same as those for **5a–f** and thus again compatible with a *BC* conformation. Force-field calculations [8] [9] again favour *BC* over *BB* with a gap of several kcal/mol [5]. Lowering the temperature of solutions of **4a** or **4e** does not lead to the detection of a second (*e.g.* *BB*) conformation. Increase of the temperature above 120–140° (*cf.* *Table 3*) produces a fast exchange of the protons of the $CH_2$ group. This ring inversion is not hindered by a *t*-Bu group at C(4) and C(8) as in compounds **5**, presumably since **4a** and **4e** lack the exocyclic O-atom.

In *Table 3*, coalescence temperatures and estimated activation energies are listed for the related structures **A** with different bridging moieties X. We tentatively correlate the high activation energies for compounds **4a** and **4e** with the unusual large O—S—O angle of 104°.

Table 3. *Estimated Free Energy of Activation for the Exchange Process e*-BC ⇄ *a*-BC *and* BC ⇄ BC *different for the Eight-Membered-Ring Heterocycles* A[a])

| X | $R^1$ | $R^2$ | $\Delta G^{\neq}$ [kcal/mol] | $T_{coalesc.}$ [°C] | Solvent | Ref. |
|---|---|---|---|---|---|---|
| P—Cl | *t*-Bu | Me | 11 | −30 | $CDCl_3/CS_2$ | [3b] |
| P—F | *t*-Bu | *t*-Bu | 11 | −40 | $(D_8)$toluene | [10] |
| S=O | *t*-Bu | *t*-Bu | 13 | +10 | $(D_8)$toluene | **5b** |
| S=O | Me | Me | 12 | −15 | $(D_8)$toluene | **5d** |
| S | *t*-Bu | Me | 18 | +120 | $(D_6)$DMSO | **4a** |
| S | Me | *t*-Bu | 19 | +140 | $(D_6)$DMSO | **4e** |
| $SiMe_2$ | *t*-Bu | *t*-Bu | 14 | +20 | $(D_8)$toluene | [1b] |
| B—Ph | *t*-Bu | *t*-Bu | > 14 | [b]) | $CDCl_3$ | [11] |

[a])



**A**

[b]) No equilibration experiment.

**Conformations of Compounds 2a and 4a in the Solid State.** – Perspective views of the molecular structures showing the conformations and the numbering scheme are presented in *Figs. 2* and *3* [12]. The bond lengths and angles are as expected within the limits of error. The only notable difference concerns the O—S—O angle in **4a** of 104.8(1). In 2,2′-(sulfinyldioxy)benzophenone, this angle amounts to 96.6° [13] and in 2,2′-(sulfonyldioxy) to 99.6° [14]. As to our knowledge, the crystal-structure analysis of **4a** is the first one of a thiodioxy derivative, no further comparison could be made.

In **4a**, the eight-membered rings adopt *BC* conformations. The molecule has a non-crystallographic plane of symmetry passing through the S-atom and the $CH_2$ group. The same type of conformations was found in a dibenzo[*d*,*g*][1,3,2]dioxaphosphocine and in a dibenz[*c*,*f*]azocine derivative [15] [16]. The dihedral angle of the planes of the two benzene rings is 120°.

In **2a**, steric interaction between the two Me groups C(23) and C(24) forces the 8-membered ring into an asymmetric form. An important feature of its conformation is that the three torsion angles O(3)—C(17)—C(12)—C(11), O(4)—C(5)—C(10)—C(11), and O(3)—S(1)—O(4)—C(5) are nearly zero. Similar forms of eight-membered rings were found in a diazaphosphorine [16], in a diazaphospholine [17], and in a dioxaphosphocine compound [18]. In the classification by *Arshinova et al.* [19], this conformation is named the *B* form. The configuration of the S-atom in the cyclic sulfides represents a slightly distorted pyramid: the deviation of the S-atom from the O(2)—O(3)—O(4) plane is 0.55 Å.

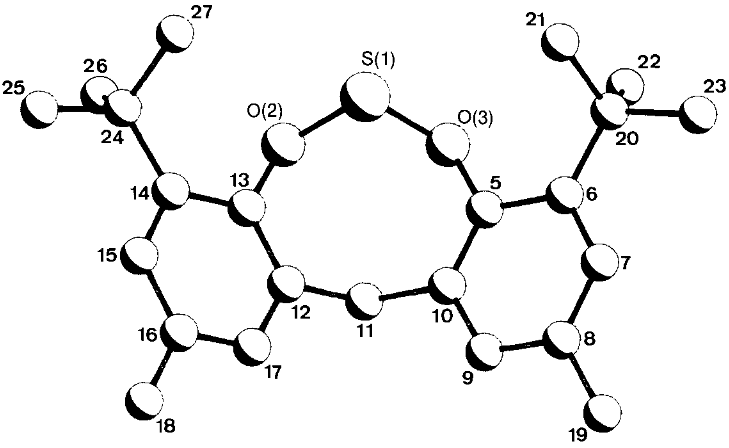


Fig. 2. *PLUTO-plot of* **2a**

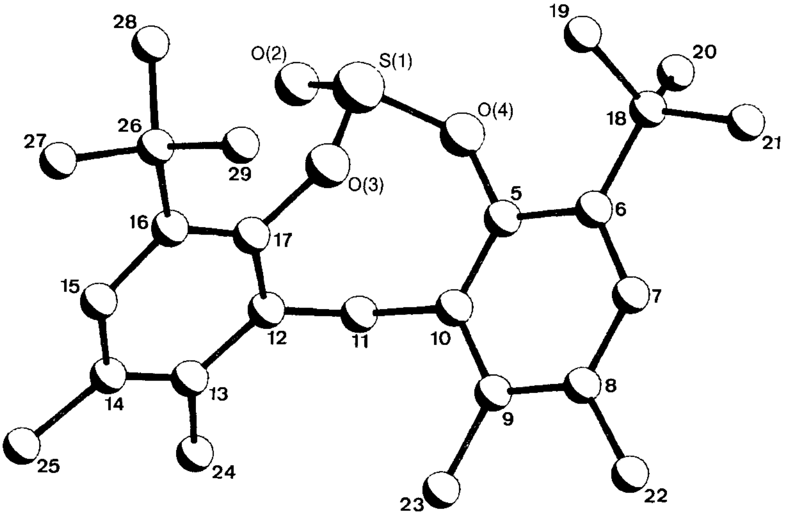


Fig. 3. *PLUTO-plot of* **4a**

The exocyclic O-atom occupies the pseudoaxial position. The distance O(4)–C(11) is 3.28 Å and S(1)–C(11) 3.20 Å which agrees well with the distances postulated by *Arshinova et al.* [3a] for *B* conformations.

## Experimental Part

1. *General.* Flash chromatography (FC) [20]: silica gel (*Merck 60*; 230–400 mesh). TLC: silica gel; $R_f$ values for hexane/AcOEt 49:1 (*A*), hexane/AcOEt 19:1 (*B*), hexane/AcOEt 9:1 (*C*). M.p.: *Tottoli* (*Büchi*); uncorrected. $^1$H-NMR spectra: *Bruker-AM200*, *-AM300*, and *-AM360* and *Varian VXR400S* spectrometers. MS: *cf.* [21].

2. *Starting Materials.* The majority of the starting materials is commercially available or can be synthesised as described in [2]. Bis[phenol] **1b** was prepared as described by *Casiraghi et al.* [22]. Bis[phenols] **1a** and **1c** were prepared by hydrogenation of the bis-*Mannich* bases derived from 1 equiv. of **1b** and 4,4′,6,6′-tetramethyl-2,2′-methylene bis[phenol], resp., 2 equiv. of formaldehyde and 2 equiv. of $Me_2NH$ [23].

3. *12*H-*Dibenzo[*d,g*][1,3,2]dioxathiocine 6-Oxides* **2a–c**. They were prepared as described in or in analogy to [1g].

**2a**: Yield 53.4%. M.p. 186–187° (2-propanol). $R_f$ 0.33 (*A*). MS: 414 ($M^{+\cdot}$), 366 ($[M-SO]^{+\cdot}$), 351, 350 ($[M-SO_2]^{+\cdot}$), 335, 310. Anal. calc. for $C_{25}H_{34}O_3S$ (414.61): C 72.42, H 8.27, S 7.73; found: C 72.42, H 8.28, S 7.83.

**2b**: MS 386 ($M^{+\cdot}$), 338 ($[M-SO]^{+\cdot}$), 323, 322 ($[M-SO_2]^{+\cdot}$), 307, 282.

**2c**: Yield 70%. M.p. 148–150° (2-propanol). $R_f$ 0.42 (*C*). MS: 330 ($M^{+\cdot}$), 282 ($[M-SO]^{+\cdot}$), 267, 266 ($[M-SO_2]^{+\cdot}$), 251 . Anal. calc. for $C_{19}H_{22}O_2S$ (330.54): C 69.06, H 6.71, S 9.70; found: C 69.15, H 6.75, S 9.92.

4. *12*H-*Dibenzo[*d,g*][1,3,2]dioxathiocines* **4a** *and* **4e** *and the 12*H-*Dibenzo[*d,g*][1,3,2]dioxathiocine 6-Oxides* **5a–f**. They were synthesised as described in [1g].

**4a**: MS: 370 ($M^{+\cdot}$), 355, 342 ($[M-CO]^{+\cdot}$), 327, 321.

**4e**: Yield 49.7%. M.p. 163° (heptane). $R_f$ 0.68 (*A*). MS: 370 ($M^{+\cdot}$), 355, 342 ($[M-CO]^{+\cdot}$), 327, 321 . Anal. calc. for $C_{23}H_{30}O_2S$ (370.56): C 74.55, H 8.16, S 8.65; found: C 74.45, H 8.22, S 8.68.

**5a**: MS: 386 ($M^{+\cdot}$), 338 ($[M-SO]^{+\cdot}$), 322 ($[M-SO_2]^{+\cdot}$), 307.

**5b**: Yield 88%. M.p. 186–187°. $R_f$ 0.61 (*B*). MS: 470 ($M^{+\cdot}$), 422 ($[M-SO]^{+\cdot}$), 406 ($[M-SO_2]^{+\cdot}$), 391. Anal. calc. for $C_{29}H_{42}O_3S$ (470.71): C 74.00, H 8.99, S 6.81; found: C 73.97, H 8.89, S 7.05.

**5c**: MS: 358 ($M^{+\cdot}$), 310 ($[M-SO_2]^{+\cdot}$), 279.

**5d**: Yield 18.1%. M.p. 202° (2-propanol). $R_f$ 0.47 (*B*). MS: 302 ($M^{+\cdot}$), 254 ($[M-SO]^{+\cdot}$), 238 ($[M-SO_2]^{+\cdot}$), 223. Anal. calc. for $C_{17}H_{18}O_3S$ (302.38): C 67.52, H 6.00, S 10.60; found: C 67.40, H 6.03, S 10.77.

**5e**: Yield 64.3%. M.p. 158–159° (2-propanol). $R_f$ 0.31 (*A*). MS: 386 ($M^{+\cdot}$), 338 ($[M-SO]^{+\cdot}$), 322 ($[M-SO_2]^{+\cdot}$), 307. Anal. calc. for $C_{23}H_{30}O_3S$ (386.55): C 71.47, H 7.82, S 8.29; found: C 71.41, H 7.88, S 8.45.

**5f**: Yield 80.8%. M.p. 128–129° (2-propanol). $R_f$ 0.25 (*A*). MS: 274 ($M^{+\cdot}$), 226 ($[M-SO]^{+\cdot}$), 210 ($[M-SO_2]^{+\cdot}$), 195. Anal. calc. for $C_{15}H_{14}O_3S$ (274.33): C 65.67, H 5.14, S 11.69; found: C 65.68, H 5.05, S 11.63 [1g].

5. *X-Ray Analyses of* **2a** *and* **4a**. Crystal data are given in *Table 4*. Intensities were collected on an automatic four-circle diffractometer *(Enraf-Nonius CAD4)* with graphite monochromated Cu*Kα* radiation and $\Theta/2\Theta$ procedure. The measured intensities were corrected for *Lorenz* and polarisation effects but not for absorption. The structures were solved by direct methods (SDP MULTAN 82) [24]. All H-atoms were found from difference *Fourier* maps. Least-squares refinements were carried out with anisotropic thermal parameters for non-H-atoms and isotropic ones for H-atoms.

Table 4. *Crystal Data of Compounds* **2a** *and* **4a**

| | **2a** | **4a** | | **2a** | **4a** |
|---|---|---|---|---|---|
| Formula | $C_{25}H_{34}O_3S$ | $C_{23}H_{30}O_2S$ | Calc. density [g/cm$^3$] | 1.195 | 1.151 |
| Crystal system | monoclinic | monoclinic | No. of reflections | 3751 | 3493 |
| Space Group | $P2_1/c$ | $C2/c$ | No. of non-zero reflections ($I > 2\sigma(I)$) | 2545 | 2717 |
| $a$ [Å] | 9.658(3) | 27.987(2) | No. of parameters | 398 | 355 |
| $b$ [Å] | 9.284(1) | 9.554(1) | Final $R$ factor | 0.089 | 0.049 |
| $c$ [Å] | 25.700(5) | 22.486(2) | Max. residual electron density [e/Å$^3$] | 0.206 | 0.194 |
| $\beta$ [°] | 90.89(1) | 134.67(2) | | | |
| $V$ [Å$^3$] | 2304 | 4276 | | | |
| $Z$ | 4 | 8 | | | |

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