*Organosulfur Compounds in Fuels*

# Terpenoid-Derived Sulfides as Ultimate Organic Sulfur Compounds in Extensively Desulfurized Fuels**

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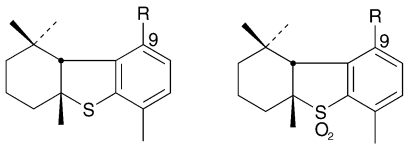
The desulfurization of fuels (for example, diesel oil) is a major concern of the petroleum industry worldwide because of the consequences for human health and the environment of high levels of sulfur dioxide emissions. In this context, a major problem encountered in refineries is the elimination of organosulfur components resistant to hydrodesulfurization processes. Although it has been shown that a substantial fraction of the organic sulfur compounds remaining after hydrodesulfurization is composed of mono- and polyalkylated dibenzothiophenes (mainly 4,6-dialkyldibenzothiophenes),[1] the lack of knowledge concerning the structures of residual highly resistant organic sulfur compounds still appears to be the greatest handicap in progressing towards higher degrees of hydrodesulfurization. We report here the identification of a series of novel, terpenoid-derived, non-dibenzothiophenic polycyclic sulfides from highly desulfurized diesel oils. These 1,1,4a,6-tetramethyl-9-alkyl-1,2,3,4,4a,9b-hexahydrodibenzothiophenes **1** (9-alkyl HDBT) were isolated from the aromatic fraction after oxidation to the corresponding sulfones **2** (9-alkyl-HDBTO$_2$).[2–4] The 9-ethyl homologue was unambiguously identified by mass spectrometry and NMR studies.




9-alkyl-HDBT **1** 9-alkyl-HDBTO$_2$ **2**

**2a** R = $C_2H_5$
**2b** R = $CH_3$
**2c** R = H

Organic sulfur compounds were studied in diesel oils from various origins and desulfurized on a mini-pilot scale to

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different levels of residual sulfur, which ranged from 400 to less than 10 ppm. They exclusively occur in the aromatic fractions of the oils (generally in the 10–30% range), which were separated by silica gel column chromatography. The difficulty of the analytical problem was circumvented by transforming the sulfides into their more polar sulfone counterparts by using the persulfate-based oxidant oxone ($2\,KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$).[2–4] This reagent was not only extremely selective, barely affecting aromatic hydrocarbons, but also gave quasi-quantitative reactions, even for extremely low concentrations. The resulting mixture of sulfones was easily separated from the untouched hydrocarbon matrix by chromatography on silica gel. GC-MS investigation[5] of the sulfone fractions revealed the presence of a series of unknown sulfur compounds besides the usually predominant 4,6-dialkyldibenzothiophene 5,5-dioxides. The EIMS spectra of all homologues are characterized by a major fragment at $m/z = 109$ and molecular ions ranging from $m/z = 278$ to 334 and corresponding to the general formula $C_{16+n}H_{22+2n}SO_2$ ($n = 0$–4). Since no further structural information could be obtained from the fragmentation pattern in the mass spectrum, these new compounds were isolated as sulfones from a diesel oil strongly depleted in sulfur compounds (50 ppm S) by a combination of liquid chromatography on silica gel and reversed-phase HPLC,[4] which gave pure **2a–c**.

About 1 mg of pure **2a** was obtained, and this enabled its complete characterization by 1D and 2D NMR studies including homonuclear ($^1H,^1H$ COSY and NOESY) and heteronuclear ($^1H,^{13}C$ HSQC and HMBC) correlation experiments. These studies permitted us to unambiguously establish the structure and relative configuration of 9-ethyl-HDBTO$_2$ (**2a**) and to assign the signals of all protons and carbon atoms (Table 1).

The $^{13}C$ NMR, $^1H$-noise-decoupled, and DEPT spectra indicate the presence of an aromatic ring bearing one methyl, one ethyl, and two vicinal protons, as well as an aliphatic part composed of two quaternary carbon atoms, and one methine, three methylene, and three methyl groups. The carbon skeleton of 9-ethyl-HDBTO$_2$ was finally established mainly on the basis of a long-range ($^{2,3}J$) correlation experiment (Figure 1a) and $^1H,^1H$ COSY and heteronuclear $^1H,^{13}C$ ($^1J$) correlation experiments. The presence of a nuclear Overhauser effect (NOE) between H-9b and protons of the C-4a-methyl group clearly indicates a *cis* junction between the cyclohexane ring and the sulfurized five-membered ring (Figure 1b). The NOEs observed between H-9b and protons respectively located on C-2 and C-4 indicate the axial position of H-9b on the cyclohexane ring. Consequently, the C-4a-methyl group must be equatorial.

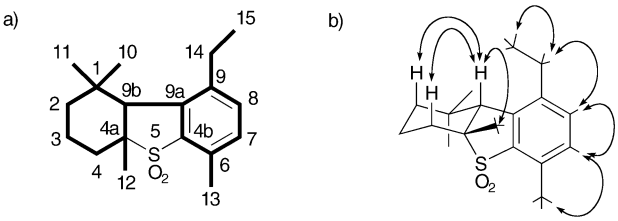


***Figure 1.*** a) Carbon sequence (bold) established from the inverse long-range $^1H,^{13}C$ correlation experiment; b) spatial representation of **2a** showing the most important NOEs observed.

Two lower homologues **2b** and **2c**, showing the typical fragmentation pattern of 9-alkyl-HDBTO$_2$ in their mass spectra,[6] were isolated in small amounts that enabled 1D $^1H$ NMR studies. The $^1H$ NMR spectrum[6] of **2b** has numerous similarities to that of **2a** and shows a singlet methyl signal with a chemical shift characteristic of a benzylic position, which replaces the ethyl group on C-9 of **2a**. This $^1H$ NMR spectrum allowed us to propose the structure of 9-methyl-HDBTO$_2$ for compound **2b**. The structure of 9-dealkylated-HDBTO$_2$ could be assigned to compound **2c**, since its $^1H$ NMR spectrum[6] shows the same aliphatic part and the signals of three aromatic protons (one triplet, two doublets) and of one benzylic methyl group.

Other homologues and isomers belonging to this novel series were detected in trace amounts by GC-MS in the fractions enriched in 9-alkyl-HDBTO$_2$ by HPLC from a diesel oil with 50 ppm residual sulfur. These compounds were identified on the basis of their mass spectra, which show the typical fragmentation pattern of 9-alkyl-HDBTO$_2$ dominated by the $m/z = 109$ fragment. In particular, we were able to detect and tentatively identify higher homologues with multiple substitution or longer side chains, in particular 9-(iso)propyl ($m/z = 320$ [$M^+$]) and 9-(iso)butyl-HDBTO$_2$ ($m/z = 334$ [$M^+$]), in accordance with the biological origin proposed below.

It clearly appears that the structures of these compounds are not the result of extensive molecular reorganization, as might be the case for dibenzothiophene-type structures, but are directly inherited from biological precursors related to terpenoids. These biological precursors could be derived from an unsaturated diterpenoid such as retinol or more likely from carotenoid precursors, which give rise to numerous molecular fossil counterparts[7] and in this case may

***Table 1:*** $^1H$ (500.1 MHz) and $^{13}C$ (125.8 MHz) NMR spectroscopic data for compound **2a** (Bruker ARX 500; in $CD_2Cl_2$, $\delta$ in ppm relative to TMS).

| C | $\delta(^{13}C)$ [ppm] | $\delta(^1H)$ | C | $\delta(^{13}C)$ [ppm] | $\delta(^1H)$ [ppm] |
|---|---|---|---|---|---|
| 1 | 36.4 | | 9 | 140.6 | |
| 2 | 40.1 | 1.52 (m, α, eq)–1.38 (m, β, ax) | 9a | 138.5 | |
| 3 | 18.7 | 2.01 (m, α, ax)–1.54 (m, β, eq) | 9b | 55.1 | 3.04 (s, β, ax) |
| 4 | 30.4 | 2.44 (m, α, eq)–1.59 (m, β, ax) | 10 | 35.1 | 1.07 (s, 3H, eq Me) |
| 4a | 62.3 | | 11 | 22.5 | 0.54 (s, 3H, ax Me) |
| 4b | 136.0 | | 12 | 30.5 | 1.23 (s, 3H) |
| 6 | 133.4 | | 13 | 16.6[a] | 2.54 (s, 3H) |
| 7 | 130.9 | 7.17 (d, $^3J = 7.5$ Hz) | 14 | 25.7 | 2.67 (dq, $^2J = 14.0$ Hz, $^3J = 7.0$ Hz)<br>2.84 (dq, $^2J = 14.0$ Hz, $^3J = 7.0$ Hz) |
| 8 | 133.2 | 7.36 (d, $^3J = 7.5$ Hz) | 15 | 16.5[a] | 1.13 (t, $^3J = 7.0$ Hz, 3H) |

[a] Values may be interchanged.

  

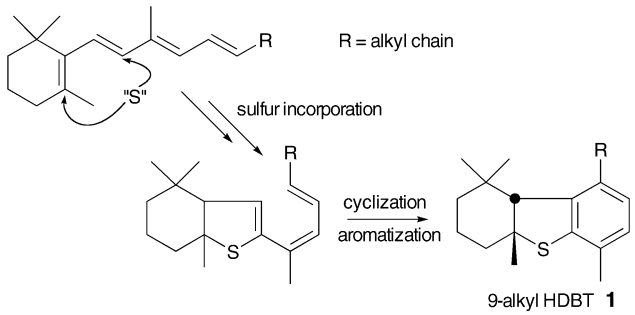


***Figure 2.*** Possible mode of formation of 9-alkyl-HDBT **1** from biological terpenoids (e.g., carotenoids).

have undergone sulfurization followed by cyclization and aromatization (Figure 2).

In a first step, the sulfurized five-membered ring could have been formed by early diagenetic reactions of double bonds of the precursor lipid with reduced inorganic sulfur species formed by bacterial sulfate reduction.[8] In a later stage, formation of the fused aromatic ring might be explained by cyclization and aromatization of polyunsaturated intermediates following a process often observed in sediments and petroleum and leading, for instance, from functionalized hopanoid precusors to sedimentary benzohopanoids[9] or from biological carotenoids to sedimentary polycyclic aromatic carotenoid derivatives.[7a] Oxidation reactions or biodegradation occurring in the early stages of diagenesis, as well as thermal processes involving cracking reactions at a later stage of burial, might explain the partial or total loss of the side chain leading to HDBT series **1**. Since these compounds are derived from biological molecules, their presence and distribution in diesel oils may be strongly dependent on the origin of the parent crude oil and may eventually be used as geochemical source indicators.

Comparison of the distribution of 9-alkyl-HDBTO$_2$ by GC-MS in diesel oils of the same origin, but desulfurized to different levels, clearly showed their relative increase as the amount of residual sulfur decreased, which shows that they are extremely resistant to hydrodesulfurization. In highly desulfurized fuels, 9-alkyl-HDBTs **1** can clearly become the predominant organosulfur compounds, even more abundant than 4,6-dimethyldibenzothiophene (Figure 3).

The reactivity of organic sulfur compounds towards hydrodesulfurization is significantly influenced by steric hindrance and the electron density on the sulfur atom.[10] These factors explain, for example, the known resistance of 4,6-dimethyldibenzothiophene towards hydrodesulfurization. In the case of 9-alkyl-HDBT, the presence of methyl groups at the 4a- and 6-positions, as well as the *cis* ring junction, could hinder the S atom sterically and thus prevent its interaction with the solid catalyst surface. This would explain the survival of these organic sulfur compounds under extreme hydrodesulfurization conditions. Their removal and hence the production of highly or even totally desulfurized fuels will require adaptation of existing hydrodesulfurization processes (e.g., new catalysts) or development of new desulfurization methods working under economically viable conditions,[11] a goal which can now be pursued based on precise knowledge of their structures.

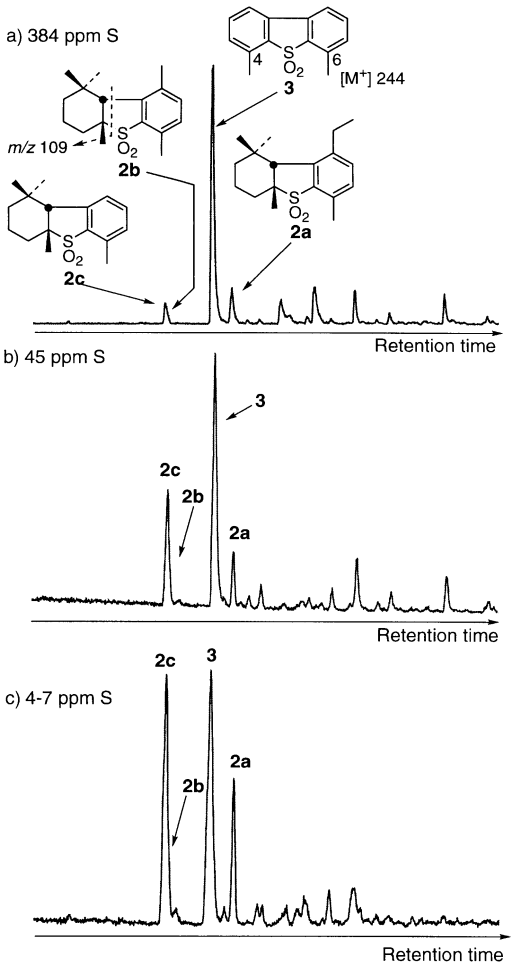


***Figure 3.*** Sum of the partial mass chromatograms $m/z = 109$ (tentatively assigned) and $m/z = 244$ (GC-MS, EI 70 eV, MAT TSQ 700 mass spectrometer connected to a Varian 3400 gas chromatograph, conditions as in ref. [5]) showing the distribution of HDBTO$_2$ and 4,6-dimethyldibenzothiophene-5,5′-dioxide (**3**) in the organic sulfur compounds isolated as sulfones from the same diesel oil desulfurized to three different levels: a) 384 ppm, b) 45 ppm c) 4–7 ppm residual sulfur. The observed relative intensities are very similar to those measured by gas chromatography (flame ionization detector), that is, they reflect the relative amounts.

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[3] Typically, 2.00 g of oxone (Aldrich) in 20 mL water was added to a mixture of acetone (20 mL) and 1.00 g of aromatic fraction isolated from a diesel oil by chromatography on a silica gel column ($0.05 < R_f < 0.90$, TLC, SiO$_2$/hexane). The reaction

  

mixture was stirred and heated to reflux for 4 h. After addition of water, extraction with $CH_2Cl_2$, and removal of the solvent under reduced pressure, the crude mixture was fractionated on a silica gel column ($CH_2Cl_2$) to give the sulfone fraction.

[4] After oxidation of the aromatic fraction isolated from a diesel oil with 50 ppm residual sulfur and separation of the sulfone fraction, **2a–c** were obtained by a sequence of chromatographic separations involving liquid chromatography on silica gel and reverse-phase HPLC steps (DuPont Zorbax ODS, 7 μm, 9.4 × 250 mm, $CH_3OH/H_2O$ 9:1).

[5] GC-MS analyses were performed on a Finnigan MAT TSQ 700 mass spectrometer, connected to a Varian 3400 gas chromatograph (on-column injector, J&W DB-5 column, 60 m × 0.25 mm, 0.1 μm film thickness). Mass spectra were recorded at 70 eV; helium was used as carrier gas.

[6] **2a**: for NMR see Table 1, MS (Finnigan MAT TSQ 700, EI, 70 eV): *m*/*z* (%): 306 (100) [$M^+$] ($C_{18}H_{26}SO_2$), 289 (32), 224 (57), 185 (35), 179 (38), 157 (37), 109 (99). **2b**: $^1$H NMR (500 MHz, $CD_2Cl_2$, 25 °C): $\delta = 0.58$ (s, 3H, H-11), 1.08 (s, 3H, H-10), 1.21 (s, 3H, H-12), 2.36 (s, 3H, H-14), 2.54 (s, 3H, H-13), 3.01 (s, 1H, H-9b), 7.13 (d, $^3J$(H,H) = 7.5 Hz, 2H, H-7 or H-8), 7.30 ppm (d, $^3J$ (H,H) = 7.5 Hz, 2H, H-7 or H-8); MS (EI, 70 eV): *m*/*z* (%): 292 (100) [$M^+$] ($C_{17}H_{24}SO_2$), 275 (29), 210 (42), 171 (35), 165 (41), 157 (24), 109 (98). **2c**: $^1$H NMR (500 MHz, $CD_2Cl_2$, 25 °C): $\delta = 0.71$ (s, 3H, H-11), 1.16 (s, 3H, H-10), 1.21 (s, 3H, H-12), 2.73 (s, 3H, H-13), 6.99 (d, $^3J$ (H,H) = 7.5 Hz, 1H, H-9 or H-7), 7.18 (d, $^3J$ (H,H) = 7.5 Hz, 1H, H-7 or H-9), 7.27 ppm (t, $^3J$ (H,H) = 7.5 Hz, 1H, H-8). MS (EI, 70 eV): *m*/*z* (%): 278 (79) [$M^+$] ($C_{16}H_{22}SO_2$,), 261 (8), 179 (10), 157 (25), 143 (19), 109 (100).

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