HIGHER ALKYLATED DIBENZOTHIOPHENES IN SOME CRUDE OILS AND HYDRODESULFURIZED FUELS

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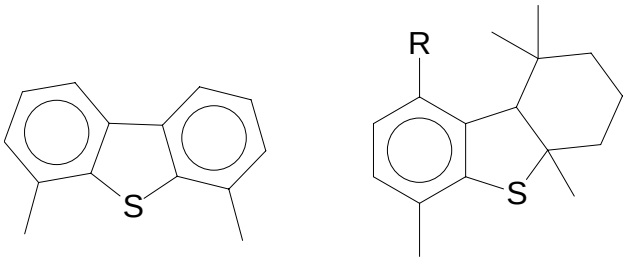
Introduction

The lowering of the legal limits for sulfur in fuels has led to a massive research effort to find catalysts that can remove sulfur down to the required levels. In the European Union this means that by 2005 gasoline and diesel fuels must meet a limit of 150 ppm with a goal of reducing it further to 10 ppm by 2009. In the USA, the gasoline limit is 120 ppm (2004) and 30 ppm (2006) and 15 ppm by 2007 for diesel[1]. Huge investments in refinery technology have allowed oil companies in Germany to exclusively offer fuels with a sulfur concentration below 10 ppm already by the year 2003. This amount is so low that such fuels are sometimes called "sulfur free fuels", although this is, of course, not correct.

Of the different forms of sulfur in fuel, the sulfur bound in aromatic structures is among the most difficult to remove catalytically. Within the aromatic sulfur species a certain selectivity can also be observed. Of the two most prominently occurring aromatic families of sulfur compounds, benzothiophenes and dibenzothiophenes, the former are generally more easily desulfurized than the latter. A further role is played by alkyl substituents which can exert some steric hindrance to the ability of the substrate to reach the catalyst surface. Thus dibenzothiophenes with alkyl groups in the 4- and/or 6-positions (**Figure 1**) are more difficult to hydrodesulfurize than other isomers and tend to accumulate in the product.

Recently members of a different class of sulfur compounds were shown to possess a high degree of recalcitrance to the catalytic process (**Figure 1**)[2]. They were all found to be 1,1,4a,6-tetramethyl-9-alkyl-1,2,3,4,4a,9b-hexahydrodibenzothiophenes with different alkyl groups in the 9 position.



R = H, CH_3, C_2H_5, iso-Pr, iso-Bu

Figure 1: Compounds showing steric hindrance to hydrodesulfurization. 4,6-Dimethyldibenzothiophene (left) and 1,1,4a,6-tetramethyl-9-alkyl-1,2,3,4,4a,9b-hexahydrodibenzothiophene (right)

In such compounds the sulfur is not part of an aromatic ring. Probably due to considerable steric hindrance, this sulfur atom shows a very pronounced resistance toward the hydrodesulfurization process and such compounds therefore accumulate when the sulfur content in fuels is reduced.

We were interested in identifying the sulfur compounds that show this recalcitrance to hydrodesulfurization and have started a program to identify them[3]. Monomethyldibenzothiophenes have long been studied. In this report we therefore concentrate on C_2- to C_4-substituted dibenzothiophenes.

Several C_2-, C_3- and C_4-substituted dibenzothiophenes, with the number denoting the total number of carbon atoms in the alkyl substituents, were synthesized as reference compounds, in most cases from an appropriately alkylated thiophenol and a suitable bromocyclohexanone[4]. In Table I, the compounds thus prepared are listed. The use of reference compounds is necessary for the assignments of unknown peaks in the gas chromatogram and for an estimation of the behavior of compounds with steric hindrance around the sulfur atom on chromatography on the palladium(II) column that was used to separate the sulfur heterocycles from the polycyclic aromatic hydrocarbons.

Table I. Compounds synthesized and studied in this work

<u>C_2-DBT</u>
4-ethyl

<u>C_3-DBT</u>
1,3,7-trimethyl
1,4,6-trimethyl
1,4,7-trimethyl
1,4,8-trimethyl
2,4,6-trimethyl
2,4,7-trimethyl
3,4,6-trimethyl
3,4,7-trimethyl
3,4,8-trimethyl
4-ethyl-6-methyl

<u>C_4-DBT</u>
1,4,6,8-tetramethyl
2,4,6,8-tetramethyl
2,4,6,7-tetramethyl
6-ethyl-2,4-dimethyl

Experimental

The aromatic fraction was isolated from the whole sample by chromatography on silica gel (6-7 g, 10 mm x 100 mm) using cyclohexane (40 mL) to elute the aliphatic compounds and cyclohexane:dichloromethane (3:1, 40 mL) to isolate the polycyclic aromatic compound fraction. After a reduction of the volume to 10 mL on a rotary evaporator, the volume of the solvent was further reduced to ca 500 µL with a slow stream of dry nitrogen. Separation into a PAH and a PASH fraction on a column with the palladium(II) complex of chemically bonded 2-aminocyclopentene-1-dithiocarboxylic acid was performed according to Ref. 5. The fraction eluting with cyclohexane:dichloromethane (7:3) contained the polycyclic aromatic hydrocarbons and the fraction coming with (1.0 % isopropanol in cyclohexane):dichloromethane (7:3) was taken as the aromatic sulfur fraction.

The gas chromatographic analysis was performed on either a DB-5 or a DB-17ms capillary column (30 m x 0.25 mm i.d., the film thickness was 250 µm) with hydrogen (FID) or helium (MSD) as carrier gas. 2-Fluorodibenzothiophene was used as internal standard (IS) for quantification purposes[6]. Mass spectra were recorded using a Finnegan GCQ mass selective detector.

Results and discussion

In Figure 2, the gas chromatogram of the sulfur aromatic fraction of a commercial diesel fuel with a sulfur content of 70 ppm is depicted. Those polycyclic aromatic sulfur heterocycles (PASH) that were identified through direct comparison with the synthesized standards are indicated through their structural formulas or in the legend. Several other components could be assigned to a general substitution pattern through their mass spectra but the exact structure has not yet been elucidated. Work is in progress to extend the identification to these peaks.

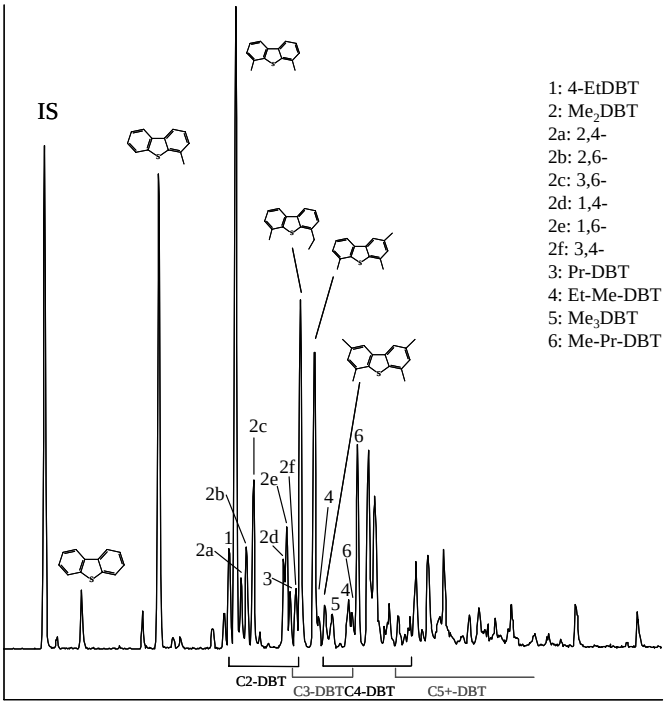


Figure 2. Gas chromatogram with mass selective detection of the polycyclic aromatic sulfur fraction of a commercial diesel fuel containing 70 ppm sulfur. Stationary phase: DB 17ms. IS = 2-fluorodibenzothiophene as internal standard. The following dimethyldibenzothiophenes (Me_2DBT) were identified: *2a*: 2,4-, *2b*: 2,6-, *2c*: 3,6-, *2d*: 1,4-, *2e*: 1,6-, and *2f*: 3,4-dimethyldibenzothiophene

The criteria for these assignments were that the M^+ ion had to correspond to the molecular mass of the congener. This ion is also the base ion (100 %) for polymethyldibenzothiophenes. If an ethyl group is present, the base ion is formed through loss of a methyl group, giving rise to $[M-15]^+$ as the base ion. A propyl group is indicated through the fragment $[M-29]^+$ which corresponds to the formation of the stabilized tropylium ion and is the base peak. This is illustrated in Figure 3 which shows the mass spectrum of peak number 3 in Figure 2. Likewise, the peak we assign to a methylpropyldibenzothiophene shows similar features typical of the two alkyl groups with m/z 211 as the base ion, corresponding to loss of an ethyl group, 226 (76 %) through loss of a CH_2 fragment and an M^+ ion at 240 (23 %).

It is well known that a methyl group in the 4-position of dibenzothiophene exerts enough steric hindrance to the approach of the sulfur atom to the active center on the catalyst surface to lower

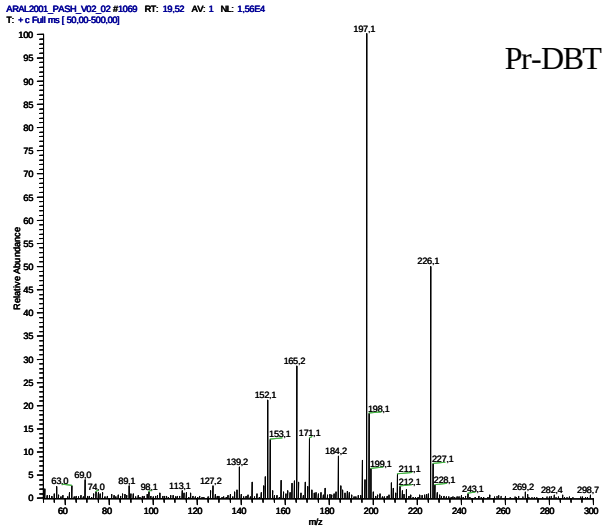


Figure 3. The mass spectrum of peak number 3 in Figure 2, assigned to a propyldibenzothiophene.

the rate of dehydrosulfurization appreciably. The result is that among the mono-methyldibenzothiophenes, only the 4-isomer is found in desulfurized products. In deeply desulfurized fuels, this congener also is removed.

Among the C_2-substituted dibenzothiophenes, 4,6-dimethyldibenzothiophene is always particularly prominent in desulfurized fuels, unlike most crude oils where other isomers are more prominent. 4-Ethyldibenzothiophene, normally a minor peak in the gas chromatogram, also attains some prominence. As can be seen in Figure 2, all the identified dimethyldibenzothiophenes have at least one methyl group in the 4- or 6-position. Gas chromatographic retention index data are available for many lower alkylated dibenzothiophenes[7].

A similar situation is found for the higher alkylated compounds. As shown in Figure 2, we have identified 4-ethyl-6-methyldibenzothiophene as the major C_3 congener, followed by 2,4,6-trimethyldibenzothiophene. Both these compounds exhibit the pattern of 4,6-disubstitution. This knowledge makes it highly probable that the indicated propyldibenzothiophene is substitued in the 4-position.

Sulfur heterocycles have been shown to be useful to identify the source of an oil spill in the environment. The PASH pattern was of particular use to correlate the pattern of the spilled oil with that of suspected sources[8,9] since different oil fields produce crudes with different PASH signatures. However, it is as yet unclear how strongly the provinence of the crude influences the pattern of the desulfurized product. At this time it can only be speculated that much information of this kind is lost through the removal of many sulfur congeners.

As illustrated above, a desulfurized fuel can be distinguished from non-desulfurized fuels not only through the lower sulfur concentration but also the pattern of the congeners. This should also show up in air pollution as the trend toward lower sulfur content in vehicle fuels is gaining ground. This proposal is now under active investigation and the results will be compared with the PASH pattern of commercial desulfurized fuels.

Conclusions

The hydrodesulfurization of crude oil fractions strongly influences the pattern of alkyldibenzothiophenes in fuels such as diesel. Congeners substituted in the 4- and/or 6-positions are enriched in relation to the crude used. In residues from the distillation of crudes, this effect is still more pronounced and alkylated sulfur heterocycles in the less volatile fractions can be considerably more difficult to desulfurize. The change in PASH pattern through desulfurization has consequences for the pattern of PASHs found in the environment.

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