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Bridgehead alkylated 2-thiaadamantanes: novel markers for sulfurisation processes occurring under high thermal stress in deep petroleum reservoirs

Sylvie Hanin,[a] Pierre Adam,[a] Isabelle Kowalewski,[b] Alain-Yves Huc,[b] Bernard Carpentier[b] and Pierre Albrecht*[a]

[a] *Laboratoire de Géochimie Bioorganique, ECPM, CNRS/Univ. Louis Pasteur, 25 rue Becquerel, 67087 Strasbourg, France. E-mail: albrecht@chimie.u-strasbg.fr; Fax: (33-3) 90 24 26 35; Tel: (33-3) 90 24 26 34*

[b] *Institut Français du Pétrole, Dépt. de Géologie et Géochimie, 1-4 rue de Bois Préau, 92852 Rueil-Malmaison, France. E-mail: Isabelle.Kowalewski@ifp.fr; Fax: (33-1) 47 52 60 00; Tel: (33-1) 47 52 70 00*

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Two bridgehead-alkylated 2-thiaadamantanes (1,5-dimethyl and 1-methyl) have been identified in petroleum; these compounds give clues to sulfurisation processes affecting petroleum which has undergone high thermal stress.

Organo-sulfur compounds are often abundant in petroleum derived from sediments deposited in anoxic environments where they are formed by early diagenetic sulfurisation processes.[1] We report here on the identification in petroleum of a series of tricyclic sulfides which are obviously the result of sulfurisation processes occurring under high temperature conditions in deeply buried petroleum reservoir-rocks. 1,5-Dimethyl-2-thiaadamantane **1** was characterised by NMR after isolation from petroleum. The structure of 1-methyl-2-thiaadamantane **2** was established by comparison with a standard obtained by synthesis.

Aliphatic sulfide fractions of several petroleum samples from the Jurassic Smackover formation (USA) or from the Devonian Nisku formation (Canada) were obtained by chromatography on silver nitrate impregnated silica gel. Analysis by gas chromatography-mass spectrometry revealed in all the samples selected, the presence of a homologous series of sulfides characterised by molecular ions at [M$^+$] 154 + ($n \times 14$) which appear as mixtures of several isomers for each homologue. The mass spectra are characterised by an intense molecular ion and minor fragments at m/z 93 and m/z 107. High resolution mass spectrometry gave an elemental composition of $C_{9+n}H_{14+2n}S$ compatible with sulfurised structures with three degrees of unsaturation. Since the fragmentation pattern shows similarities with that of alkyladamantanes,[2] it was envisaged that these sulfides were sulfurised analogues of alkyladamantanes.

The major isomer among the C_{11} homologues **1** ([M$^+$] 182, $C_{11}H_{18}S$) could be isolated in the milligram range.†Compound **1** was fully characterised as 1,5-dimethyl-2-thiaadamantane‡ by 1D and 2D NMR experiments including ^1H–^1H homonuclear (COSY and NOESY), as well as heteronuclear ^1H–^{13}C correlation experiments (HMBC and HSQC).

The DEPT 135 and the HSQC experiments indicated the presence of two methines, two methyls and five methylenes. This observation was compatible with the structure of a dimethyl-2-thiaadamantane where both methyl groups would be located on quaternary carbon atoms. The HMBC experiment permitted the establishment of a partial sequence of the skeleton (Fig. 1). The COSY experiment (Fig. 1) gave unambiguously the connection between the partial structure obtained from the HMBC and the remaining methines and methylenes. The COSY experiment showed also numerous $^4J_{H-H}$ attesting that the structure was actually a fusion of four cyclohexane-like structures (Fig. 1). Furthermore, the NOESY experiment confirmed that the methyl groups were located at the bridgehead of a sulfurised adamantane-like structure.

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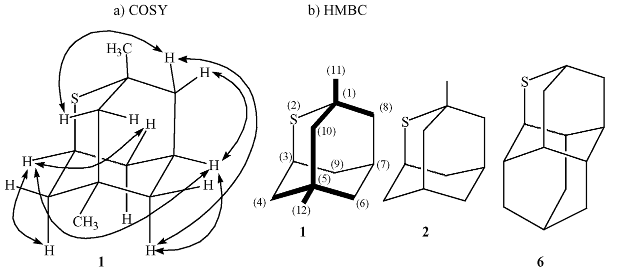
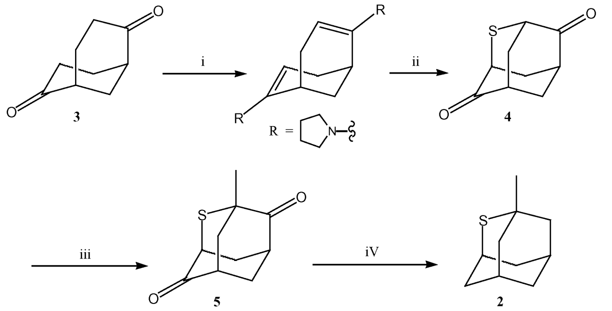


Fig. 1 1,5-Dimethyl-2-thiaadamantane **1**, 1-methyl-2-thiaadamantane **2** and 2-thiadiamantane **6**. (a) Spatial representation of **1** showing the most important couplings observed. (b) Carbon sequence (bold) of **1** established from inverse long-range ^1H–^{13}C correlation experiment.

Analysis by GC-MS of the alkylthiaadamantanes from petroleum samples showed that only three dimethylthiaadamantane isomers were present. Since the major isomer was alkylated at the bridgehead and since there were only three possible dimethylated bridgehead alkylated isomers, we infer that all the dimethyl-2-thiaadamantane present are alkylated at these positions.

To confirm the hypothesis that the major monomethyl-2-thiaadamantanes also bears a bridgehead methyl group, we have synthesised 1-methyl-2-thiaadamantane **2**, starting from bicyclo[3.3.1]nonane-2,6-dione **3** following the procedure described by Stetter and Held[3a] (Scheme 1) for the construction of the 2-thiaadamantane skeleton. After bisenamination with pyrrolidine and heterocyclisation with sulfur dichloride yielding the diketone **4**, one position α to the sulfur atom of the diketone **4** could be methylated with LDA–CH_3I. The resulting methylated diketone **5** was reduced by a Wolff–Kishner reaction[3b] yielding 1-methyl-2-thiaadamantane **2**.

2-Thiaadamantane-4,8-dione **4** and 1-methyl-2-thiaadamantane-4,8-dione **5**‡ were fully characterised by complete NMR



Scheme 1 Synthesis of 1-methyl-2-thiaadamantane: i, pyrrolidine, p-TSA, C_6H_6; ii, SCl_2, Et_3N, $CHCl_3$; iii, LDA, THF, then CH_3I; iv, hydrazine, NaOH, ethylene glycol, MeOH.

studies comprising homo (^{1}H–^{1}H, COSY, NOESY) and heteronuclear (^{1}H–^{13}C, HMBC, HSQC) correlation experiments. The ^{1}H-NMR chemical shifts for 2-thiaadamantane-4,8-dione were consistent with values from the literature.[4] Due to the high tendency of 1-methyl-2-thiaadamantane **2** to sublime, we were not able to obtain a NMR spectrum of the final product. GC-MS‡ analysis is consistent with the expected structure.

Unambiguous identification of the major monomethyl-2-thiaadamantane occurring in petroleum as 1-methyl-2-thiaadamantane was based on comparison of mass spectra and chromatographic behaviours (coelution in GC on a DB5 J&W column: 30 m × 0.25 mm, 0.1 μm) of the synthetic and of the naturally occurring compound.

2-Thiaadamantane has already been isolated from an Iranian kerosine[5] and several routes have been proposed for its synthesis[3] and that of homologues alkylated at positions 4 and 8,[6] but never at the bridgehead. Nevertheless, this position seems to be the most stable as is the case with bridgehead alkylated adamantanes[7] which are reported to be more resistant to thermal stress than the other isomers.[8]

Mass spectral study of the fractions containing alkylated 2-thiaadamantanes suggested that the minor compounds present in these fractions could be alkylthiadiamantanes (related to **6**). These compounds obviously were sulfides (retained on silver nitrate impregnated silica gel) and their mass spectra were, similarly to those of alkyl-2-thiaadamantanes, characterised by a predominant peak corresponding to a molecular ion ([M$^+$] 206 + (n × 14)) compatible with sulfurised structures with five degrees of unsaturation. This was confirmed by high resolution mass spectrometry ($C_{13+n}H_{18+2n}S$). The mass spectra showed also a typical diamantane fragment at m/z 105.[2]

Thiadiamandoids might have been formed by acid catalysed rearrangement of tricyclic sulfides as described for diamondoid hydrocarbons which can be formed by drastic rearrangement of polycyclic hydrocarbons.[9] It has indeed been proven that polycyclic structures in petroleum could be converted to adamantanes by zeolite-catalysed isomerisation[10] and clays present in small amounts in petroleum reservoirs might be acidic enough to catalyse these rearrangements at high temperature.[10] However, the possibility of formation of diamondoid hydrocarbons in petroleum reservoirs under high temperature is still the subject of debate. Indeed, pyrolysis experiments reported recently in the literature[8] seem to indicate that diamondoids are not formed under high temperature conditions prevailing in reservoirs and that their enrichment in petroleum relative to other hydrocarbons which have undergone high thermal stress might rather be the result of their high stability and resistance towards cracking reactions.[8] Several observations, however, support the hypothesis that thiadiamondoids are formed in deeply buried reservoirs which have undergone the effects of Thermal Sulfate Reduction (TSR), a high temperature process in which organic matter from petroleum is oxidised by sulfates (anhydrite) from the reservoir-rocks which in turn are transformed to reduced sulfur species such as hydrogen sulfide and elemental sulfur.[11] Indeed, a set of petroleum samples originating from the same source rock (Smackover Formation, Gulf of Mexico, USA) but having migrated in different reservoir-rocks which have undergone different thermal histories during burial has been investigated for thiaadamantanes. The latter could only be detected in petroleum altered by TSR.[12] Furthermore the isotopic composition of sulfur (δ^{34}S / CDT)[13] from thiaadamantanes (+21 to +22‰) is similar to that of the sulfates (+18 to +24‰) from the reservoir thus clearly indicating that these structures are formed by sulfurisation processes involving reduced sulfur species formed by TSR.[14] These values differ from those of organic sulfur compounds occurring in less mature petroleum (in general significantly depleted in ^{34}S as compared to sulfate). The latter results from the interaction of biological compounds with reduced sulfur species formed by bacterial sulfate reduction at early stages of burial. Hence our data suggest that alkylthiaadamantanes are molecular indicators of TSR occurring in deeply buried petroleum reservoirs.[1]

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Notes and references

† Compound **1** was isolated by a sequence of chromatographic separations including liquid chromatography on silver nitrate impregnated silica gel (CH_2Cl_2 followed by AcOEt) and high performance liquid chromatography (Du Pont Zorbax Silica, 250 × 4.6 mm, hexane: 1 ml min^{-1}). As solvent could not be evaporated without loss of compound **1** by sublimation, the product was concentrated by filtration on a micro-column of silver nitrate impregnated silica gel. Non deuterated solvents were removed from the column by elution with deuterated benzene. 1,5-dimethylthiadamantane **1** was finally recovered and directly collected in the NMR tube by elution with small amounts of perdeuterated acetone.

‡ *Analytical data* 1,5-dimethyl-2-thiaadamantane **1**: ^{1}H-NMR (500 MHz, CD_3COCD_3) δ ppm: 0.78 (3H, H-12), 1.22 (3H, H-11), 1.46 (1H, H-6(a)), 1.50 (1H, H-6(b)), 1.60 (1H, H-10(b)), 1.78 (1H, H-8(b)), 1.82 (2H, H-4(b) and H-10(a)), 1.95 (1H, H-4(a)), 1.98 (1H, H-9(a)), 2.09 (1H, H-8(a)), 2.16 (1H, H-9(b)), 2.18 (1H, H-7), 3.27 (1H, H-3). ^{13}C-NMR and DEPT 135 (125 MHz, CD_3COCD_3) δ ppm: 11.8 (C-12), 29.8 (C-7), 32.4 (C-11), 34.7 (C-5), 37.0 (C-9), 39.1 (C-3), 43.1 (C-6), 43.5 (C-1), 44.7 (C-4), 45.4 (C-8), 53.1 (C-10). GC-MS (Finnigan MAT INCOS 50) (EI, 70eV), m/z (rel.int.) 182 ([M$^+$], 100%), 125 (65), 107 (37), 93 (35). HR-MS: $C_{11}H_{18}S$, mass 182.1127, calculated mass 182.1129.

1-Methyl-2-thiaadamantane-4,8-dione **5**: ^{1}H-NMR (500 MHz, CD_2Cl_2) δ ppm: 2.06 (s, 3H, H-11), 2.07 (d, 1H, ^2J = 13.0Hz, H-9(b)), 2.13 (br s, 2H, H-10), 2.17–2.18 (m, 2H, H-6), 2.23 (m, 1H, H-9(a)), 2.66 (m, 2H, H-5 and H-7), 2.79 (d, 1H, ^3J = 7.0Hz, H-3). ^{13}C-NMR (125 MHz, CD_2Cl_2) δ ppm: 12.8 (C-11), 37.5 (C-9), 38.9 (C-6), 43.1 (C-10), 46.1 (C-7), 48.0 (C-5), 52.0 (C-3), 56.3 (C-1), 210.5 (C-8), 211.7 (C-4). GC-MS (EI, 70 eV), m/z (rel. int.): 196 ([M$^+$], 100%), 168 (39), 153 (57), 125 (38).

1-Methyl-2-thiaadamantane **2**: GC-MS (EI, 70 eV), m/z (rel. int.): 168 ([M$^+$], 49%), 125 (100), 93 (16).

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