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Further Bridged Sulfur Compounds of the Kerosine Boiling Range of Middle East Distillates

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Earlier (*1*) an account was given of the identification of a number of thiophenes and mono- and polycyclic sulfides in the sulfurous oil obtained in the process of refining Middle East (Agha Jari) kerosine. Of special interest were two of the sulfides which were solids, possessing a structure in which a carbon ring is bridged by a sulfur atom. The probable presence of other sulfides of similar structure was indicated and further work has now confirmed their presence. The compounds identified, either tentatively or definitely, are listed in Table I; several possess the atomic-bridged structure. Although two polycyclic sulfides, thianaphthene (*12*) and 1,8-dimethyldibenzothiophene (*6*), have been identified in crude oils and also some hydrocarbons possessing an atomic-bridged structure (*11*), these are the only sulfur compounds of this type that have so far been identified in naturally occurring materials. It is of interest, however, to compare their structure with those of the tropane group of alkaloids—e.g., tropane and granatanine.

PREPARATION OF CLOSE BOILING FRACTIONS

The preparation, in the refinery, of the sulfur compound concentrate used in this investigation has been fully described (*1*). Subsequent processing and precise fractional distillation of a portion of this concentrate were also described, and three fractions obtained by this process (XX, XXIV, XXVII, Table II) have been re-examined in the course of this work. In addition a further portion of the sulfur compound concentrate was fractionally distilled to obtain a quantity (15 liters, n_D^{20} 1.4811) of material in the 180° to 192° C. range. Following Dualayer solutizer treatment (*8*) to remove mercaptans, fractionation with 0.7M aqueous mercuric acetate solution (*1*) (five extractions each of 25 volume %) yielded, after regeneration of the extracts, a bicyclic sulfide concentrate, 2.5 kg., n_D^{20} 1.4856, which was distilled through a 100-plate column under reduced pressure. The fractions from this distillation (A-I, Table III) were used to obtain concentrates of polycyclic sulfides. Distillation, under reduced pressure, of the raffinate from this extraction left a residue of the same acetoxymercurithiophenes as those described previously (*1*).

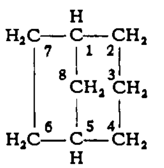
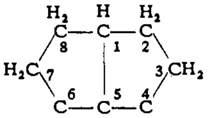
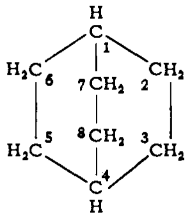
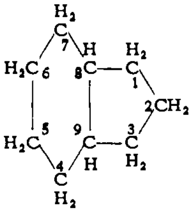
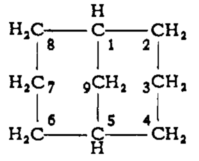
CONCENTRATION OF POLYCYCLICS PRESENT IN CLOSE-BOILING FRACTIONS

Because the primary objective was to investigate the polycyclic compounds, the first need was to separate these from the associated monocyclic compounds, which were in general the largest component of the fractions. An attempt to separate mono- and bicyclic compounds by elution chromatography using alumina was only partially successful and similar results were obtained with the corresponding sulfones. The methods finally used were based on the use of the mercury salt complexes of the sulfides, the first stage being fractional extraction with aqueous mercuric acetate solution. It was shown that the previously used method, involving a two-stage acid regeneration (*1*), caused some decomposition of the polycyclic sulfides—e.g., a portion of the tar oil, boiling point, 193° C., was refluxed for 2 hours with aqueous mercuric acetate solution and regenerated by the addition of hydrochloric acid; the loss of bicyclic sulfides was indicated by a fall in refractive index, n_D^{20}, from 1.4932 to 1.4872. The process of fractionation had therefore to depend entirely upon the selectivity of the extraction process.

The fraction was extracted with an amount of aqueous mercuric acetate solution, sufficient only to extract a small percentage of the sulfides, by vigorous agitation, preferably with a high-speed stirrer, for 10 minutes. After water-washing to remove the mercuric acetate complexes remaining dissolved in the sulfide layer, the combined extracts were regenerated by addition to a refluxing aqueous solution of sodium sulfide, followed by removal of the steam-distilled sulfides using an oil-water separator. The raffinate was similarly extracted with further small quantities of mercuric acetate solution until the refractive index of the regenerated sulfide showed that it contained only a small amount of bicyclic compound. By retreatment of bulked fractions it was possible to obtain materials of high refractive index consisting essentially of polycyclic compounds. While recovery of polycyclic sulfides by this procedure was incomplete, the concentrates obtained were undoubtedly representative of the types present, as little separation of individual polycyclics appears to occur during this process.

A further method for the concentration of polycyclic sulfides was based upon the formation and separation of the mercuric chloride complexes. It had been observed that the mercuric chloride complexes of synthetic bicyclic sulfides were almost invariably extremely insoluble and it was found that the least soluble portion of the complexes formed from the tar oil fractions or concentrates (using a high molar ratio of mercuric chloride to sulfide) contained a high proportion of bicyclic sulfides. By further crystal-

Table I. Polycyclic Sulfides in Kerosine Range

Sulfur Compound	B.P., °C.	M.P., °C.	Formula of Analogous Hydrocarbon
8-Thiabicyclo[3.2.1]-octane[a]	195[b]	172–173	
6-Thiabicyclo[3.2.1]-octane	197[b]	173–174.5	
2-Thiabicyclo[3.2.1]-octane	197[b]	166–167	
3-Thiabicyclo[3.2.1]-octane	196±2[b]	174–175	
x-Methyl-8-thiabicyclo-[3.2.1]octane	...	...	...
cis-3-Thiabicyclo-[3.3.0]octane	198[b]	-17	
2-Thiabicyclo[2.2.2]-octane	...	209–10	
cis-1-Thiahydrindane[a]	214	-44	
trans-1-Thiahy-drindane[a]	213	-11.5	
9-Thiabicyclo[3.3.1]-nonane	...	155.5–158	
Tricyclics $C_9H_{14}S$ $C_{10}H_{16}S$	...	170–172	...
Tricyclics (2) $C_{10}H_{16}S$	...	185	...

[a] Isolation of these compounds described (*1*).

[b] Values determined at atmospheric pressure. Elsewhere values at atmospheric pressure have been obtained by conversion from pressures between 10 and 40 mm. using a standard hydrocarbon vapor pressure–temperature graph.

lization a bicyclic concentrate, or occasionally an individual bicyclic sulfide, was obtained as its mercuric chloride complex. The use of ethyl alcohol as a solvent was unsatisfactory, because large quantities of solvent were required and recovery of the complex from the crystallization mother liquors involved considerable loss of sulfide, presumably because of decomposition of the complex and loss of sulfide by distillation with the solvent. In place of ethyl alcohol, Carbitol (the monoethyl ether of diethylene glycol) proved to be a very satisfactory solvent, as it had a high solubility both for mercuric chloride itself and for its complexes with sulfides. In addition, the sulfide could be recovered from the crystallization mother liquors by addition of the Carbitol solution to refluxing sodium sulfide solution.

The treatment of the fractions by these methods and the composition of the bicyclic concentrates obtained are detailed in Tables II and III.

IDENTIFICATION OF POLYCYCLIC SULFIDES

The fractionation process having given separation into fractions consisting essentially of polycyclic compounds, the problem of identification remained. The procedure adopted was to desulfurize the bicyclic concentrate and identify the hydrocarbons formed. The structure of the naphthenes gave an indication of the probable structure of the sulfides, which were synthesized if they were not already available under the program of preparation of sulfur compounds related to petroleum in progress in these laboratories (*4*). The infrared spectra of the synthetic sulfides were used to give positive identification of the sulfides in the bicyclic concentrates. As an example of this method, one of the products of desulfurization of the lower boiling fractions was shown to be cycloheptane and the postulate that this was derived from 8-thiabicyclo-[3.2.1]octane was confirmed by synthesis of the sulfide.

Fortunately, in the course of this work the powerful tool of gas liquid chromatography (*9*) became available, which made possible separation and identification of the Raney nickel desulfurization products obtained from a small amount of sulfide (0.1 gram). Because of the difficulty of separating small amounts of hydrocarbons from the ethanolic distillate, the original technique (*1*) was modified. Using Carbitol as solvent, desulfurization could be effected by heating to 100°C. for 90 minutes. Water was then added and the desulfurization products were steam-distilled through a short glass-packed column (Carbitol is not steam-volatile) into a receiver containing pentane, which dissolved the hydrocarbons and scrubbed the hydrogen evolved during the reaction. After careful removal of the bulk of the pentane, the residual desulfurization products were

Table II. Polycyclic Sulfides Identified in 210° to 250°C. Range

Fraction					Bicyclic Concentrate				
No.	B.P., °C.	n_D^{20}	Wt., Grams	Bicyclic[a] Content	Method[b]	n_D^{20}	Wt., Grams	Naphthene on Desulfurization	Sulfide Identified
XX	210–212	1.4973	253	35	a		25		
						→ Solid	0.6	Cyclo-octane	9-Thiabicyclo[3.3.1]nonane
			25	...	b				
						→ Liquid 1.5206	0.2	...	9-Thiabicyclo[3.3.1]nonane *cis*- and *trans*-1-Thiahydrindane
XXIV	237–239	1.5090	510	40	a	Solid (>1.5310)	20	C_9 and C_{10} Bicyclic	C_9 Tricyclic *x*-Methyl-C_9 Tricyclic
XXVII	245–249	1.5158	1050	65	a	>1.5305	180		
		>1.5305	180	...	b	Solid	97	C_{10} Bicyclics	C_{10} Tricyclics

[a] Approximate percentage by refractive index.

[b] a. Extraction by aqueous mercuric acetate, efficient stirring.
b. Formation and crystallization of mercuric chloride complex.

Table III. Polycyclic Sulfides Identified in 180° to 192° C. Range

Fraction					Bicyclic Concentrate				
No.	B.P., °C.	n_D^{20}	Wt., Grams	Bicyclic[a] Content	Method[b]	n_D^{20}	Wt., Grams	Naphthene on Desulfurization	Sulfide Identified[c]
A	180–183	1.4845	465	10	a	1.5030	1.5	Cycloheptane	8-Thiabicyclo[3.2.1]octane (40)
B	186.5–187	1.4864	83	12	...	...	...	Cycloheptane Methylcyclohexane Ethylcyclopentane	... ...
C	187.5–188	1.4894	74	20	...	...	...	As in B	...
D	188–188.5	1.4928	155	25	b	Semisolid >1.5200	22		
						m.p. 175–6 °C.	3.1	Cycloheptane Methylcyclohexane	8-Thiabicyclo[3.2.1]octane (90) 6-Thiabicyclo[3.2.1]octane (10)
		Semi-solid	22		c				
						Semisolid	15	Cycloheptane Methylcyclohexane Ethylcyclopentane Methylcycloheptane	8-Thiabicyclo[3.2.1]octane (10) 6-Thiabicyclo[3.2.1]octane (15) 2-Thiabicyclo[3.2.1]octane x-Methyl-8-Thiabicyclo[3.2.1]-octane (50)
E	188.5–189	1.4960	83	30	a,c	Semisolid	7.2	...	8-Thiabicyclo[3.2.1]octane 6-Thiabicyclo[3.2.1]octane (13) 2-Thiabicyclo[3.2.1]octane x-Methyl-8-Thiabicyclo[3.2.1]-octane
F	189–189.5	1.4963	39	30	d,c	...	...	Methylcylohexane Ethylcyclopentane *cis*-1,2-Dimethyl-cyclopentane *cis*-1,3-Dimethyl-cyclopentane	
G	189.5–190	1.4960	46	30	c	Solid	0.6		6-Thiabicyclo[3.2.1]octane (85) 3-Thiabicyclo[3.2.1]octane 2-Thiabicyclo[3.2.1]octane *cis*-3-Thiabicyclo[3.3.0]-octane (15)
H	190–191	1.4940	39	30	b,c	Solid (1.524)	2.5		6-Thiabicyclo[3.2.1]octane (70) 2-Thiabicyclo[3.2.1]octane *cis*-3-Thiabicyclo[3.3.0]-octane (10)
I	191–192.5	1.4894	120	20	b,c	Solid	1.7	Methylcyclohexane Ethylcyclopentane *cis*-1,2-Dimethyl-cyclopentane	6-Thiabicyclo[3.2.1]octane (10) 2-Thiabicyclo[3.2.1]octane 2-Thiabicyclo[2.2.2]octane

[a] Approximate percentage by refractive index.

[b] a. Extraction by aqueous mercuric acetate, hand shaking.
b. Extraction by aqueous mercuric acetate, efficient stirring.
c. Formation and crystallization of mercuric chloride complex.
d. Chromatographic separation using alumina.

[c] Figures in brackets refer to estimated percentage of sulfide in concentrate as determined by infrared and composition of desulfurization products. Where no figure is quoted, amount is small and could not be estimated.

examined by gas liquid chromatography. A Carbitol solution of the mercuric chloride complex or an aqueous solution of the mercuric acetate complex could be desulfurized equally well by this technique, thus enabling the course of a separation to be followed without the necessity of regenerating the sulfide. In general, the gas liquid chromatography was carried out using a column operating at 78.5 °C., although for some of the higher fractions the column was operated at 134 °C. The three stationary phases employed were benzyldiphenyl (a mixture of the *o*- and *p*-compounds), *n*-hexatriacontane, and a silicone oil, for all of which retention volumes of a considerable number of hydrocarbons were known (*7*). Where any doubt as to the identity of any particular hydrocarbon occurred, it was separated from the mixture by the chromatographic column and the cracking pattern in the mass spectrometer was compared with that of the synthetic material. The naphthenes obtained on desulfurization of the bicyclic concentrates and the parent sulfur compounds are included in Tables II and III.

DISCUSSION

The advantages and disadvantages of the use of a spent refining agent as a source of sulfur compounds present in a petroleum distillate have been argued. Although the authors believe that all the compounds identified in this work were present in the original distillate, it is probable that some compounds have been lost in the course of refining—e.g., some thiophenes and aromatic sulfides—and in the course of recovery from the spent reagent, especially by reaction with aqueous mercuric acetate. [Neither *cis*- nor *trans*-2-thiabicyclo[3.3.0]octane (*3*, *5*) has been identified, and both compounds show some instability to mercuric salts]. The contention that the identified compounds are present in the original distillates is supported by the fact that the authors have been able to isolate thiaadamantane (0.08 gram) directly from the appropriate fraction (3 liters) of an unrefined Agha Jari kerosine (91 liters) by fractional extraction with aqueous mercuric acetate solution and regeneration with sodium sulfide.

Of the sulfides listed in Table I, the identification of two is not so precise as the remainder. The first, a methyl-8-thiabicyclo[3.2.1]octane, was obtained together with identified thiabicyclo[3.2.1]octanes by a combination of mercuric acetate extraction and repeated crystallization of mercuric chloride complexes. The hydrocarbons obtained on desulfurization of this fraction contained 70% of methylcycloheptane and microanalysis of the sulfides indicated a mixture of 70% of $C_8H_{14}S$ and 30% of $C_7H_{12}S$. As the infrared spectrum showed absorption at 7.26 microns, which is characteristic of a methyl group and is not present in any of the parent thiabicyclooctanes, it is certain that the compound is one of the methyl-8-thiabicyclo[3.2.1]octanes. It is surprising that its boiling point is so close to that of the parent sulfide, but this is confirmed by the fact that their retention volumes on a silicone oil are identical.

The other sulfide, not rigorously identified, 9-thiabicyclo[3.3.1]nonane, was obtained as a solid of constant melting point 155.5-58°C., analyzing correctly as $C_8H_{14}S$. As it gives only cyclo-octane on desulfurization, its most probable structure is that given or 9-thiabicyclo[4.2.1]-octane. An indication that it is the former is given by the fact that it has been prepared in the authors' laboratory (*13*), although in very low yield, by the method of Yur'ev (*14*) involving the reaction of *N*-methylgranatanine and hydrogen sulfide over alumina at 350°C.

No structure has been allocated to the sulfides comprising the two tricyclic fractions, because no synthetic compounds are available for comparison. Microanalysis indicated that the first of these, which was not purified to constant melting point owing to the smallness of the sample, contained 25% of the $C_9H_{14}S$ compound, and infrared spectra on various crystallization portions indicated that the $C_9H_{14}S$ compound did not contain a methyl substituent whereas the $C_{10}H_{16}S$ compound did. As the minor component of the desulfurization product had a retention volume identical with bicyclo[3.3.1]nonane, it is probable that the $C_9H_{14}S$ sulfide is an isomer of thiaadamantane. The identity of the remaining tricyclic fraction, which analyzed as $C_{10}H_{16}S$, is unknown, although it is known from gâs liquid chromatography of the sulfides and their desulfurization products to consist of two components in the ratio of 2 : 3. Extensive crystallization of the sulfides and the desulfurization product (melting point, 35°C.) failed to produce any appreciable separation of these components. The infrared spectrum had absorption at 7.26 microns, so that it is possible that they are methyl derivatives of thiaadamantane.

The opinion has been expressed that a relationship exists between the structure of sulfur compounds and hydrocarbons present in petroleum. Although this can only be speculative, in view of the paucity of data on both types of compounds, it is remarkable that the hydrocarbons and sulfur compounds possessing the adamantane and bicyclo-[3.3.0]- and -[3.2.1]octane structures should be present in crude oils (*2, 10, 11*) unless there is some common point of origin. An additional correlation, although less striking, exists in the occurrence of the monocyclic hydrocarbons and their sulfur analogs. Should it prove that a relationship does exist between the sulfur bodies and hydrocarbons present in a petroleum distillate, knowledge as to the structure of the sulfur compounds may well prove a useful pointer to the nature of certain of the hydrocarbons.

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