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SULFUR COMPOUNDS IN FOSSIL FUELS I

Anellated thiophenes in crude oils, oil shales, tar sands, syncrudes, and extracts from coals

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Fossil fuels and products made from them vary in sulfur content according to different origins and refining operations. The following sulfur contents are known: 0.05–13.95% for crude oils[1], 0.2–12% for oil shales[2,16], 0.4–11.5% for tar sands[3] and 0.03–1% for syncrudes from coals[4,5]. The low sulfur contents of syncrudes from coals originate in the hydrogenation processes by which the coals are liquefied and at the same time partially desulfurized.

In fossil fuels the organic sulfur is represented by the various structures given on page 123 to 157. R, R^1, R^2 stand for alkyl, cycloalkyl, or aromatic substituents. The cyclic compounds can occur unsubstituted or have one or several substituents (R_x). Systems bearing R_x generally represent a large number of individual compounds with the exception of the thiazoles **7**, benzothiazoles **68**, and thiochinolones **69**, of which a small number has been identified. References are given in brackets below the structures. In petroleum fractions certain sulfur compounds are dominating with respect to boiling range. The distribution of sulfur compounds is as follows.

Fractions boiling below 150°C: alkane- and cycloalkanethiols **1**, dialkyl, alkyl cycloalkyl sulfides **2**, disulfides **3**, monocyclic sulfides **4**, **5**, thiophene and thiophenes **6** with one or two short side chains.

Fractions with the boiling range 150°C to 250°C: alkane-, arene- and cycloalkanethiols **1**, dialkyl, alkyl cycloalkyl, and alkyl aryl sulfides **2**, polysulfides **3**, mono-, bi-, and tricyclic sulfides **4**, **5**, **8–14**, thiaindanes **38**, thiophenes **6** with up to four short side chains and thiophenes **70** with one anellated ring (benzothiophenes, thienothiophenes, and thienopyridines).

Fractions boiling above 250°C: thiophenes **6**, isothiaindanes **39** (two compounds with an ester group in an alkyl chain) dithienyls **6**, thiazoles **7**, thiochinolones **69**, anellated thiophenes **70** with known structure of the heterocyclus (benzothiophenes, indano- and indenothiophenes, dibenzothiophenes, naphtho-, benzonaphtho- and phenananthrothiophenes, benzodithiophenes), annellated thiophenes **70** with "probable structures".

Most of our knowledge of compounds in high-boiling oil fractions is the result of mass spectrometric investigations. Since by MS methods alone one cannot distinguish between

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isomeric structures e.g. anthracene and phenanthrene,[40] structures of compounds given in the literature are "probable structures". Sulfur compounds in high-boiling oil fractions (> 540°C), containing approximately half of the total sulfur content of crudes,[93] are estimated to be mostly thiophenes (up to 80%)[6]. According to MS investigations, thiophenes in the heavy ends of crudes are polycyclic systems with aromatic and naphthenoaromatic rings anellated to the thiophene ring (up to nine rings are known), and with side chains attached to the systems, which comprise also oxygen, nitrogen, and sulfur heterocycles. The position of the rings and of the side chains is unknown.

For refining operations, an exact knowledge of the structures of the individual sulfur compounds is not necessary for their removal. It is, however, essential to gain a deeper insight into the nature and properties of sulfur compounds in the heavy ends of refining, too, for the development of new and better desulfurization processes for crude oils, oil shales, tar sands, and syncrudes from coals, which will play (for both economical and ecological reasons) an ever-growing role in the future.

Table II contains structures of anellated thiophenes in crude oils, oil shales, tar sands, syncrudes, and extracts from coals.

The methods used for the elucidation of structures found in the literature are subdivided into a, b, c, d. Compounds whose structures have been established by methods a and/or b are to be regarded as positively identified.

The identification methods are as follows:

a) Structure identification by comparison of data of isolated sulfur compounds or their sulfones with data of authentic specimens (mixed melting point, IR, UV, NMR, MS, TLC, GC)

b) Structure identification by desulfurization with Raney-Nickel of isolated sulfur compounds and comparison of data of desulfurization products with authentic specimens or data from the literature

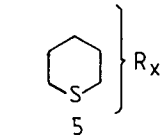
c) Suggested structure by comparison of data of isolated sulfur compounds with data from the literature

d) Probable structure of isolated sulfur compounds based on mass spectral investigations alone (no other evidence given)

Acknowledgment: We wish to thank the Deutsche Forschungsgemeinschaft for financial support.

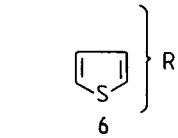
TABLE I

Sulfur Compounds in Fossil Fuels Other Than Anellated Thiophenes



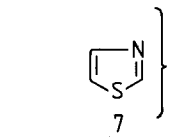
1

(1, 6–13, 17, 25, 90–92, 95)



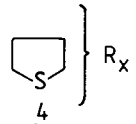
2

(1, 6–14, 17, 30, 31, 33, 36, 38, 91, 92, 94)



3

(n = 2:1, 6, 7, 10–12, 24, 91, 92, 94)(n = 3:11)



4

(1, 6–15, 17, 24, 27, 28, 30, 33–35, 91, 92)

5

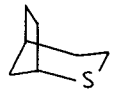
(1, 6–13, 15, 17, 24, 29–32, 34, 36, 91, 92, 94, 95)

6

(1, 6–14, 17, 19, 24, 25, 27, 28, 30–38, 40–42, 46, 47, 60, 68, 90–92, 94–96)

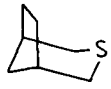
7

(18)



8

(9–11, 13, 17, 19)



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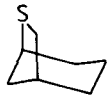
(9–11, 13, 17, 19)

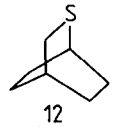


10

(6, 7, 9–11, 13, 17, 19)

11

(6, 7, 9–11, 13, 17, 19, 91)



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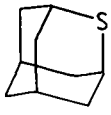
(6, 7, 9–11, 13, 17, 19)

13

(9–11, 13, 17, 19)



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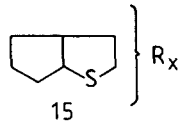
(6, 7, 9–13, 19, 20, 91)



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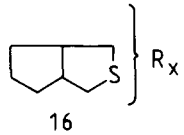
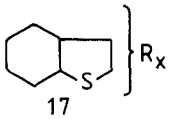
(6, 7, 10–13, 15, 17, 19, 27, 34)



16

(10, 12, 13, 19)



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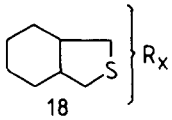
(6, 7, 9–15, 17, 19, 32–35, 95)



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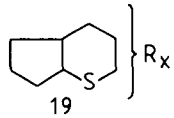

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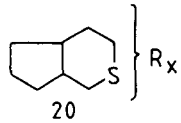
(6, 7, 10, 12)



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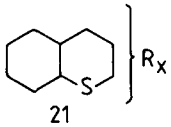
(10, 12)



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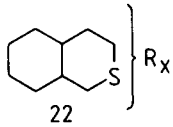

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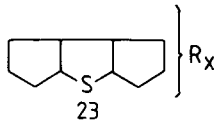

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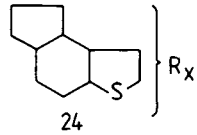

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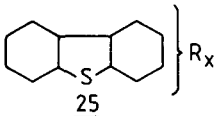

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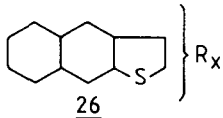

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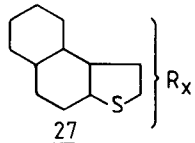

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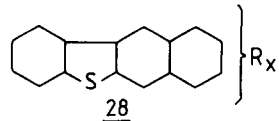

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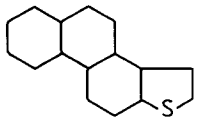
(35)

TABLE I (Continued)



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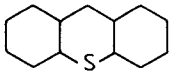

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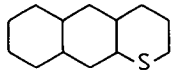

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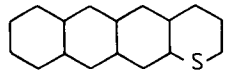

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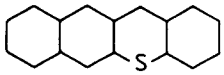

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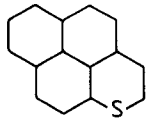

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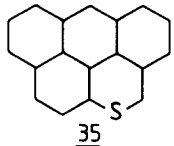

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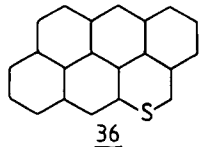

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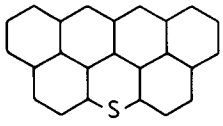

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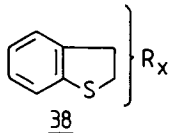

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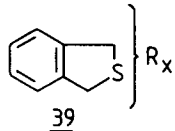
(1, 6, 7, 9, 11, 12, 14, 24, 27, 29–31, 33–38, 45, 57, 64, 90–92, 94, 106)



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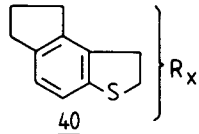

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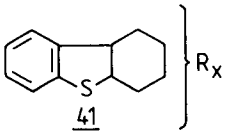

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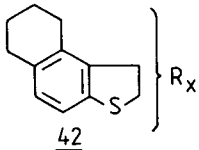

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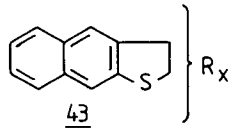

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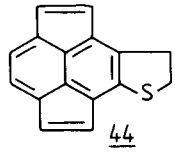

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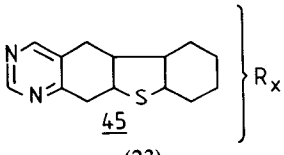

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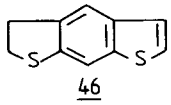

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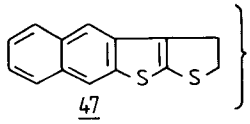

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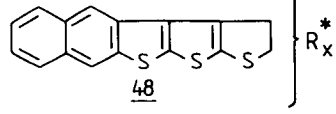
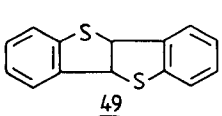


48

(24)

R_x^*: with anellated naphthene rings and sidechains



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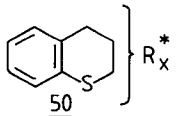
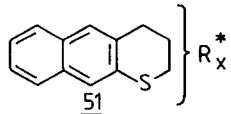


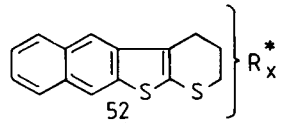
50

(24)



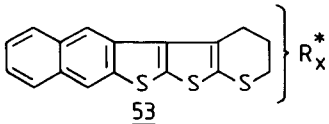
51

(24)



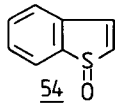
52

(24)



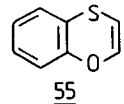
53

(24)



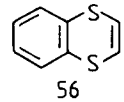
54

(38)



55

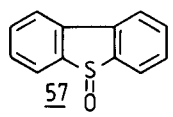
(38)

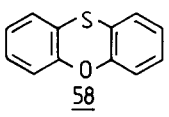


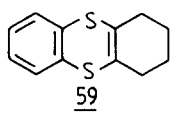
56

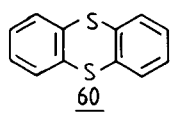
(38)

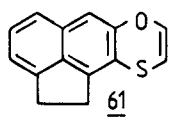
TABLE I (Continued)

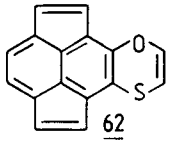

57
(38)

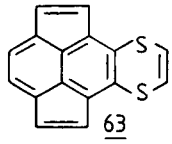

58
(38)

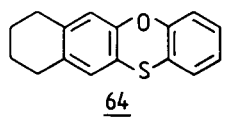

59
(38)

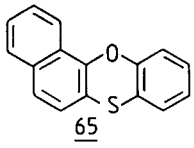

60
(38)

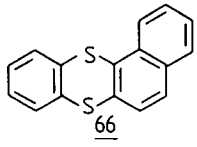

61
(38)

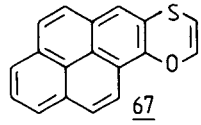

62
(38)

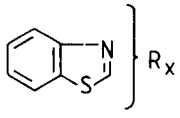

63
(38)


64
(38)


65
(38)


66
(38)


67
(38)


68
(10, 25)

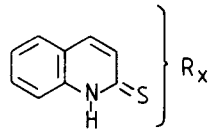

69
(26)

TABLE II

Anellated Thiophenes 70 in Fossil Fuels

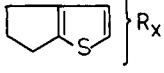
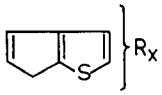
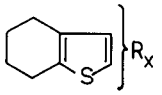
STRUCTURE	R_x	ID	ORIGIN	REF.
	H, Me	d	syncrude	25
	H, alkyl	d	crude oil	9, 24, 27
	H, Me, Et, Pr, Bu	d	syncrude	25
	H, alkyl	d	crude oil	9, 27, 39
	H, alkyl and OH	d	syncrude	40
	H	d	crude oil	28
	H	d	syncrude	41
	H, alkyl	d	crude oil	36

TABLE II (Continued)

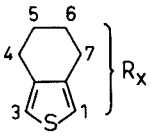
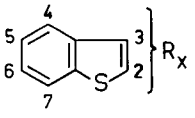
STRUCTURE	R_x	ID	ORIGIN	REF.
	1,4,4-Me_3	b	crude oil	6, 7, 11, 12, 42
	H	a	crude oil	1, 7, 9, 11, 12, 17, 43, 88
	H	a	oil shale	11, 44, 88
	H	a	syncrude	45
	2-Me	a	crude oil	1, 6, 7, 11, 13, 17, 61, 91
	2-Me	a	oil shale	44
	2-Et	a	oil shale	44
	2-Et	b	crude oil	1, 6, 7
	2-Ph	b, c	oil shale	46, 68
	2—(5-Me—2-thienyl)	b	oil shale	46
	2—(Me—2-thienyl)	b	oil shale	46
	2-benzyl	b	oil shale	46
	2-(—CH_2—2-thienyl)	b	oil shale	46
	3-Me	a, b	crude oil	1, 6, 7, 11, 12, 17
	3-Me	a	oil shale	44
	3-Me	a	syncrude	45
	3-Et	b	crude oil	1, 6, 7
	2,3-Me_2	b	crude oil	1, 6, 7
	2-Me, 3-Ph	b	oil shale	46
	2-Me, 3-Et	b	crude oil	1, 6, 7
	2-Ph, 3-Me	b	oil shale	46
	4-Me	a	oil shale	44
	4-Me	b	crude oil	1, 7
	4-Pr	b	crude oil	1, 7
	2,4-Me_2	a	oil shale	44
	2,4-Me_2	b	crude oil	1, 6, 7
	2-Me, 4-Et	b	crude oil	1, 7
	2-Et, 4-Me	b	crude oil	1, 7
	5-Et	a	oil shale, syncrude	45
	5-Pr	b	crude oil	1, 7

TABLE II (Continued)

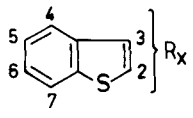
STRUCTURE	R_X	ID	ORIGIN	REF.
	2,5-Me_2	b	crude oil	1, 6, 7
	2-Me, 5-Et	b	crude oil	1, 7
	2-Et, 5-Me	b	crude oil	1, 7
	6-Me	a	oil shale	44
	2,6-Me_2	a	oil shale	44
	2,6-Me_2	b	crude oil	1, 6, 7
	7-Me	a	crude oil	1, 6, 7, 11
	7-Me	a	oil shale	44
	7-Pr	b	crude oil	1, 7
	2, 7-Me_2	a	oil shale	44
	2,7-Me_2	b	crude oil	1, 6, 7
	2-Me, 7-Et	b	crude oil	1, 7
	2-Et, 7-Me	b	crude oil	1, 7
	3,5-Me_2	a	oil shale	44
	3-Et, 5-Me	b	crude oil	1, 7
	3,6-Me_2	b	crude oil	1, 6, 7
	3-Et, 6-Me	b	crude oil	1, 7
	3, 7-Me_2	b	crude oil	1, 6, 7
	3-Et, 7-Me	b	crude oil	1, 7
	4,7-Me_2	b	crude oil	1, 6, 7
	2,3,5-Me_3	b	crude oil	1, 7
	2,3,6-Me_3	b	crude oil	1, 7
	2,3,7-Me_3	b	crude oil	1, 7
	2,4,7-Me_3	b	crude oil	1, 7
	2,4,5,6-Me_4	c	oil shale	47
	3-Et, 5,6-Me_2	c	oil shale	47
	2-(C_9H_{19}—$C_{13}H_{27}$), (4-7)Me	b	oil shale	46
	2-Me, 3-(Me-phenyl)	b	oil shale	46
	2-Me, 3-Ph, (4-7)Me	b	oil shale	46
	(2-3)C_7H_{15}—$C_{10}H_{21}$, (4-7)Me	b	oil shale	46
	2-Ph, (3-7)Et	b	oil shale	46
	2-(Me-phenyl) (4-7)Me	b	oil shale	46
	2-(5-Me-2-thienyl), (4-7)Me	b	oil shale	46

TABLE II (Continued)

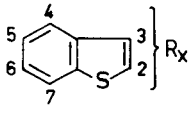
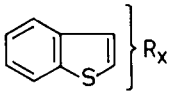
STRUCTURE	R_X	ID	ORIGIN	REF.
	2-(Me-2-thienyl), (4-7)Me	b	oil shale	46
	3-(Me-2-thienyl), (4-7)Me	b	oil shale	46
	3-(Et-2-thienyl), (4-7)Me	b	oil shale	46
	H, Me, Et	d	crude oil	59
	H, Me, Et	d	coal extract	58
	H, Me, Et, Pr, Bu	d	crude oil	61
	H, Me—C_5H_{11} and Ph	d	crude oil	60
	H, Me (isomers),	d	tar sand	62
	Me_2 (isomers), Me_3, Me and Et (isomers), Me and vinyl, Me, Et and Pr, Me_2 and Et, Me_2 and Pr, Et and vinyl, Et_2, C_5H_{11}—$C_{11}H_{23}$ (with C_5H_{11} and C_7H_{15} isomers)			
	H, Me, Me_2, naphthyl, Me and naphthyl	d	syncrude	41
	H, Me, Pr, Bu and pyridyl	d	crude oil	60
	H, Me and OH,	d	syncrude	25
	Et, Pr and OH, Et and $(OH)_2$			
	Me, Et, Pr	d	oil shale	57
	Me—$C_{20}H_{41}$	d	syncrude	25
	Et, Pr	d	coal extract	89
	Pr—C_5H_{11}	d	syncrude	56
	Pr—$C_{27}H_{55}$	d	oil shale	51
	n-C_4H_9, n-C_5H_{11}, n-C_6H_{13}, n-C_7H_{15}	d	oil shale	47
	Bu—$C_{24}H_{49}$	d	crude oil	51
	C_5H_{11}—$C_{17}H_{35}$	d	crude oil	38
	C_5H_{11}—$C_{27}H_{55}$	d	crude oil	54

TABLE II (Continued)

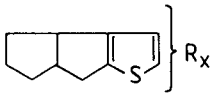
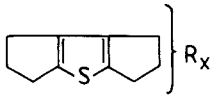
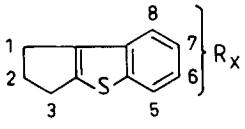
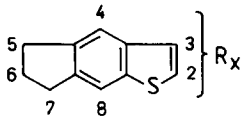
STRUCTURE	R_X	ID	ORIGIN	REF.
	$C_{15}H_{31}$—$C_{31}H_{63}$	d	crude oil	29
	$C_{22}H_{45}$ and Ph	d	crude oil	50
	$C_{10}H_{21}$ and COOH	d	crude oil	6, 63
	H, alkyl	a–d	crude oil, oil shale	48
	H, alkyl	d	crude oil	9, 14, 24, 27, 30–34, 36, 37, 39, 49, 52, 64, 88, 106
	H, alkyl	d	syncrude	53, 55, 65
	H, alkyl	d	coal extract	90
	H, alkyl and OH, $(OH)_2$	d	syncrude	40
	H, alkyl	d	crude oil	24
	H, alkyl	d	crude oil	9, 24, 27, 106
	5- or 8-Et	c	oil shale	47
	H, Me, Et, Pr	d	crude oil	60
	H, Me-$C_{17}H_{35}$	d	syncrude	25
	H, Me-C_7H_{15} and OH	d	coal extract	58
	Et, Pr, Bu	d	syncrude	56
	Et, Pr, Bu, C_6H_{13}, C_9H_{19}—$C_{12}H_{25}$, $C_{14}H_{29}$	d	crude oil	38
	H, alkyl	d	crude oil	24, 39, 52
	H, alkyl	d	syncrude	40, 53
	H, alkyl and OH	d	syncrude	40
	Pr—$C_{23}H_{47}$	d	crude oil	51
	Pr—$C_{24}H_{49}$	d	crude oil	54
	C_5H_{11}—C_8H_{17}	d	oil shale	46
	H, alkyl	d	crude oil	9, 14, 27, 30, 33, 36, 37, 66, 106
	H, alkyl	d	syncrude	55, 65

TABLE II (Continued)

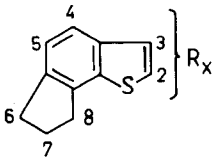
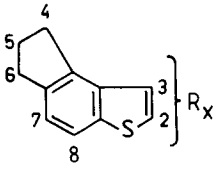
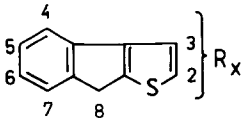
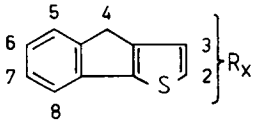
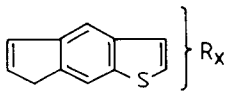
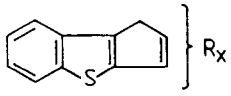
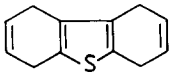
STRUCTURE	R_x	ID	ORIGIN	REF.
	2-Me	a	oil shale	47, 67
	C_5H_{11}—C_8H_{17}	b	oil shale	46
	C_5H_{11}—C_8H_{17}	b	oil shale	46
	(2-3)Bu—C_6H_{13}, (4-7)Me_2	b	oil shale	46
	H, Me—C_5H_{11}	d	coal extract	58
	H, Me—$C_{17}H_{35}$	d	syncrude	25
	Et, Bu, C_5H_{11}	d	syncrude	56
	H, alkyl	d	crude oil	39, 66
	(2-3)Bu—C_6H_{13}, (5-8)Me	b	oil shale	46
	H, Me—$C_{17}H_{35}$	d	syncrude	25
	Et—C_7H_{15}	d	crude oil	24
	H, alkyl	d	crude oil	52, 66
	H, alkyl	d	syncrude	40
	H, Me—$C_{17}H_{35}$	d	syncrude	25
	Et—C_7H_{15}	d	crude oil	24
	Et, Bu, $C_{11}H_{23}$	d	crude oil	38
	H, alkyl	d	crude oil	52, 66
	H, alkyl	d	syncrude	40
	H, C_6H_{13},	d	crude oil	38
	C_9H_{19}—$C_{15}H_{31}$			
	H, alkyl	d	crude oil	9, 27
		d	syncrude	69

TABLE II (Continued)

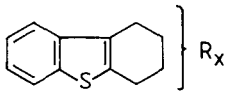
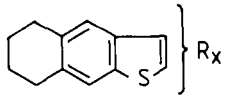
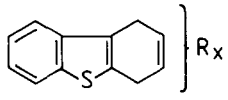
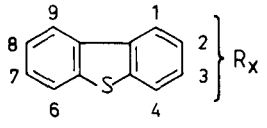
STRUCTURE	R_X	ID	ORIGIN	REF.
	Me—$C_{25}H_{51}$	d	crude oil	35
	C_6H_{13} and COOH, $C_{12}H_{25}$ and COOH	d	crude oil	6, 63
	H, alkyl	d	crude oil	49
	$C_{15}H_{31}$—$C_{28}H_{57}$	d	crude oil	29
	H, alkyl	d	crude oil	31, 32, 34, 63
	H, alkyl	d	syncrude	55
	H	a	crude oil	1, 6, 7, 11, 12, 70–73, 88, 108
	H	a	oil shale	45, 47, 68, 88
	H	a	syncrude	45, 69, 88, 104, 105
	H	a	coal extract	89, 96
	1-Me	a	crude oil	108
	1-Me	a	coal extract	107
	2-Me	a	crude oil	108
	2-Me	a	coal extract	107
	2-Me	b	crude oil	1, 6, 7, 12
	2-Me	c	crude oil	71, 72
	3-Me	a	crude oil	108
	3-Me	a	coal extract	107
	4-Me	a	crude oil	7, 11, 12, 71, 72, 77, 78, 108
	4-Me	a	coal extract	107
	4-Me	b	crude oil	1, 6, 7
	4,6-Me_2	a	crude oil	6, 7, 9, 11–13, 71, 77–79
	4,6-Me_2	c	crude oil	71, 72
	2,4,6,8-Me_4	a	crude oil	7, 11, 12, 71, 80
	2,4,7,8-Me_4	a	crude oil	7, 11, 12, 80
	3,4,6,7-Me_4	a	crude oil	7, 11, 12, 71, 81, 91
	3,4,7,8-Me_4	a	crude oil	7, 11, 12, 80
	Me	c	oil shale	47
	Et	b	oil shale	46

TABLE II (Continued)

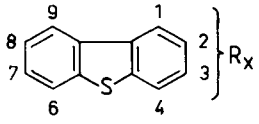
STRUCTURE	R_x	ID	ORIGIN	REF.
	Me_2	b	oil shale	46
	Me_3, Me_4	c	crude oil	80
	Me, iPr	b	oil shale	46
	Me_2, Et (isomers)	b	oil shale	46
	Me_2, Pr (isomers)	b	oil shale	46
	H	d	crude oil	74
	H	d	syncrude	75, 76
	H	d	tarsand	62
	H, Me	d	syncrude	41
	H, Me, Et, Pr	d	crude oil	59
	H, Me, Et, Pr	d	oil shale	57
	H, Me, Et, Pr	d	syncrude	69
	H, Me—$C_{15}H_{31}$	d	syncrude	25
	H, Me—$C_{16}H_{33}$	d	crude oil	24
	H, Me—$C_{20}H_{41}$	d	crude oil	29
	H, Me, Et, Pr, Bu and OH	d	syncrude	25
	Me	d	crude oil	70
	Me	d	coal extract	89, 96
	Me_2	d	crude oil	108
	Me_2	d	coal extract	96, 107
	Me (isomers), Me_2 (isomers)	d	syncrude, oil shale	45
	Me (isomers), Me_2 (isomers), Et (isomers)	d	syncrude	75
	Me_3	d	coal extract	107
	Me, Me_2, Me_3	d	tarsand	62
	Me—C_5H_{11}	d	syncrude	104
	Me—$C_{18}H_{37}$	d	oil shale	51
	Me—$C_{23}H_{47}$	d	crude oil	51
	Me, Pr, $C_{18}H_{37}$, $C_{20}H_{41}$—$C_{23}H_{47}$	d	crude oil	38
	Me—$C_{31}H_{63}$	d	crude oil	54
	Pr, Bu	d	syncrude	56

TABLE II (Continued)

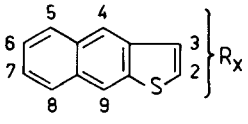
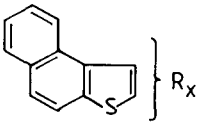
STRUCTURE	R_X	ID	ORIGIN	REF.
	$C_{10}H_{21}$,$C_{11}H_{23}$	d	crude oil	50
	Et, Pr and $(OH)_2$	d	syncrude	25
	C_9H_{19} and COOH	d	crude oil	6, 63
	H, alkyl	d	crude oil	9, 14, 27, 30–34, 37, 39, 49, 52, 61, 64, 66, 92, 106
	H, alkyl	d	syncrude	40, 53, 55, 65
	H, alkyl	d	coal extract	90
	H, alkyl and OH, $(OH)_2$	d	syncrude	40
	H	b, c	oil shale	68
	H	c	oil shale	47
	2-Me	b, c	oil shale	68
	2-Et	b	oil shale	46
	2-Me, (5-8)Me	b	oil shale	46
	2-Et, (5-8)Me	b	oil shale	46
	3-Et, (5-8)Me	b	oil shale	46
	2,3-Me_2, (5-8)Me	b	oil shale	46
	2-Me, (5-8)Me_2	b, c	oil shale	46
	2-Et, (5-8)Me	b, c	oil shale	46
	2-Et, (5-8)Et	b, c	oil shale	46
	Et	d	syncrude	75
	H, Me—$C_{16}H_{33}$	d	crude oil	24
	H, alkyl	d	crude oil	64
	H, alkyl	d	syncrude	65
	H	a	oil shale, syncrude	45
	H	c	oil shale	47
	Me, Et	c	oil shale	46
	C_5H_{11}—C_7H_{15} and Ph	d	crude oil	50

TABLE II (Continued)

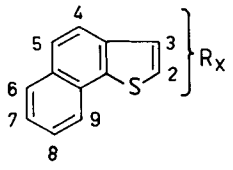
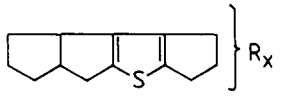
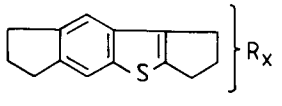
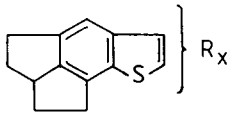
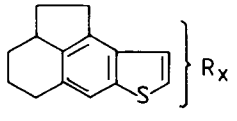
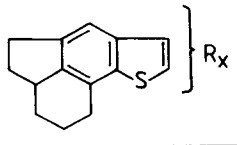
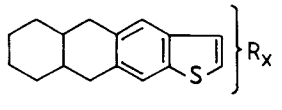
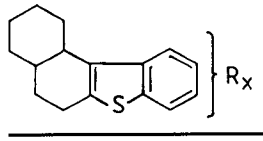
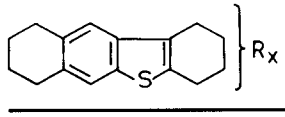
STRUCTURE	R_X	ID	ORIGIN	REF.
	H	a	oil shale, syncrude	45
	H	c	oil shale	47
	2-Me, (6-9)Me	b, c	oil shale	46
	2-Et, (6-9)Me	b, c	oil shale	46
	3-Me, (6-9)Me_2	b, c	oil shale	46
	3-Et, 6,8-Me_2	b, c	crude oil	6, 7, 11, 80, 91
	H, alkyl	d	crude oil	24
	H, Me and OH	d	syncrude	25
	H, Me—$C_{23}H_{47}$	d	crude oil	54
	Me—$C_{19}H_{39}$	d	crude oil	51
	H, alkyl	d	crude oil	14, 24, 30, 33, 36, 37, 52, 106
	H, alkyl	d	crude oil	32, 34
	H, alkyl	d	crude oil	64
	H, alkyl	d	crude oil	31
	H, alkyl	d	crude oil	49
	Et and COOH	c, d	crude oil	6, 63

TABLE II (Continued)

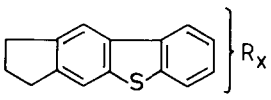
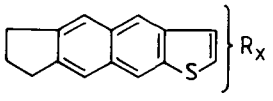
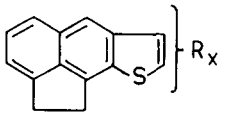
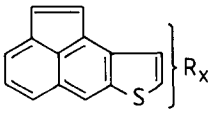
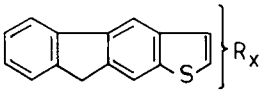
STRUCTURE	R_x	ID	ORIGIN	REF.
	H, Me, Et, Pr, Bu	d	crude oil	60
	H, Me—C_8H_{17}	d	crude oil	24
	H, Me—$C_{17}H_{35}$	d	crude oil	29
	H, Me—$C_{30}H_{61}$	d	crude oil	54
	Et—$C_{16}H_{33}$	d	crude oil	51
	H, alkyl	d	crude oil	9, 14, 27, 52, 106
	H, alkyl	d	syncrude	53, 55, 82
	H, Me—C_8H_{17}	d	crude oil	24
	H, alkyl and OH, $(OH)_2$	d	syncrude	40
	H, Me—C_5H_{11}	d	crude oil	60
	H, Me—C_5H_{11}, C_7H_{15}	d	crude oil	38
	H, Me—$C_{11}H_{23}$	d	syncrude	25
	H, Me, Et and OH	d	syncrude	25
	H, alkyl	d	crude oil	27, 30, 33, 37, 39, 66
	H, alkyl	d	syncrude	40
	H, alkyl	d	coal extract	90
	H	d	crude oil	38
	H, Me—C_6H_{13}	d	crude oil	24
	H, Me—$C_{14}H_{29}$	d	syncrude	25
	H, Me—$C_{18}H_{37}$	d	crude oil	29
	H, alkyl	d	crude oil	9, 27
	H, alkyl	d	syncrude	82
	H, alkyl	d	coal extract	90
	H, Me—C_5H_{11}	d	crude oil	60
	H, Me—C_6H_{13}	d	crude oil	24
	H, Me—$C_{13}H_{27}$	d	syncrude	25
	H, Me, Et, Pr and OH	d	syncrude	25
	Pr-C_{11} H_{23}	d	crude oil	51
	H, alkyl	d	crude oil	30, 33, 64, 106
	H, alkyl	d	syncrude	40
	H, alkyl and OH, $(OH)_2$	d	syncrude	40

TABLE II (Continued)

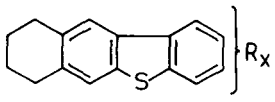
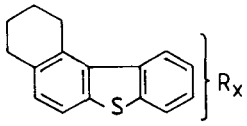
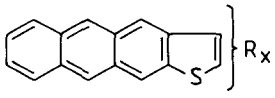
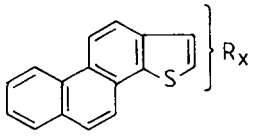
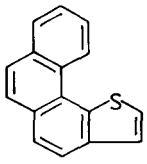
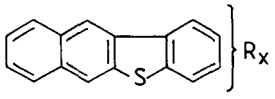
STRUCTURE	R_X	ID	ORIGIN	REF.
	H, alkyl	d	crude oil	32
	H, alkyl	d	crude oil	49
	H	d	syncrude	76
	H, Me—C_5H_{11}	d	crude oil	60
	H, Me—C_6H_{13}	d	crude oil	24
	H, alkyl	d	crude oil	39
	H, alkyl	d	syncrude	82
	H	a	oil shale, syncrude	45
	H, Me—C_5H_{11}	d	crude oil	60
	H, Me—C_6H_{13}	d	crude oil	24
	H, Me—$C_{12}H_{25}$	d	syncrude	25
	Me, Et and OH, $(OH)_2$	d	syncrude	25
	H, alkyl	d	crude oil	39
	H, alkyl	d	syncrude	53, 55, 82
		a	oil shale, syncrude	45
	H	a	oil shale	45
	H	a	syncrude	45, 104
	H	d	crude oil	38, 74
	H, Me	d	crude oil	70
	H, Me	d	syncrude	75
	H, Me, Et	d	syncrude	69
	H, Me—C_5H_{11}	d	crude oil	60
	H, Me—C_6H_{13}	d	crude oil	24

TABLE II (Continued)

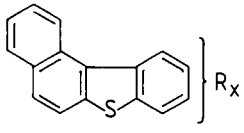
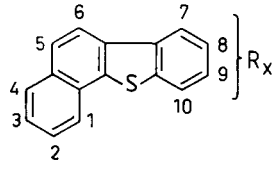
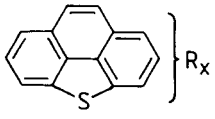
STRUCTURE	R_x	ID	ORIGIN	REF.
	Me, Me_2	d	crude oil	85
	Et—$C_{11}H_{23}$	d	crude oil	51
	C_9H_{19} and COOH	d	crude oil	6, 63
	H, alkyl	d	crude oil	22, 32–34, 106
	H, alkyl	d	coal extract	90
	H	a	crude oil	108
	H	a	syncrude	104
	H	d	crude oil	74
	H	d	oil shale, syncrude	45
	H, Me	d	syncrude	75
	H, Me, Et	d	syncrude	69
	H, Me, Et, Pr	d	crude oil	38
	Me, Me_2	d	syncrude	45
	Me, Me_2	d	crude oil	85
	H, alkyl	d	crude oil	49, 50
	H	a	crude oil	6, 7, 11, 12, 70, 73, 74, 77, 78, 80, 84–86, 88, 91, 108.
	H	a	oil shale	45
	H	a	syncrude	45, 75, 104
	1-Me	a	crude oil	6, 87
	4-Me	a	crude oil	6, 87
	10-Me	a	crude oil	6, 87
	Me, Et, Pr, Bu	d	syncrude	104
	H, alkyl	d	crude oil	9, 27, 29, 50, 92
	H	a	crude oil	70, 83, 108
	H	a	syncrude	104
	H	c	coal extract	89, 90
	H	d	crude oil	73, 88
	H	d	oil shale	45, 57
	H	d	syncrude	41, 45, 69, 88
	Me	d	oil shale	45
	Me	d	syncrude	45, 69, 104
	Ph	d	crude oil	73

TABLE II (Continued)

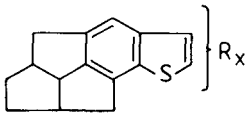
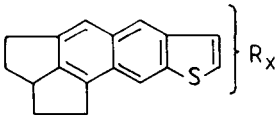
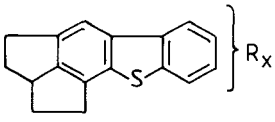
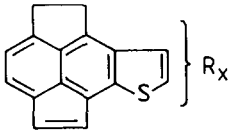
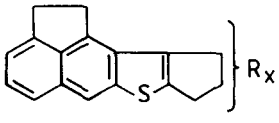
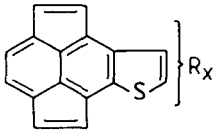
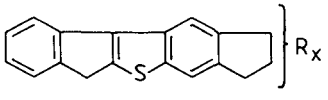
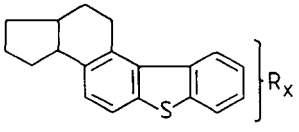
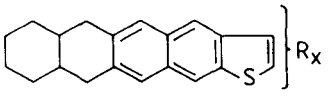
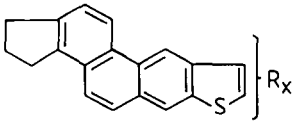
STRUCTURE	R_x	ID	ORIGIN	REF.
	H, Me, Et	d	crude oil	29
	Et—$C_{19}H_{39}$	d	crude oil	51
	H, alkyl	d	crude oil	24, 52, 54
	H, Me—C_7H_{15}	d	crude oil	24
	H, Me—C_7H_{15}	d	crude oil	24
	H, Me-$C_{13}H_{27}$	d	crude oil	51
	H, alkyl	d	crude oil	52, 54
	H, alkyl	d	syncrude	55
	H, Me-C_6H_{13}	d	crude oil	24
	H, Me, Et, Pr	d	crude oil	60
	H	d	crude oil	22
	H, Me, Et, Pr	d	crude oil	24
	H, Et, Pr, Bu, C_5H_{11}	d	crude oil	38
	H, alkyl	d	crude oil	9, 27
	H, Me—C_6H_{13}	d	crude oil	24
	H, alkyl	d	crude oil	49
	H, alkyl	d	crude oil	32
	H, Me, Et, Pr, Bu	d	crude oil	24, 60
	H, alkyl	d	syncrude	53

TABLE II (Continued)

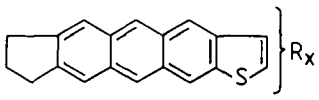
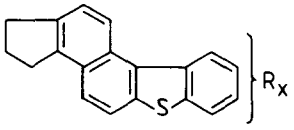
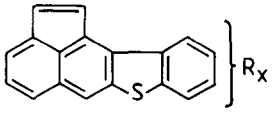
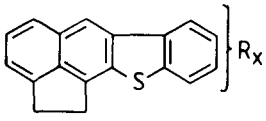
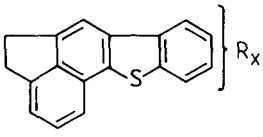
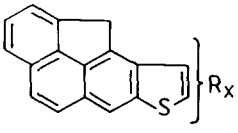
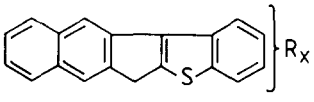
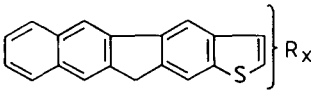
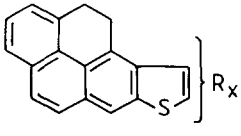
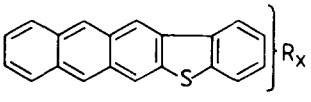
STRUCTURE	R_x	ID	ORIGIN	REF.
	H, Me, Et, Pr, Bu	d	crude oil	24
	H, alkyl	d	crude oil	39
	H, alkyl	d	crude oil	49
	H, Me—C_5H_{11}	d	crude oil	60
	H, Me—C_5H_{11}	d	crude oil	60
	Et—C_8H_{17}	d	crude oil	51
	H, alkyl	d	crude oil	30, 33, 34, 38, 52
	H, alkyl	d	crude oil	29
	H, Me—$C_{11}H_{23}$	d	syncrude	25
	H, alkyl	d	syncrude	55
	H, alkyl	d	crude oil	24
	H, alkyl	d	crude oil	24
	Et, Pr and OH	d	syncrude	25
	H, Me	d	crude oil	24

TABLE II (Continued)

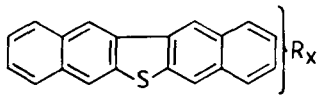
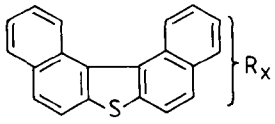
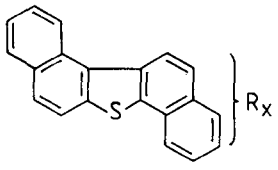
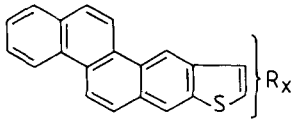
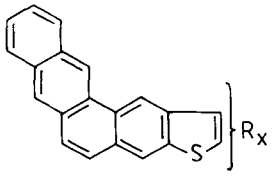
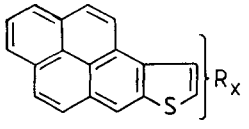
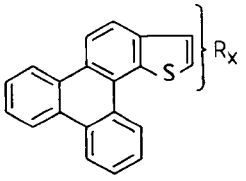
STRUCTURE	R_X	ID	ORIGIN	REF.
	H,	d	syncrude	76
	H, Me	d	crude oil	24
	H, Me	d	syncrude	41
	H, Me, Et, Pr, Bu	d	crude oil	60
	H, alkyl	d	crude oil	52, 64
	H, Me	d	crude oil	24
	H, alkyl	d	crude oil	38
	H, Me	d	crude oil	24
	$C_{16}H_{33}$	d	crude oil	50
	H, alkyl	d	crude oil	29
	H, Me	d	crude oil	24
	H, Me—C_5H_{11}	d	syncrude	25
	Me, Et, Pr, Bu and OH	d	syncrude	25
	H, alkyl	d	crude oil	39
	H, Me	d	crude oil	24
	H	a	crude oil	83
	H, Me	d	crude oil	24
	H, Me, Et, Pr, Bu	d	crude oil	38
	H, Me, Et, Pr, Bu, C_5H_{11}	d	crude oil	60
	H, Me, Et and OH	d	syncrude	25
	H, alkyl	d	crude oil	9, 22, 27, 29, 39
	H, Me	d	crude oil	24

TABLE II (Continued)

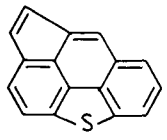
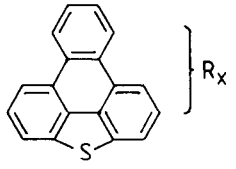
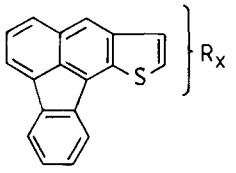
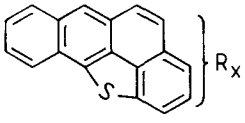
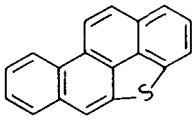
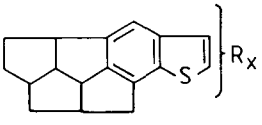
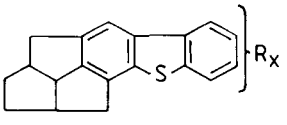
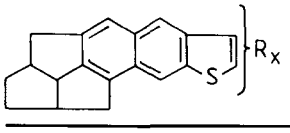
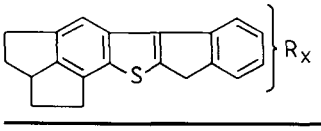
STRUCTURE	R_x	ID	ORIGIN	REF.
		d	crude oil	73
	H	a	crude oil	70, 83, 108
	H	a	syncrude	45, 104
	Me, Me_2	d	crude oil	108
	H, Me—C_5H_{11}	d	crude oil	60
	H, Me	d	crude oil	24
	H, Me—C_5H_{11}	d	crude oil	60
	H	a	syncrude	104
	Me, Et	d	syncrude	104
		a	syncrude	104
	Et—$C_{17}H_{35}$	d	crude oil	51
	Pr, Bu	d	crude oil	29
	H, alkyl	d	crude oil	24, 52, 54
	H, alkyl	d	crude oil	24, 52, 54
	Me—$C_{10}H_{21}$	d	crude oil	51
	H, alkyl	d	crude oil	24, 52, 54
	H, Me, Et, Pr, Bu	d	crude oil	24

TABLE II (Continued)

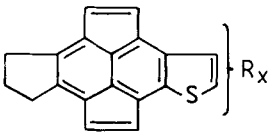
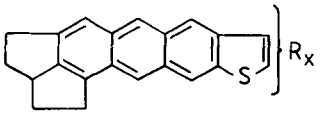
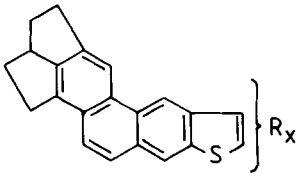
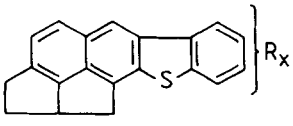
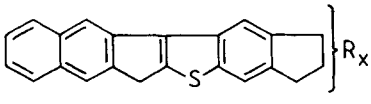
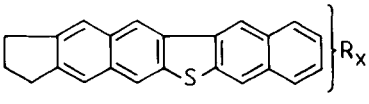
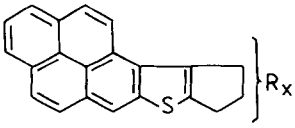
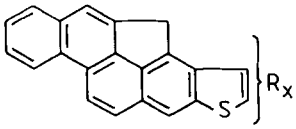
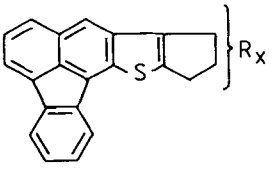
STRUCTURE	R_X	ID	ORIGIN	REF.
	H, alkyl	d	crude oil	24
	H, Me, Et, Pr, Bu	d	crude oil	24
	H, Me, Et, Pr, Bu	d	crude oil	24
	H, alkyl	d	syncrude	53
	H, Me—C_7H_{15}	d	crude oil	51
	H, alkyl	d	crude oil	24, 33, 34, 52
	H, alkyl	d	crude oil	24
	H, alkyl	d	crude oil	52
	H, Me	d	crude oil	24
	H, Me, Et, Pr	d	crude oil	60
	H, Me—C_5H_{11}	d	syncrude	25
	Me, Et, Pr and OH	d	syncrude	25
	H, Me	d	crude oil	24

TABLE II (Continued)

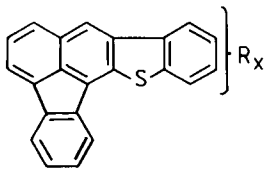
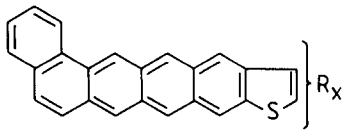
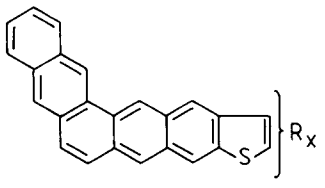
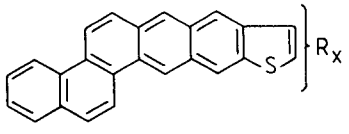
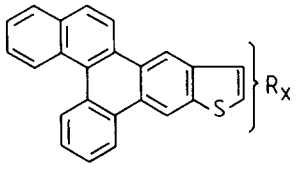
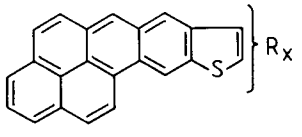
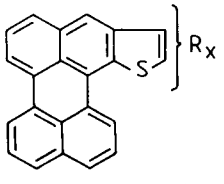
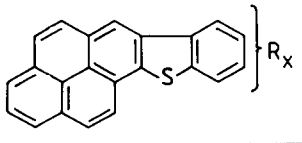
STRUCTURE	R_x	ID	ORIGIN	REF
	H, Me, Et, Pr	d	crude oil	60
	H, alkyl	d	crude oil	24
	H, alkyl	d	crude oil	24
	H, Me, Et H, alkyl	d d	syncrude crude oil	25 24
	H, alkyl	d	crude oil	24
	H, Me H, Me, Et, Pr Me, Et, Pr, Bu H, Me, Et and OH	d d d d	crude oil crude oil syncrude syncrude	24 60 25 25
	H, Me H, alkyl	d d	crude oil syncrude	24 53
	H, alkyl	d	crude oil	29

TABLE II (Continued)

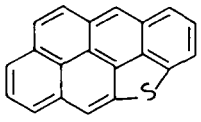
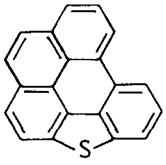
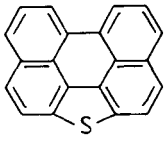
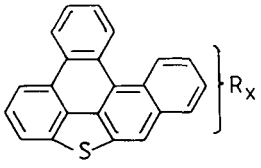
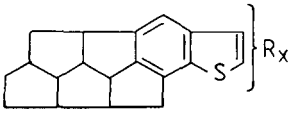
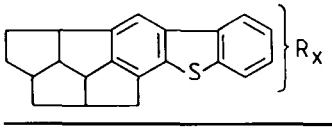
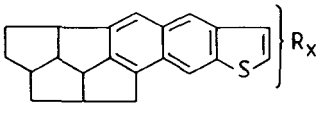
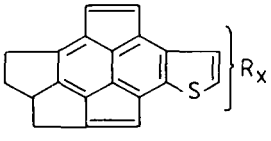
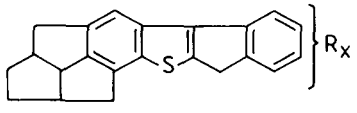
STRUCTURE	R_x	ID	ORIGIN	REF.
		a	crude oil	83
		a	crude oil	83
		d	crude oil	73
	H, Me, Et, Pr	d	crude oil	60
	Et	d	crude oil	29
	Et—$C_{14}H_{29}$	d	crude oil	51
	H, alkyl	d	crude oil	24, 52, 54
	H, alkyl	d	crude oil	24, 51, 52, 54
	H, alkyl	d	crude oil	24
	H, alkyl	d	crude oil	24
	H, Me, Et, Pr, Bu	d	crude oil	24

TABLE II (Continued)

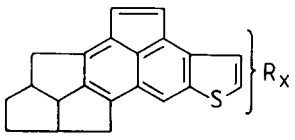
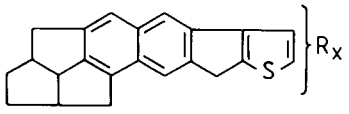
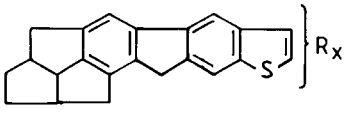
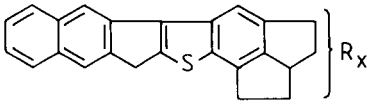
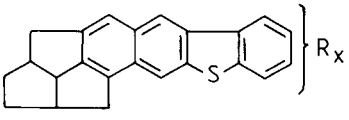
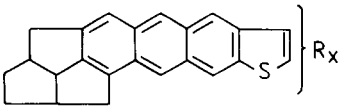
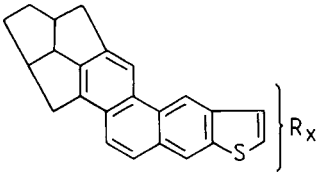
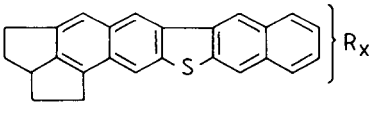
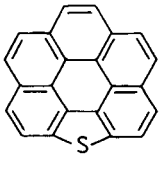
STRUCTURE	R_x	ID	ORIGIN	REF.
	H, Me, Et, Pr, Bu	d	crude oil	24
	H, Me, Et, Pr, Bu	d	crude oil	24
	H, alkyl	d	crude oil	24
	H, alkyl	d	crude oil	24
	H, Me, Et, Pr, Bu H, alkyl	d d	crude oil crude oil	51 52
	H, Me, Et, Pr	d	crude oil	24
	H, Me, Et, Pr H, alkyl	d d	crude oil syncrude	24 53
	H, alkyl	d	crude oil	52
		a d	crude oil crude oil	83 73

TABLE II (Continued)

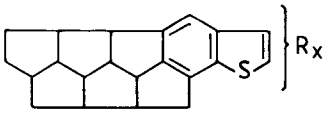
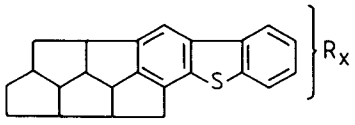
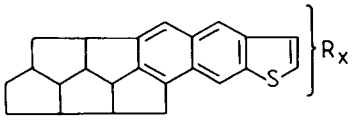
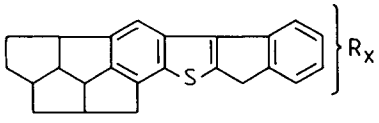
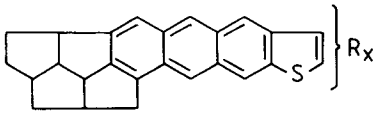
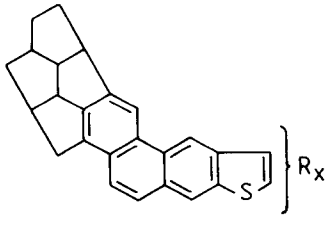
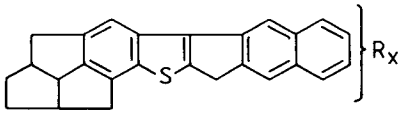
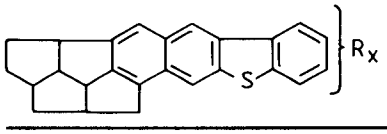
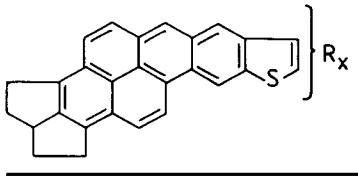
STRUCTURE	R_x	ID	ORIGIN	REF.
	H, alkyl	d	crude oil	54
	H, alkyl	d	crude oil	24, 52, 54
	H, alkyl	d	crude oil	24, 52
	H, Me, Et, Pr	d	crude oil	24
	H, alkyl	d	crude oil	24
	H, alkyl	d	crude oil	24
	H, alkyl	d	crude oil	24
	H, alkyl	d	crude oil	52
	H, alkyl	d	crude oil	52

TABLE II (Continued)

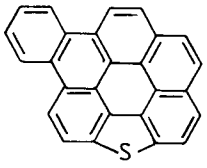
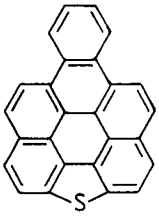
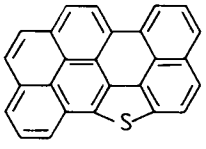
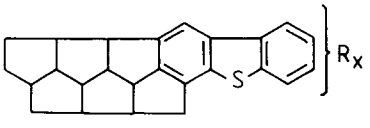
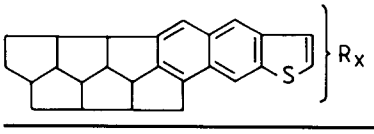
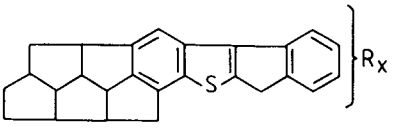
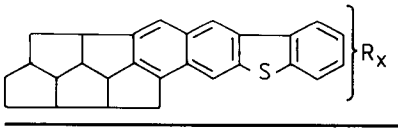
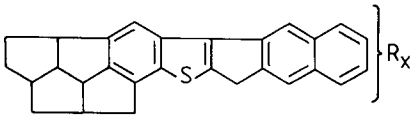
STRUCTURE	R_x	ID	ORIGIN	REF.
		d	crude oil	97
		d	crude oil	97
		d	crude oil	97
	H, alkyl	d	crude oil	24, 54
	H, alkyl	d	crude oil	24
	H, alkyl	d	crude oil	24
	H, alkyl	d	crude oil	52
	H, alkyl	d	crude oil	24

TABLE II (Continued)

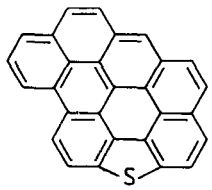
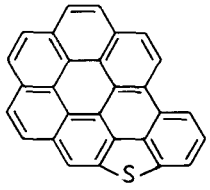
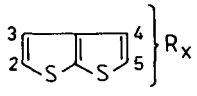
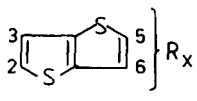
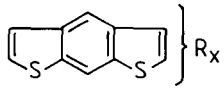
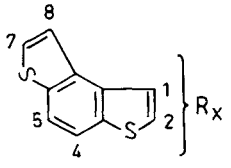
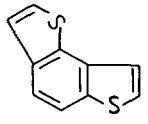
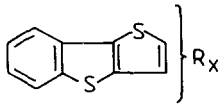
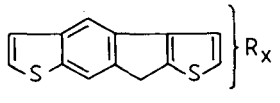
STRUCTURE	R_x	ID	ORIGIN	REF.
		d	crude oil	97
		d	crude oil	97
	3-Me	b	crude oil	1, 6, 7, 11
	(2-5)Me_3, Et	c	oil shale	47
	2-Me	b	crude oil	1, 6, 7, 11
	2,3,6-Me_3, 5-Et	c	oil shale	47
	Me_2	d	oil shale	46
	Et, Pr, Bu	d	syncrude	25
	H, alkyl	d	crude oil	38
	H	c	oil shale	47
	2-Me	b,	oil shale	68
	Me_2	d	oil shale	46
	Me_2 and Pr—C_6H_{13}	c	oil shale	46
		c	oil shale	47
	H, alkyl	d	crude oil	38
	H, alkyl	d	crude oil	24

TABLE II (Continued)

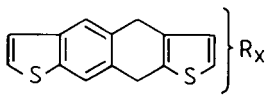
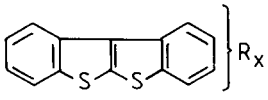
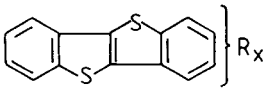
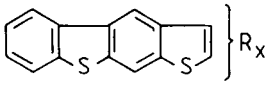
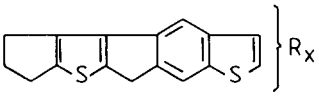
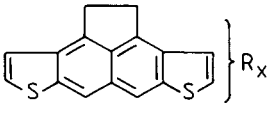
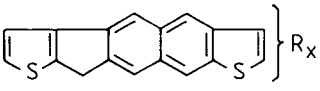
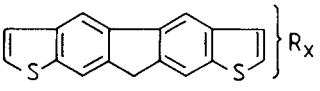
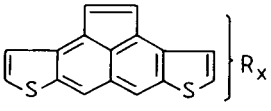
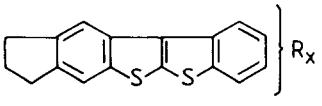
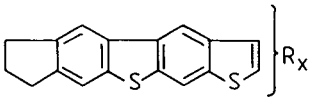
STRUCTURE	R_X	ID	ORIGIN	REF.
	Me, Et	d	syncrude	25
	Me, Et, Pr	d	syncrude	25
	H, alkyl	d	crude oil	29, 39
	Pr	d	crude oil	98
	Pr, Bu	d	crude oil	38
	H, alkyl	d	crude oil	9, 22, 27, 32
	H, Me—C_6H_{13}	d	crude oil	24
	Pr, Bu	d	crude oil	38
	H, alkyl	d	crude oil	24
	Me, Et, Pr	d	syncrude	25
	H, Me—C_6H_{13}	d	crude oil	24
	H, Me—C_6H_{13}	d	crude oil	24
	H, Me—C_9H_{19}	d	syncrude	25
	H, Me—C_6H_{13}	d	crude oil	24
	H, Me—$C_{10}H_{21}$	d	crude oil	25
	H, alkyl	d	crude oil	29
	H, Me, Et, Pr, Bu	d	crude oil	24

TABLE II (Continued)

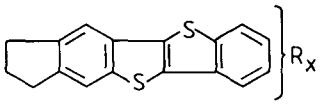
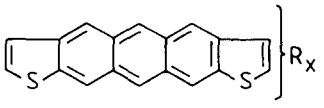
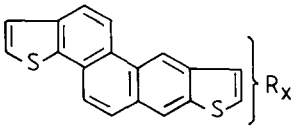
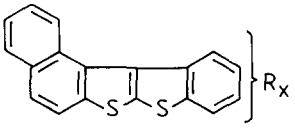
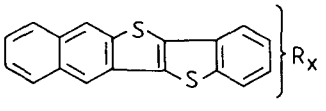
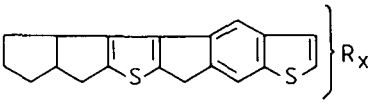
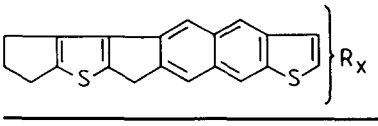
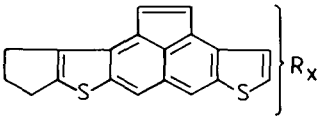
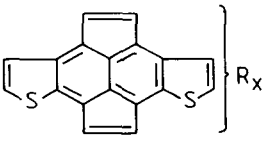
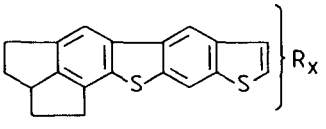
STRUCTURE	R_X	ID	ORIGIN	REF.
	H, alkyl	d	crude oil	98
	H, Me—C_6H_{13}	d	crude oil	24
	H, Me—C_6H_{13}	d	crude oil	24
	H, Me—$C_{12}H_{25}$	d	syncrude	25
	H, Me, Et, Pr	d	crude oil	38
	H, alkyl	d	crude oil	29
	H, alkyl	d	crude oil	9, 27
	H, alkyl	d	crude oil	24
	H, Me—C_6H_{13}	d	crude oil	24
	H, Me—C_6H_{13}	d	crude oil	24
	H, alkyl	d	crude oil	24
	H, Me, Et, Pr	d	crude oil	24

TABLE II (Continued)

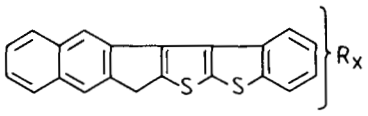
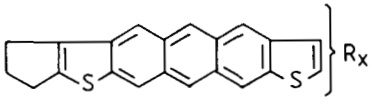
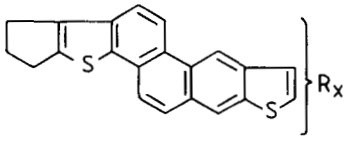
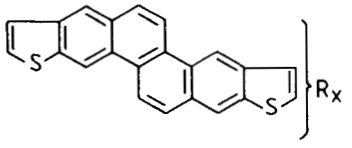
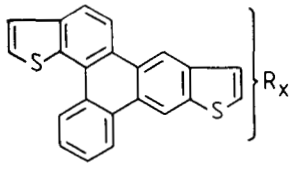
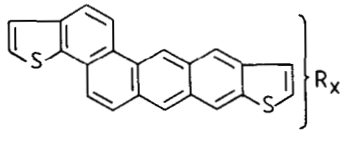
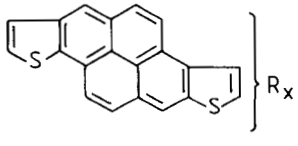
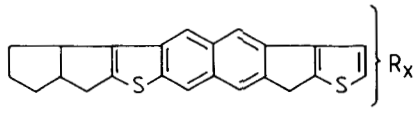
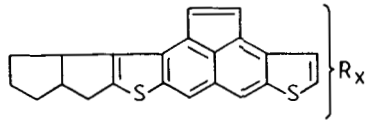
STRUCTURE	R_x	ID	ORIGIN	REF.
	H, alkyl	d	crude oil	24
	H, Me, Et, Pr, Bu	d	crude oil	24
	H, alkyl	d	crude oil	52
	H, Me, Et, Pr, Bu	d	crude oil	24
	$Me—C_{10}H_{21}$	d	syncrude	25
	H, alkyl	d	crude oil	52
	H, Me, Et	d	syncrude	25
	H, alkyl	d	crude oil	24
	H, alkyl	d	crude oil	24
	H, alkyl	d	crude oil	24
	$Et—C_8H_{17}$	d	syncrude	25
	H, Me, Et, Pr, Bu	d	crude oil	24
	H, Me, Et, Pr, Bu	d	crude oil	24

TABLE II (Continued)

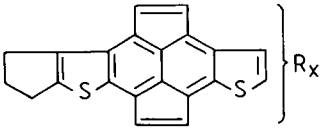
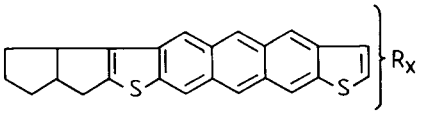
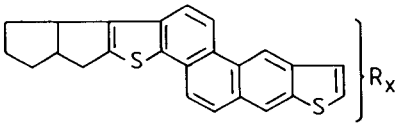
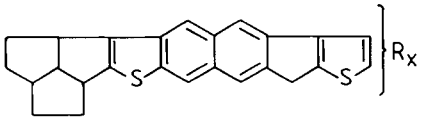
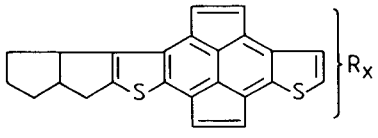
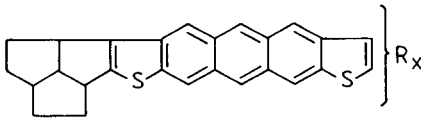
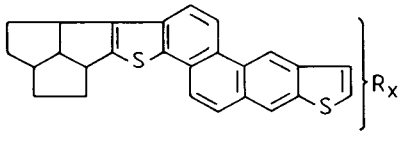
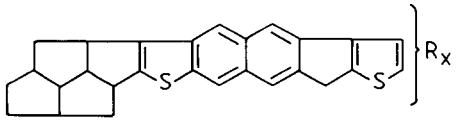
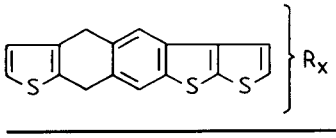
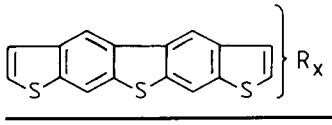
STRUCTURE	R_x	ID	ORIGIN	REF.
	H, alkyl	d	crude oil	24
	H, Me, Et, Pr	d	crude oil	24
	H, alkyl	d	crude oil	52
	H, Me, Et, Pr	d	crude oil	24
	H, alkyl	d	crude oil	52
	H, Me, Et, Pr, Bu	d	crude oil	24
	H, alkyl	d	crude oil	24
	H, Me	d	crude oil	24
	H, Me	d	crude oil	24
	H, Me	d	crude oil	24
	Me, Et	d	syncrude	25
	H, Me—C_6H_{13}	d	crude oil	24

TABLE II (Continued)

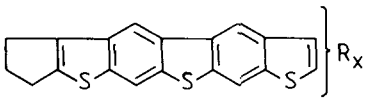
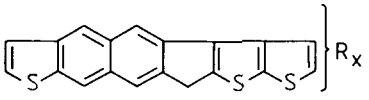
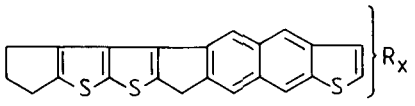
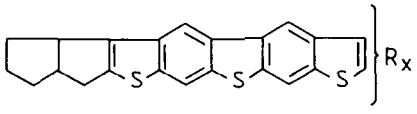
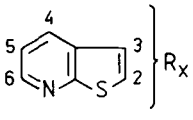
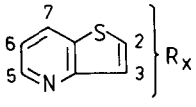
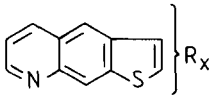
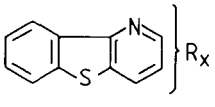
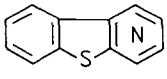
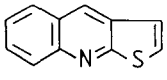
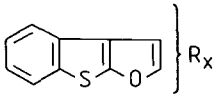
STRUCTURE	R_x	ID	ORIGIN	REF.
	H, Me, Et, Pr	d	crude oil	24
	H, alkyl	d	crude oil	24
	H, alkyl	d	crude oil	24
	H, Me	d	crude oil	24
	6-Me	b	oil shale	99
	5-Me	b	oil shale	99
	$2,5\text{-Me}_2$	b	oil shale	99
	H, alkyl	d	crude oil	100, 101
	H, alkyl	d	crude oil	100
		b, d	crude oil	102
		d	crude oil	103
	Pr, Bu	d	syncrude	25

TABLE II (Continued)

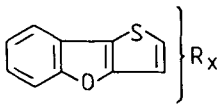
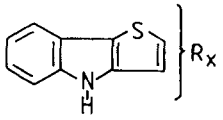
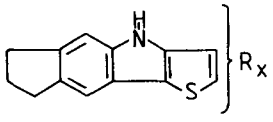
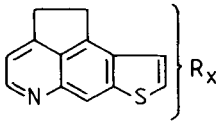
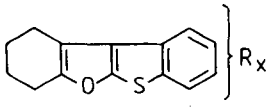
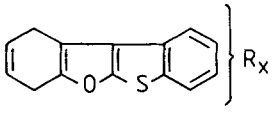
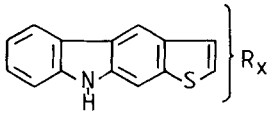
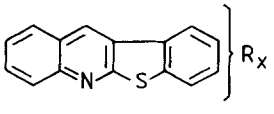
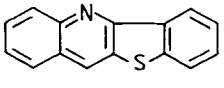
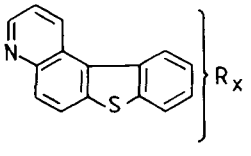
STRUCTURE	R_x	ID	ORIGIN	REF.
	H, alkyl	d	crude oil	38
	H, Me—C_5H_{11}	d	coal extract	58
	H, alkyl	d	crude oil	100
	H, alkyl	d	crude oil	100
	H, Me, Pr, Bu	d	crude oil	60
	H, alkyl	d	syncrude	25
	Me, Et, Pr	d	syncrude	25
	H, Me, Et, Pr	d	crude oil	60
	H, alkyl	d	crude oil	101
		d	crude oil	102
	H, alkyl	d	crude oil	23

TABLE II (Continued)

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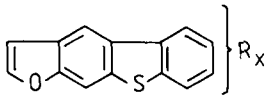
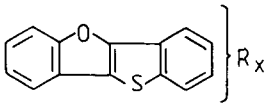
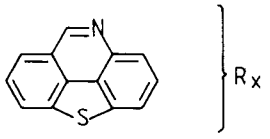
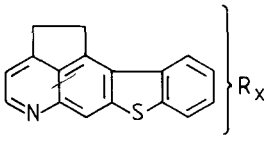
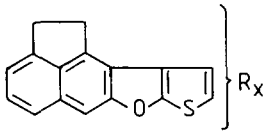
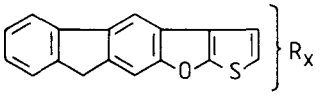
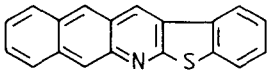
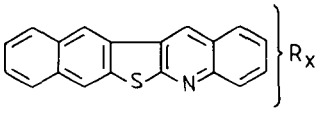
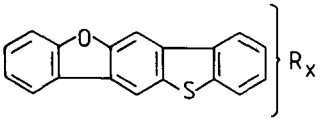
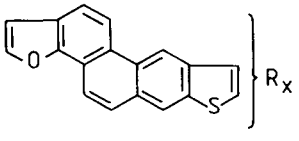
	Me, Et, Pr	d	syncrude	25
	H, alkyl	d	crude oil	38
	Pr—C_6H_{13}	d	syncrude	25
	H, Me, Et	d	crude oil	60
	H, Me—C_5H_{11}	d	syncrude	25
	H, Me, Et, Pr	d	syncrude	25
		d	crude oil	103
	H, Me, Et, Pr	d	syncrude	25
	H, alkyl	d	crude oil	100
	H, Me, Et	d	syncrude	25

TABLE II (Continued)

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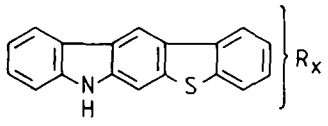
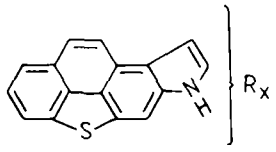
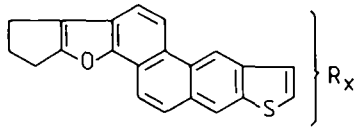
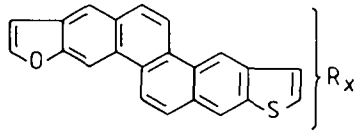
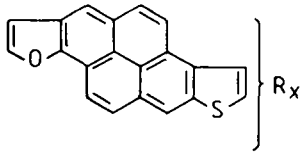
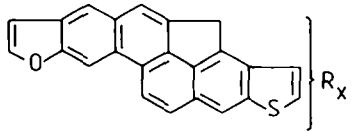
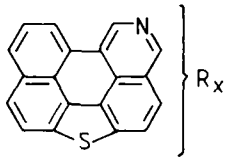
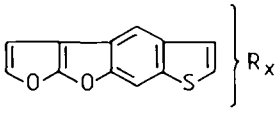
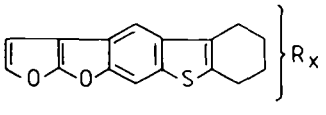
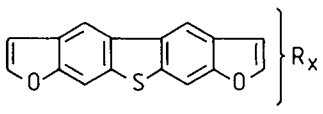
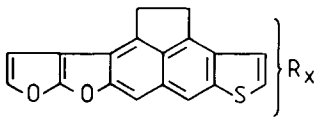
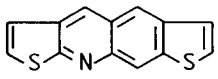
	H, alkyl	d	crude oil	23
	H, Me, Et, Pr	d	crude oil	60
	H, Me, Et	d	syncrude	25
	H, Me, Et	d	syncrude	25
	Me, Et	d	syncrude	25
	H, Me, Et, Pr	d	syncrude	25
	Bu, C_5H_{11}	d	syncrude	25
	H, Me, Et	d	syncrude	25
	H, Me, Et	d	syncrude	25

TABLE II (Continued)

STRUCTURE	R_x	ID	ORIGIN	REF.
	H, Me, Et, Pr	d	syncrude	25
	H, Me, Et	d	syncrude	25
		d	crude oil	103

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