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SOME AROMATIC BASIC CONSTITUENTS OF COAL SOOT

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Abstract—Coal soot has been found to contain a complex mixture of aromatic bases which with one exception fit the three homologous series of pyridine, quinoline and indoline bases.

In Ref 1 and earlier papers we described the isolation of nitrophenolic and other compounds from coal soot and now wish to record the isolation of basic compounds from the same source.

The soot has come from coals of different quality and been extracted with warm dilute HCl and the resulting sludge filtered, basified (NaOH) and steam distilled.

On adding NaOH (40%) to the clear distillate a milky solution results from which ether extracts a mixture of aromatic bases giving no positive test for primary or secondary bases. The mixture distils (2 mm) over a wide range of temperature and no effective separation has been effected by chromatography over Al_2O_3 or SiO_2 or by picrate formation from the various fractions.

Mass spectrometry on the lower b.p. fractions gave 13 molecular ions with masses corresponding to pyridine and its methyl homologues whilst the higher b.p. fraction also gave 13 ion values including those corresponding to quinoline and its methyl homologues.

In addition to the pyridine and quinoline series the M.W. values obtained when fractionation is done at 2 mm show the presence of a third series of bases but to a lesser relative extent, whose M.W. values fit the indoline **1** or triazole **2** series.

The bases will have come presumably from the breakdown of the nitrogenous complexes in the coals.

Mass spectrometry shows the basic mixture is very complex but does not distinguish between say the six isomeric dimethylpyridines.

Pyridine can usually be detected by the pink colour given with an acidified solution of *p*-dimethylaminobenzaldehyde and evidence on the presence and position of Me groups in the 2, 4, & 6, positions of the pyridine molecule and the 2 and 4, positions in quinoline can be obtained by making use of their reactivity with aldehydes.

Very valuable help in identifying some of the bases however, has been obtained by a combination of GLC and mass spectrometry techniques as detailed in the Experimental.

Table 2 (M.W. values obtained on an AEI MS9 mass spectrometer) shows that the lutidine, collidine and methyl collidine are the major constituents and the only member which does not fit into the 3 series is one with M.W. value 183 which is present to only a small extent.

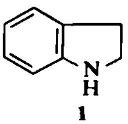
The condensations were most conveniently done with metanitrobenzaldehyde in the presence of acetic anhydride and the reaction products furnish proof for the presence of α-picoline, 2:4-lutidine and of 2:3:4- and 2:3:6-collidine and its monomethylhomologue 2:3:4:6-tetramethylpyridine, and probably of 2:3:4:5:6-pentamethylpyridine. An indication of the possible presence of a C_2 or C_3 substituent to a small extent is given by M.W. 163 and M.W. 167.

The third series. In order to gain an insight into the nature of these compounds the action of potassium on the mixture of bases was examined and two crystalline products obtained. These gave almost identical mass spectra and the C, H, and N values point to an indole complex such as **3**. Accurate mass measurements prove the third series to be indolines.

EXPERIMENTAL

M.W. values. Pyridine (79), picolines (93), lutidines (107) Collidines (121), Quinoline (129), methylquinolines (143).

Extraction. 2 kg of fresh dry soot was stirred wich conc



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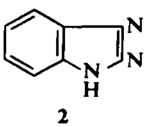

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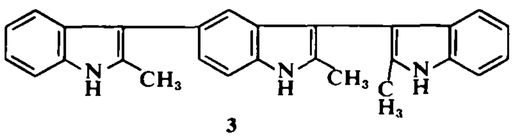

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Table 1

Fraction	GLC peak	% of fraction (as determined by analytical GLC)	Composition as determined by MS–GLC	Composition as determined by preparative GLC and NMR
a	1	24	monomethyl- and dimethylpyridine	2:6 and 3:4 dimethylpyridines in 1:2 ratio
	2	33	dimethylpyridine	2:4 dimethylpyridine (+ some monomethylpyridine)
	3	8	trimethylpyridine	———
	4*	11	trimethylpyridine (+ some dimethyl) pyridine)	mixture of 2, 4, 6 and 2, 3, 6 trimethylpyridine (1:1 ratio) (+ unknowns)
	5*	7	trimethylpyridine (+ some dimethyl) pyridine)	
b	4*	24	*	
	5*	20	*	
	6	3	trimethylpyridine or methylethylpyridine	———
	7	11	tetramethylpyridines (or isomer)	2:4:5 trimethyl and 2:3:4:5 tetramethylpyridine (1:1 ratio)
	8	3	tetramethylpyridines (or isomer)	equivocal result (tetramethylpyridine?)
c	9	4	tetramethylpyridines (or isomer)	
	10	6	tetramethylpyridines (or isomer)	
	11	12	tetramethylpyridines (or isomer)	
	12	8	pentamethyl pyridine (or isomer)	
	13	32	quinoline	quinoline plus at least one other component
	14	7	not identified	
	15	20	methylquinoline	2 methylquinoline
	16	4	methylquinoline	
	17	4	dimethylquinoline	
	18	1	dimethylquinoline	
	19	1	dimethyl or ethylquinoline	
	20	1	dimethyl or ethylquinoline	

*In a and b that appeared to be identical by analytical GLC and GLC–MS.

HCl (200 ml) and hot H_2O (8 l) and filtered after standing 3 hr. The filter cake was stirred with conc HCl (25 ml) and hot H_2O (2 l). The combined filtrates was basified in ½ l lots with NaOH (20 ml of 40%) and steam distilled until 200 ml of distillate was obtained. The addition of NaOH (40%) to the distillate gave a milky suspension from which ether extracted 3 g of bases in all which gave 2·8 g b.p. 25°–125°/2 mm 'A'.

The last trace of distillate gave a mixture of picrates (m.p. 60°–65°) with basic M.W. values 121, 129, 143, 157, 171. Extraction of the residues after steam distillation with C_6H_6 gave 0·33 g b.p. up to 190°/2 m of which only 0·2 g 'B' was soluble in dilute HCl.

Fractionation of 'A'. This gave 0·19 g b.p. 23–25°/2 mm, fr I; 0·53 g, b.p. 65°–70°/2 mm, fr II; 0·71 g b.p. 80°–5°/2 mm fr III; and 1·1 g b.p. up to 125°/2 mm fr IV.

A similar batch of bases 'A' when distilled at 12 mm gave approx. equal amounts of fractions 'a', 'b' and 'c' bp b.p. 80°–90°, and up to 140° with appreciable residue.

GLC examination of 'a', 'b' and 'c'. This was carried out on a Pye 104/64 dual FID gas chromatograph using a 5′ × ¼″ column packed with 5·0% SE30 on Gas Chrom Q with column oven temp 80°C (a[4] and b) and 120° (C). An identical chromatograph and column was used for the GLC/MS examination the effluent being split to an FID monitor and thence via a silicone membrane separator to an AEI MS902 mass spectrometer. Samples for NMR examination were obtained from a Pye 104/2 chromatograph fitted with a 7′ × ⅜″ preparation column packed with 15% SE 300A chromosorbler and spectra were obtained with $CDCl_3$ solutions on a Varian HA-100D Spectrometer.

The twenty resolved components, their composition and the percentage of the respective fractions that they represent are listed in Table 1.

The condensations with MNB in acetic anhydride were done in narrow sealed glass tubes heated to 195°–205° (temp. in reaction mixture) for 8 hr appr. Thus α-picoline gave 2-(3-nitrostyryl) pyridine as colourless plates from MeOH m.p. 128–9°. (Found: C, 68·8; H, 4·3; N, 12·3. Calc. for $C_{13}H_{10}O_2N$; C, 69·0; H, 4·4; N, 12·4%).

γ-Picoline gave 4-(3-nitrostyryl) pyridine as plates from EtOH m.p. 142°. (Found: C, 68·55; H, 4·3; N, 12·2; Calc. for $C_{13}H_{10}O_2N$; C, 68·9; H, 4·4; N, 12·4%). When the heating was kept at 140°–5° in addition to the above a sparingly soluble product was also obtained as brown plates from EtOH m.p. 205°–207° of a salt with γ-picoline and m-nitrobenzoic acid. (Found: C, 59·8; H, 4·1; N, 10·7. $C_{13}H_{11}O_4N_2$ requires: C, 59·7; H, 4·2; N, 10·8%).

2:4-Lutidine gave 2:4-bis-(3-nitrostyryl) pyridine as colourless plates from EtOH m.p. 248°. (Found: C, 68·1; H, 3·65; N, 11·0; $C_{21}H_{15}O_4N_3$ requires: 67·5; H, 4·0; N, 11·2%).

2:5-Lutidine gave 2-(3-nitrostyryl) 5-methylpyridine as plates from MeOH m.p. 134°–5°. (Found: C, 69·4; H, 4·85; N, 11·4. $C_{14}H_{12}O_2N$ requires: C, 70·0; H, 5·0; N, 11·6%).

2:4:6-Collidine gave 2:4:6-tri-(3-nitrostyryl) pyridine as small colourless aggregates from pyridine m.p. 312–314°. (Found: C, 66·6; H, 3·5; N, 10·8; M.W. 520. $C_{29}H_{20}O_6N_4$ requires: C, 66·9; H, 3·8; N, 10·8, M.W. 520. In this case the product usually separates out well up the tube although it does not sublime under the reaction conditions.

Quinaldine gave 2-(3-nitrostyryl)-quinoline as plates from EtOH mp 154–5°. (Found: C, 74·3; H, 4·5; N, 10·2. $C_{17}H_{12}O_2N_2$ requires C, 73·9; H, 4·4; N, 10·2%). In addition to the M.W. value 276 the M.W. 290 showed the presence of a few % of an homologue.

With all five fractions (Table 2) containing at least 13 different compounds, many with reactive Me groups the reaction mixtures with M.N.B. are complex and it has not been possible or indeed necessary to effect a full separation since the M.W. values obtained reveal the compounds present in the mixtures.

M values for a picoline condensation product, 226, a lutidine di-condensation product 373, a 2:4:6-collidine tricondensation product 520, a methylquinoline condensation product 276 and a 2:4-dimethylquinoline condensation product 423.

Fraction 1. The most soluble part of the reaction mixture gave plates from MeOH, m.p. 128°–9° (M226) not depressed by admixture with 2-(3-nitrostyryl) pyridine. The less soluble gave granules from EtOH m.p. 158–160°, MW 373, 387, 401, 415, Mol % 79·5, 18·4, 1·8, 0·3, and the least soluble aggregates from pyridine m.p. 275°–295°.

Fraction 2. The material separating from EtOH, m.p. 220° approx. MW 387, 401, 415, 423, 437, 451, mol % 24·9, 20·7, 6·5, 37·9, 8·9, 1·1, and the residual dark material did not crystallise from pyridine.

Fraction 3. The part which separated from EtOH, m.p. 210–215, had M values as for 2 above and the remainder gave small prisms from pyridine m.p. 302–310°, MW 520, 534 and 548, mol % 89·0, 10·2, 0·7.

Fraction 4. The more soluble part of the reaction mixture gave prisms from EtOH m.p. 145–150° MW 373, 387, 401, mol % 46·1, 51·4, 2·5 and the remainder gave small prisms from pyridine m.p. 305–8° MW 373, 387, 401, 415, 520 and 534, mol % 50·9, 44·5, 2·7, 0·4, 1·3, 0·2.

Fraction B. Three fractions were obtained from the reaction, a non-crystalline one, one from EtOH m.p. from 200°, and the least soluble from pyridine m.p. 285–290°. MW values 276, 290, 301, mol % 64·5, 32·3 and 3·2; and

Table 2. Condensations with m-nitrobenzaldehyde (M.N.B.) and the examination of fractions 1, 2, 3 and 4, and of B.

	1	2	3	4	Residual 'B'	
M.W.			Mol %			Mol %
79	Trace					
93	2·75	0·99	1·05	0·90		
107	20·05	3·52	3·35	9·51	107	1·4
119	0·99	0·92	0·19	2·06	119	0·9
121	44·88	15·18	4·52	27·52	121	7·5
129	2·57	13·38	11·30	16·26	129	27·7
133	2·27	5·11	1·75	4·50	133	3·8
135	17·06	15·11	3·66	13·26	135	6·1
143	2·60	20·11	31·57	14·64	143	34·8
147	1·74	5·39	3·51	3·00	147	13·6
149	3·44	5·99	1·79	3·21	149	2·5
157	0·66	7·40	23·77	3·30	157	9·1
161	0·42	2·82	2·88	1·13	161	0·7
163	0·57	1·76	1·05	0·71	163	1·1
171		1·34	6·32		171	0·3
175		0·70	1·29		175	0·3
177		0·28	0·32		177	0·1
183			0·66			
185			1·02			

The M.W. values show the presence of 3 homologous series:

Pyridines 79, 93, 107, 121, 135, 149, 163, 177
Quinolines 129, 143, 157, 171, 185
Iodolines 119, 133, 147, 161, 175

373, 387, 401 and 415 mol % 23·5, 69·1, 6·8, 0·6, and 520, 534, 546 and 560 mol % 86·0, 7·5, 6·1 and 0·4 respectively.

The action of K *on the basic mixture.* To the basic mixture in ether clean K shavings were added and left to stand for 3–4 days during which the shavings turned brown. The ether soln was decanted, the ether removed and then the unreacted bases removed under reduced pressure. The residual crystalline material gave two products m.p. 70° and 134°. Both gave appr. the same mass spectrum with main peaks 130, 259, 389 and homologues at 144, 273, 403 and 417.

A structure such as **3** has MW 389, and a two indole complex 259. *Accurate* mass measurements gave 119·0722 whilst the theor value for **1** is 119·0735 and for **2** 119·0484 thus establishing the indoline structures.

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