[CONTRIBUTION FROM THE SYNTHETIC FUELS RESEARCH BRANCH, BUREAU OF MINES]

THE ISOLATION OF CORONENE FROM A COAL-HYDROGENATION OIL

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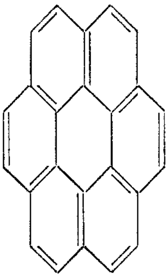
Received November 17, 1952

INTRODUCTION

Coronene, (I) is the simplest compound containing a benzene ring completely surrounded by fused benzene rings and thus containing no hydrogen atoms on the center nucleus. Despite the widespread interest in this compound, it is not readily available; five syntheses (1–5) have been reported, but these have been conducted on a very small scale.



Coronene (I)

There have been numerous reports (6) to the effect that coronene was isolated from certain fractions of oil produced by the hydrogenation of coal in Germany, but details of the isolation are not available. Operation of the Bureau of Mines 200-barrel/day coal-hydrogenation plant at Louisiana, Missouri, provided the opportunity to investigate the occurrence of coronene in such oils, and this paper reports its successful isolation.

The coronene-rich fractions were segregated by the technique of co-distillation of the coronene-containing oil with a selected fraction of a commercial polyglycol. Such co-distillation has proved effective for purification of certain polynuclear compounds. Thus, ethylene glycol and anthracene co-distill at atmospheric pressure, and purification of this tricyclic hydrocarbon is best achieved on a large scale in this fashion (7). Phenanthrene has been purified by azeotropic distillation with diethylene glycol at selected sub-atmospheric pressures (8). Because of the high boiling point of coronene, it was necessary to employ the very low pressures achieved with the molecular still. It was found that a commercial polyglycol, of approximately 750 average molecular weight, distills with coronene at about 0.025 mm. pressure; whether this is a co-distillation or a genuine azeotropic distillation was not determined. The concentration of coronene in the distillate was not more than about 0.5 per-cent. Although large quantities of glycol are thus required, the method has the advantage that the

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distillate is liquid, and no problems arising from the high melting point of coronene are encountered. Furthermore, it is possible to process large quantities of solution in a well-designed molecular still.

In the conventional coal-hydrogenation process, crushed coal is dispersed in a heavy recycle oil, catalyst is added, and the resulting slurry is fed into a hot (450–500°) reactor along with hydrogen at high pressure (300–700 atmospheres). After a suitable reaction period (5 to 60 minutes), the reactor contents pass to a vessel called the "hot catchpot"; this vessel is held at a prescribed temperature (440°), and collects all the solids (unconverted coal, catalyst, and ash), in addition to all the less volatile components. The material still in the vapor phase passes from the hot catchpot to a "cold catchpot", where the products which are liquid under normal conditions are condensed. The contents of the hot catchpot are "let down" to atmospheric pressure and collected. This black, tarry, viscous material, which is called the "heavy-oil let-down" or H.O.L.D., served as a sample for the present investigation. The particular H.O.L.D. studied was produced when the plant was processing a coal found in western Kentucky (9).

PREPARATION OF SAMPLE

To a 5-liter three-neck flask containing 1470 g. of H.O.L.D. and equipped with a stirrer there was added 1750 ml. of carbon disulfide. After one hour of stirring, the mixture was allowed to stand for two days, whereupon separation into two phases, both very dark, occurred. The upper layer was siphoned off, and the residual material was stirred with 1750 ml. of fresh carbon disulfide for two hours. After standing overnight, the mixture was filtered, and the insoluble, black, solid material was discarded. The combined carbon disulfide solutions were evaporated and the residue was poured into 5 liters of cold mixed hexanes (b.p. 60–65°). The sticky material which separated was stirred with the supernatant liquid for several hours and the mixture was left standing overnight. The supernatant liquid was decanted and discarded. The black, tarry residue, consisting of carbon disulfide-soluble, hexane-insoluble material, was dissolved in carbon tetrachloride and precipitated by pouring the solution into hexane. This treatment gave a brownish-black amorphous precipitate, which was easy to filter and which, after air-drying, weighed 287 g.

ISOLATION OF CORONENE

To 230 g. of the above brownish-black powder was added 2.3 liters of "propylene polyglycol 400".[2] The mixture was heated to about 100°, filtered, and the filtrate was transferred to a D.P.I. cyclic molecular still.[3] Four distillate fractions, each weighing about 450 g., were collected at 24 microns (0.024 mm.) pressure, while the rotor temperature was raised from 100° to 210°. The residue consisted of about 600 g. A measured volume (0.1 cc.) of each distillate sample was diluted with benzene and the ultraviolet spectrum of the fraction was determined. The first three fractions gave similar spectra, which indicated the probable presence of a substituted pyrene; but no absorption peak at 3420 Å, characteristic of coronene (10), was present. The fourth fraction gave a spectrum with maxima at 3050 Å and 3420 Å, indicating the presence of coronene; quantitative calculations using absorbance values at 3420 Å indicated that coronene was present to the extent of about 0.1 to 0.5% in this fraction, the balance of the material (99%) being propylene polyglycol of an estimated average molecular weight of 700. It is thus apparent that coronene co-distills with a polyglycol of about 700 molecular weight.

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[2] Obtained from the Dow Chemical Co., Midland, Michigan.

[3] Model CMS-5, Distillation Products Inc., Rochester, N. Y.

The portion of the sample which was insoluble in hot "polyglycol 400" was now treated with hot "polyglycol 750" and the mixture was filtered. The filtrate was combined with the residue (600 g.) from the "polyglycol 400" distillation, and the combined solution was distilled at 24 microns in the molecular still. The temperature of the rotor was gradually raised from 150 to 240° while six more distillate fractions were collected. A small portion of each of these fractions was diluted with benzene and examined by ultraviolet spectrophotometry. The spectrum of the fourth fraction (395 g.; rotor temperature about 200°) showed that the absorbing material, which was mainly coronene, was present in a concentration of about 0.1%. The whole fraction was poured into a mixture of 2 liters of methanol and 2 liters of water. After standing for several weeks, the oil and the small quantity of crystals that precipitated were separated by filtration and taken up in benzene. Evaporation of the benzene gave 4.6 g. of a dark oil. The material was redissolved in benzene and chromatographed on alumina. The chromatogram was developed and the adsorbed material eluted by the

TABLE I

DIFFRACTION DATA FOR CORONENE

FROM COAL			SYNTHETIC	
[a]vS	(3)	9.5[b]	vS	9.5
vS	(2)	7.3	vS	7.3
w		5.2	M	5.1
w		4.86	w(br)	4.90
w		4.43	w	4.41
vS		3.98	vS	3.95
vw		3.65		
vS	(3)	3.51	vS	3.50
M		3.44	M	3.43
vS	(1)	3.08	vS	3.05
vw		2.95	vw	2.93
M		2.66	M	2.65
			vvw	2.50
vvw(br)		2.31	vvw	2.27
vvw		2.23	vvw	2.22
			vvw	2.18
M		2.13		
w		2.07	vw	2.04
			w	1.99
			vw	1.94
w		1.90	w	1.89
vvw		1.86		
w		1.77	vw	1.76
vvw		1.605	vw	1.64
vvw		1.53		
vvw		1.30		
			vvw	1.25
			vvw	1.215
vvw		1.11		
vvw		1.07		

[a] Intensity where S = Strong, M = Medium; w = weak; v = very and br = broad or two unresolved lines. [b] Interplanar spacings; d computed from Bragg's Law: $\lambda = 2d$ *sin* e.

continuous addition of hexane containing 5% of benzene. The first fraction was collected when a yellow color appeared in the eluate; thereafter, seven fractions were arbitrarily collected. Evaporation of the second and third fractions gave 0.36 and 0.50 g., respectively, of yellow crystalline material; the other fractions gave oily residues on evaporation, and only the third fraction was further investigated. This fraction was recrystallized twice from benzene, giving 0.4 g. (approximately 0.2% based on starting powder) of nicely crystalline coronene, melting point about 425° [Literature (2) reports m.p. 438–440°]. The melting point was difficult to ascertain because of some darkening and sublimation before melting.

Anal.[4] Calc'd for $C_{24}H_{12}$: C, 96.0; H, 4.0.
Found: C, 95.3; H, 4.7.

The sample was sublimed *in vacuo*, recrystallized from benzene and sealed in a nitrogen-filled capillary tube. This sample had a melting point of about 435° but again darkening occurred and the melting point was difficult to ascertain. The *complex* with *trinitrofluorenone* (11) formed small red needles (from benzene), m.p. 332–334°.

Anal.[4] Calc'd for $C_{37}H_{17}N_3O_7$: C, 72.2; H, 2.8.
Found: C, 73.0; H, 3.0.

An authentic specimen of pure synthetic coronene, secured through the generosity of Dr. Wilson Baker (3, 4) gave an ultraviolet spectrum identical with that of our sample. The molar extinction coefficient of our sample at 3050 Å (the major absorption maximum) was 221,800, compared to 232,800 for Dr. Baker's sample;[5] this indicates a maximum purity of about 95% for our sample. The ratio of the extinction coefficients at 3050 Å and 3420 Å was approximately the same for both samples, which indicates that the purity was probably not much less than 95%. The spectra of both samples were identical with that previously reported by Clar (12).

The x-ray diffraction patterns of both coronene samples are compared in Table I. These data show that the sample isolated from coal-hydrogenation oil is nearly pure coronene, with a minor amount of contaminant.

Casual examination of other distillate fractions by ultraviolet spectrophotometry indicated the probable presence of the following compounds: Pyrene, methylpyrenes, and 1,2-benzperylene; but no attempt was made to isolate or confirm their presence.

Acknowledgment. We wish to thank Peter Pantages for assistance with the molecular distillation; Dr. R. A. Friedel and Robert Zange for the ultraviolet spectra; and Dr. L. J. E. Hofer and Mrs. W. C. Peebles for the x-ray analysis.

SUMMARY

The isolation of coronene from the high-boiling portion of an oil produced by the hydrogenation of coal was achieved by co-distillation of a carbon disulfide-soluble, hexane-insoluble fraction of the oil with polypropylene glycol of average molecular weight of 750. The distillation was conducted in a cyclic molecular still operating at about 0.024 mm. Hg pressure and a temperature of about 200°. The identity of the coronene was established by comparing its ultraviolet spectrum and its x-ray diffraction pattern with those of an authentic specimen.

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[4] Microanalyses by G. L. Stragand, University of Pittsburgh.

[5] Dr. Baker has indicated his intention of publishing and discussing the details of the ultraviolet spectrum of coronene.

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