JLR-33-50, No. 3.

Serial Number 18842.

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May 18, 1944

Bz-1:Bz-1'-Dibenzanthronyl
(Preparation in Alkyl Sulfuric Acids)

Problem Report

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Bz-1:Bz-1'-Dibenzanthronyl
(Preparation in Alkyl Sulfuric Acids)
(Project No. 2408)

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JLR-33-50, No. 3. Serial Number 18842.

Object of the Investigation:

To obtain sufficient data for a patent application covering the use of methyl sulfuric acid in the oxidation of benzanthrone to Bz-1:Bz-1'-dibenzanthronyl. This is described in tentative Chambers Works process for the manufacture of Bz-1:Bz-1'-dibenzanthronyl Crude, Serial Number 18734-A.

Period Covered by the Report:

November 20, 1943 to May 18, 1944.

Use:

Bz-1:Bz-1'-Dibenzanthronyl is used in the manufacture of Ponsol Direct Black 3G.

Historical Background:

In JLR-33-50, No. 2, Serial Number 18,734 the work is described leading to an improved process for the manufacture of Bz-1:Bz-1'-dibenzanthronyl, whereby benzanthrone, dissolved in methyl sulfuric acid, is treated with manganese dioxide. On the 100% pure basis, as determined by the analytical method described in JLR-33-50, No. 1, Serial Number 18,733, the savings were estimated at 23% of the former cost, where benzanthrone is oxidized in 17 parts of 85% sulfuric acid. The improved process employs 5 parts of methyl sulfuric acid, affording a 34% increase in production capacity, and a 20% increase in yield, on the 100% pure basis. Inasmuch as the Patent Report (AN-2336) bearing on this case concluded that the process contained new and possibly patentable matter, it was considered desirable to extend the principle to obtain sufficient data for a patent application. The present report describes this work.

Conclusions:

The object was attained. Invention Memo OR-1665 has been written and submitted.

Summary:

The following factors were investigated:

1 - Evaluation of the Prior Art.
2 - Kinds of alkyl sulfuric acids
3 - Limits of the reaction when using methyl sulfuric acid
4 - Preparation of dibenzanthronyl derivatives
5 - Kind of oxidizing agent

Patent Situation:

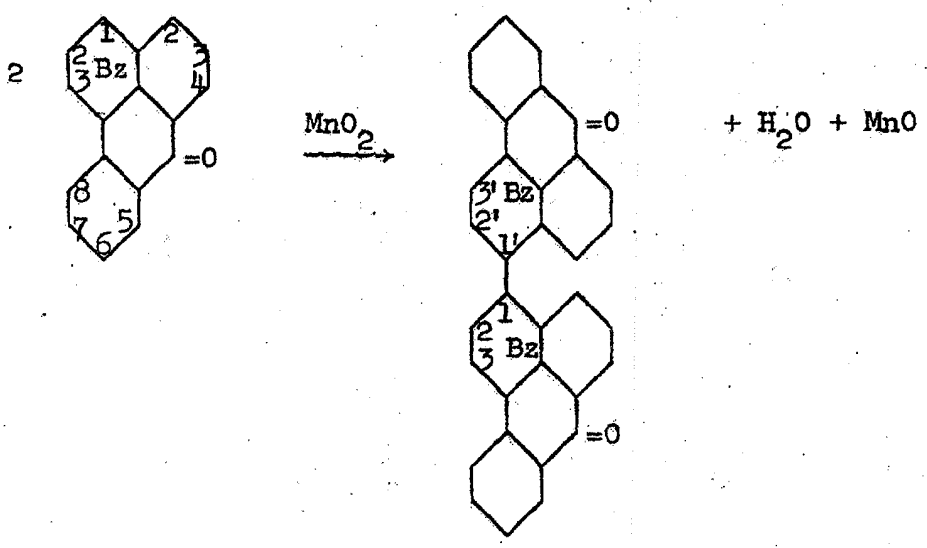
This is covered in Patent Report AN-2336 in which it was concluded that we are free to operate the improved process and that it contains new and possibly patentable matter. Invention Memo OR-1665 has been submitted covering the patentable features.

Plans for Future Work:

At present no further work is contemplated relative to the patent situation.

Theoretical Discussion:

In the oxidation of benzanthrone in sulfuric acid or methyl sulfuric acid by means of manganese dioxide, the principal product is Bz-1:Bz-1'-dibenzanthronyl, according to the following reaction:



Under the very best conditions found, the yield (on the 100% pure basis) is not much in excess of 70% of theoretical. The balance of the material consists of hydroxy-benzanthrone and hydroxy-dibenzanthronyls of unknown constitution, referred to as oxy bodies. They occur in the reaction as oxo bodies but are for the most part converted to hydroxy bodies by the sulfurous acid treatment in the finishing step. Up to 5% unchanged benzanthrone may also be present.

Experimental Data:

1 - Evaluation of the Prior Art:

The procedures of the following references were repeated and yield of dibenzanthronyl (100% pure basis) was determined in each case.

D. 431,774 (I.G. 1922) - Treats benzanthrone in 26 part of 72% sulfuric acid with chromic anhydride.

U.S. 1,607,491 (Thomson et al to S.D. 1926) - Treats benzanthrone dissolved in 17.4 parts of concentrated sulfuric acid with manganese dioxide at 60°C.

B. 278,112 (S.D. 1927) - Treats benzanthrone dissolved in concentrated sulfuric acid with manganese dioxide at low temperature, e.g. 0°C.

D. 515,327 (I.G. 1930) - Treats benzanthrone dissolved in 66% sulfuric acid with manganese dioxide. The product is an oxobenzanthrone.

U.S. 2,001,063 (Howell to DuPont 1935) - Treats benzanthrone dissolved in 80-90% sulfuric acid with manganese dioxide at 2-5°C. or in 93% sulfuric acid with a decreased proportion of manganese dioxide, the conditions being such that approximately 30-40% unchanged benzanthrone remains in the reaction product and is recovered for re-use. The advantage of this is that less oxy bodies are formed and higher yield is obtained on the benzanthrone actually consumed. If 85% acid is used, substantially complete reaction may be obtained. There is no example of this in the patent, but it is covered in the claims.

The benzanthrone used in these tests and throughout the rest of the investigation was purified material produced in the plant, containing not more than 1% of insoluble or 1% of anthraquinone. The manganese dioxide used throughout was plant material analyzing 81.6% MnO_2.

Testing of the products obtained from the prior art procedures was greatly facilitated by the analytical method described in JLR-33-50, No. 1, Serial Number 18,733, Appendix 1. This method, making use of chromatography and spectrophotometry, provides a much greater ease and certainty in arriving at the absolute purity of crude dibenzanthronyl than any method heretofore available.

In Table 1 are given the results of the various procedures described in the prior art. The figures in the Table are weight percentages based on the weight of the initial benzanthrone. Since in some cases considerable unchanged benzanthrone is present in the products, and since this is a recoverable, re-usable material, the figures in the fifth column, the sums of the yield of dibenzanthronyl and benzanthrone, are given to show the total useful material obtained from the methods. On the other hand, the amount of degradation is shown in the column headed "Oxy Bodies".

Table 1

Patent	Bz-1: Bz-1'-Dibenzanthronyl %	Benzanthrone %	Oxy Bodies %	Sum of Dibenzanthronyl & Benzanthrone %	Reference JLNB - Page
D. 431,774	9.0	25.4	57.8	34.4	4308-121
U.S. 1,607,491	38.4	18.1	46.2	56.2	4308-103
B. 278,112	50.7	7.2	42.2	57.9	4308-105
*U.S. 2,001,063	57.8	6.0	30.0	63.8	4264-9
Present Case	71.0	4.5	25.0	75.5	4264-41

*Using 85% sulfuric acid (not in the examples of this patent, but covered in claims). Process as currently run in plant.

Thus the decrease in oxy bodies is reflected in the increase in yield of dibenzanthronyl and dibenzanthronyl plus unchanged benzanthrone, with each succeeding improvement. By comparison with the prior art it is obvious that the present case is well justified in laying claim to improvement.

2 - Kinds of Alkyl Sulfuric Acids

Under optimum conditions described later, typical results obtained from the first two members of the series are shown in Table 2.

Table 2

Reference JLNB-Page	R-HSO_4	Minimum Operable Parts	Yield Dibenzanthronyl 100%	Benzanthrone
4264-77	$MeHSO_4$	5.0	70.7	5.4
4264-33	$EtHSO_4$	7.5	72.0	7.1

Thus although a slightly higher yield was obtained with ethyl sulfuric acid, the proportion of this acid could not be decreased much below 7.5 parts on account of solidification of the reaction mass. The preferred medium accordingly appears to be methyl sulfuric acid.

Attempts were made to extend the principle to the preparation of other alkyl sulfuric acids. The general method was to add the anhydrous alcohol to chloro-sulfonic acid with cooling. In Table 3 are shown the results obtained with several alcohols.

Table 3

Reference JLNB-Page	Alcohol	Analysis of Product % $RHSO_4$	% H_2SO_4	% Cl	Yield Pure $RHSO_4$ % of Theory
4264-31	Methyl	93.29	5.64	.29	91.5
4264-29	Ethyl	91.45	5.85	.21	91.0
4264-37	Isopropyl	*	-	-	-
4264-45	Glycol	77.5	23.48	.18	75.5
4264-81	n-Propyl	49.4	28.5	.01	49.1
4264-75	n-Butyl	43.1	28.18	.02	40.8

*The product consisted almost entirely of isopropyl chloride.

The preparation of the alkyl sulfuric acids with any degree of success was apparently confined to the methyl and ethyl. The glycol, n-propyl and n-butyl acids were tried in the benzanthrone oxidation, but gave no reaction in the case of the glycol, 7.8% and 9.4% in the case of the n-propyl and n-butyl, respectively. JLNB-4264, pages 49, 83, 89.

The attempts to prepare a purer butyl sulfuric acid were as follows: The experiment was repeated, adding n-butyl alcohol to chloro-sulfonic acid, but using a lower temperature (-20 - -15°). The product analyzed 10.82% H_2SO_4 and 73.9% $C_4H_9HSO_4$. In attempting to eliminate the sulfuric acid, the crude product was dissolved in water and treated with the calculated amount of barium hydroxide to precipitate the sulfuric acid. The resulting barium sulfate was filtered off, and the water was removed from the filtrate by evaporation under vacuum. It came off at 29° at 27 mm. When the residue was analyzed, however, it was found to contain more sulfuric acid than at the start, apparently due to hydrolysis. A portion of the original crude was next distilled under 10-11 mm. pressure, and about 20% came over at 29°. It was apparently butyl alcohol. The resudue then had the following composition: $BuHSO_4$ 53.79%, H_2SO_4 19.42% (Ba method). These results were also worse than the original ones. This material was used in the oxidation of benzanthrone, but gave no conversion and 76.2% unchanged benzanthrone. The original crude butyl sulfuric acid was also tried and it gave no conversion.

Limits of the Reaction:

Proportion of Alkyl Sulfuric Acids

As little as 5 parts of methyl sulfuric acid gave good results. Lower than this required an increase in the proportion of manganese dioxide and gave a thicker reaction mass. There appeared to be no advantage in using more than 5 parts. In the case of ethyl sulfuric acid good results were obtained with 7.5 parts. Less than this gave thickening. At 5 parts the reaction mass solidified. A mixture of the methyl and ethyl sulfuric acids (total of 5 parts) remained fluid in the reaction mass, but the yield dropped to 61.4%. The optimum proportion for methyl sulfuric acid therefore appears to be 5 parts, and for ethyl sulfuric acid, 7.5 parts.

Influence of Free Sulfuric Acid

An important factor is the amount of free sulfuric acid present in the alkyl sulfuric acid. Table 4 shows the relation between this factor and the resulting yield of dibenzanthronyl.

Table 4

Reference JLNB-Page	% Free H_2SO_4 in $MeHSO_4$	Yield Dibenzanthronyl % of Theory (100% Basis)
4264-3	19.76	61.2
4264-65	7.55	70.6
4264-41	5.64	71.4
4264-79	1.58	60.4

As the sulfuric acid content is decreased, the yield increases to a certain point, and then decreases. It therefore appears to be an advantage to have 5-7% of free sulfuric acid present, when using methyl sulfuric acid.

Influence of Alcohol

20% of methyl alcohol added to methyl sulfuric acid entirely inhibited the reaction (JLNB-4264, page 11). It was also observed that the presence of water tended to inhibit the reaction and cause thickening.

Proportion of Oxidizing Agent

When using 7.5 parts of methyl sulfuric acid, 3 moles of manganese dioxide (100% basis) were required to give substantially complete consumption of the benzanthrone. With 5 parts of methyl sulfuric acid, 4 moles of manganese dioxide were required to give the same degree of reaction. The reason for this is possibly that the water liberated by the reaction is sufficient to partially inhibit the reaction in the case of the smaller proportion of solvent, and that this dilution would not be as great in the case of a greater proportion of solvent. JLNB-4212, page 157; JLNB-4264, page 3.

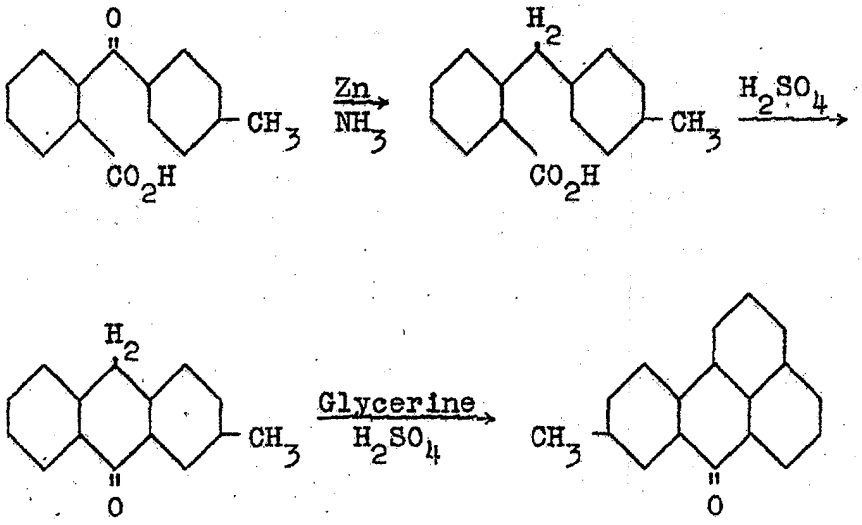
Temperature

The optimum temperature for the oxidation appeared to be from minus 5° to plus 5° in methyl sulfuric acid. At lower temperatures, the velocity of the reaction gradually fell off, and at higher temperature (25°) the formation of degradation products was already excessive. JLNB-4264, pages 21, 23, 91.

Preparation of Derivatives:

6-Methyl-Benzanthrone

This was prepared from p'-methyl-o-benzoyl-benzoic acid according to the following series of reactions:



The crude 6-methyl benzanthrone was recrystallized from solvent naphtha with Darco. The over-all yield of crystals from methyl-ortho-benzoyl-benzoic acid was 63% of theoretical.

M.P. Literature - 170°
Found - 171.2°

The product consisted of yellow micro crystals. The color in concentrated sulfuric acid was similar to that of benzanthrone. The optical absorption in mono-chloro-benzene compared with that of benzanthrone is given in Table 5 and is plotted in Figure 1. JLNB-4158, pages 185; JLNB-4214, pages 51, 52.

6-Chloro-Benzanthrone

This was prepared from p'-chloro-ortho-benzoyl-benzoic acid by a series of reactions analogous to those used in the preparation of the 6-methyl derivative. The crude product was recrystallized from ortho-dichloro-benzene with Darco, and was obtained in the form of yellow micro crystals in 13.5% of theoretical yield based on p'-chloro-ortho-benzoyl-benzoic acid. A further crop of crystals was obtained from the mother liquor giving a total yield of 24.3% of theoretical.

M.P. Literature - 186-187°C.
Found - 189.5°C.

Chlorine Calculated - 13.4%
Found - 13.9%

The optical absorption in mono-chloro-benzene compared with that of benzanthrone is given in Table 5 and is plotted in Figure 1. JLNB-4214, pages 35, 111; JLNB-4308, pages 39, 157.

Bz-2-Methoxy-Benzanthrone

This was prepared by methylation of Bz-2-hydroxy-benzanthrone. The latter was obtained by diazotization and hydrolysis of Bz-2-amino-benzanthrone, according to D. 507,359 (I.G. 1930). The yield was about 50% of theoretical.

M.P. Literature - 172°C.
Found - 174.4°C.

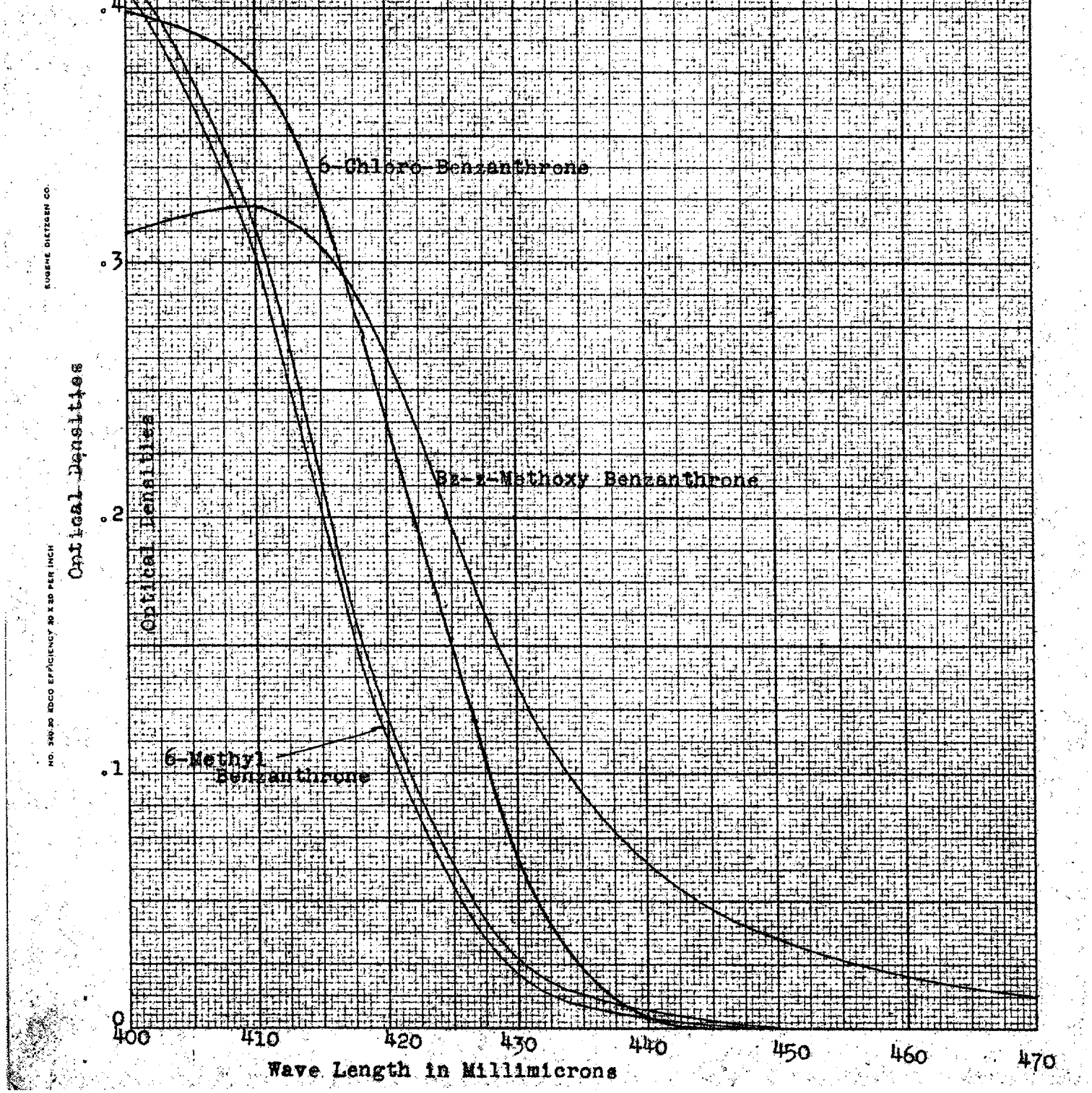
The optical absorption in mono-chloro-benzene compared with that of benzanthrone is given in Table 5 and is plotted in Figure 1.

Table 5

Wave Length Milli-microns	Optical Density of Solution in Mono-chloro-benzene .01 mg. per cc.; 1 cm. cell			
	Benzanthrone	6-Methyl Benzanthrone	6-Chloro Benzanthrone	Bz-2-Methoxy-Benzanthrone
400	.4136	.4073	.3987	.3116
405		.3773		.3180
410	.3143	.3039	.3764	.3226
415	.2136			.3056
416		.1808		
420	.1204	.1169	.2364	.2627
422			.1985	
430	.0252	.0197	.0647	.1346
440	.0055	.0033	.0028	.0627
450	.0023	.0009	.0000	.0352
460	.0015			.0193
470	.0011			.0133
480	.0009			.0106

Referring to Figure 1, the curves advance toward the red end of the spectrum in the order: 6-methyl-benzanthrone, benzanthrone, 6-chloro-benzanthrone and Bz-2-methoxy-benzanthrone. All but the

latter apparently have maxima just over in the ultra-violet, whereas the Bz-2-methoxy group causes a shift in the curve so that its maximum is just inside of the visible region.



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6:6'-Dimethyl-Bz-1:Bz-1'-Dibenzanthronyl

25 Grams of 6-methyl-benzanthrone, M.P. 171.2°, was dissolved in 187.5 grams of methyl sulfuric acid analyzing 95.11% $MeHSO_4$, 4.38% H_2SO_4, and .2% Cl. The temperature was lowered to 5° and 38.2 grams of 81.6% MnO_2 was added in portions during 3-4 hours at 2-5°C. The mass was stirred 19 hours at 1-2° and was diluted into 1000 cc. water containing 50 grams of sodium bisulfite. 25 Cc. of 96% sulfuric acid was added, and after bringing to the boil, the slurry was filtered and washed acid free. The filter cake was pebble milled, retreated with aqueous bisulfite, acidified, boiled, filtered, washed acid free and dried. Yield dry crude - 28 grams. The crude product was semi-purified by extraction with 37.5 parts of 5% aqueous pyridine bases containing 1% caustic soda. This removed a large part of the oxy-bodies, giving 24.5 grams of a very light yellowish-brown material. This was further purified as follows: 10 Grams of the semi-purified product was dissolved in 150 grams of 96% sulfuric acid. 28 Cc. of water were added at such a rate that the temperature went to 75-80°. The solution was then allowed to cool to room temperature with stirring. The microscope showed beautiful 40-60 micron rods. These were filtered on a sintered glass funnel and were washed with 50 cc. of 80% sulfuric acid. The filter cake was digested with water, filtered, and washed acid-free. The filter cake was digested in 5% aqueous pyridine bases with 1% caustic soda, and was filtered, and washed with water until alkali free. Yield of dry crystals - 7.22 grams. This contained the silica and other ash components, so was dissolved in 145 grams of nitrobenzene at 205° with the addition of Darco, and was filtered hot through paper. The filtrate was allowed to cool giving golden yellow crystals which were filtered off, washed with nitrobenzene, and alcohol and were dried.

Yield dry crystals - 5.3 grams
Spectral absorption
In 96% sulfuric acid - maxima at 428 and 542 millimicrons
In mono-chloro-benzene - maximum at 416 millimicrons

The spectral absorption data is given in Tables 6 and 7 with other derivatives, and are plotted in Figures 2 and 3.

Based on this data and on that for 6-methyl-benzanthrone in Table 5, the following equations could be set up for the simultaneous determination of 6:6'-dimethyl-Bz-1:Bz-1'-dibenzanthronyl and 6-methyl-benzanthrone in the presence of each other.

$$X = 100\ (2.5844\ d_2 - 1.1472\ d_1)$$
$$Y = 100\ (4.0393\ d_1^2 - 3.5691\ d_2^1)$$

where X = % dimethyl dibenzanthronyl
Y = % methyl benzanthrone

d_1 = optical density (corrected to .01 milligrams per cc. in mono-chloro-benzene, 1 cm. cell) of the sample at 400 millimicrons
d_2 = the same at 416 millimicrons.

By running the solution of the sample through a chromatograph column of aluminum hydroxide activated at 200°, the oxy bodies were removed and the above components then determined by means of the spectrophotometer using the above equations. (For a more detailed description of this method used in connection with the parent compounds, see JLR-33-50, No. 1, Serial Number 18733.)

Using this method on the semi-purified material, the results were as follows:

6:6'-Dimethyl-Bz-1:Bz-1'-dibenzanthronyl -	71.2%
6-Methyl-benzanthrone	0.7%
Ash	11.4%
Oxy Bodies (by diff.)	16.7%
Yield of pure dimethyl dibenzanthronyl	17.35 grams
Theoretical yield	24.9 grams
Percent of theoretical	69.7%

Thus the yield of pure product is very close to that obtained in the case of the parent compound, and accordingly this experiment may well serve as an example in the patent application. JLNB-4308, page 151.

6:6'-Dichloro-Bz-1:Bz-1'-Dibenzanthronyl

25 Grams of purified 6-chloro-benzanthrone, M.P. 189.5° was dissolved in 187.5 grams of methyl sulfuric acid analyzing 94.67% $MeHSO_4$, 4.01% H_2SO_4, and 0.11% Cl. The solution was cooled to 5° and 35.4 grams of 81.6% manganese dioxide were added in portions during a period of 2-3 hours, and the mass was stirred 20 hours at 0-5°. The product was isolated and semi-purified as in the case of the dimethyl derivative. Further purification was carried out as follows: The dichloro-dibenzanthronyl was found to be less soluble in diluted sulfuric acid than was the dimethyl derivative, so that this procedure had to be modified. The net result was that 10 grams of the semi-purified material was dissolved in 360 grams of 97.1%

sulfuric acid and 28 cc. of water was added drop by drop (to 90% sulfuric acid) at such a rate that the temperature went to 75-80°C. On cooling, beautiful, thick 20-40 micron orange colored prisms separated. These were filtered on a sintered glass funnel and washed with 75 grams of 90% sulfuric acid. The filter cake was digested in water, filtered and washed. The cake was extracted with 5% aqueous pyridine bases containing 1% caustic soda, and was washed alkali free and was dried. Yield of crystals: 6.815 grams. The dry crystals were dissolved in 200 grams of boiling nitrobenzene with Darco, and the solution was filtered hot through paper. The orange yellow crystals from the filtrate weighed 3.6 grams.

Chlorine Calculated - 13.4%
Found - 12.73%

Spectral absorption
In 96% sulfuric acid
Maxima at 432 and 557 millimicrons
In mono-chloro-benzene - 422 millimicrons

The spectral absorption data is given in Tables 6 and 7 and is plotted in Figures 2 and 3. Based upon this data and that for 6-chloro-benzanthrone, Table 5, the following equations were set up for the quantitative determination of 6-chloro-benzanthrone and 6:6'-dichloro-Bz-1:Bz-1'-dibenzanthronyl in the presence of each other.

$$X = 100\ (2.921\ d_2 - 1.454\ d_1)$$
$$Y = 100\ (4.120\ d_1 - 3.238\ d_2)$$

where X and Y = the percentages of dichloro-dibenzanthronyl and chloro-benzanthrone, respectively, and d_1 and d_2 are the optical densities (corrected to standard conditions) of the mono-chloro-benzene solutions of the sample at 400 and at 422 millimicrons, respectively. The effluent from the chromatograph was the solution used.

Using this method on the semi-purified material the results were as follows:

6:6'-Dichloro-Bz-1:Bz-1'-dibenzanthronyl -	82.7%
6-Chloro-benzanthrone	1.8%
Ash	9.67%
Oxy Bodies (by diff.)	5.8%
Yield of pure dichloro-dibenzanthronyl -	20.33 grams
Theoretical yield	24.9 grams
% of theoretical	81.7 grams

This is a more favorable yield than either that of the parent compound or of the methyl derivative, suggesting that the chlorine is in the position partly attacked during the formation of the oxy bodies. This experiment makes an excellent example for the proposed patent application. JLNB-4308, pages 81, 164.

Bz-2:Bz-2'-Dimethoxy-Bz-1:Bz-1'-Dibenzanthronyl

10 Grams of purified Bz-2-methoxy-dibenzanthronyl, M.P. 174.4°, was dissolved in 75 grams of methyl sulfuric acid analyzing 94.67% $MeHSO_4$, 4.01% H_2SO_4 and .11% Cl. 14.35 Grams of 81.6% manganese dioxide were added in portions during 2-3 hours at 2-4°. The mass was stirred 20 hours at 2-4° and the product was isolated as above giving 10 grams of crude material. The product did not lend itself well to purification by the extraction with aqueous pyridine bases. A small sample of the crude, however, was fused at 120° in alcoholic potash. This gave almost immediate ring-close to Bz-2:Bz-2'-dimethoxy-dibenzanthrone. Dyeings of the latter were fast to acid and alkali, proving that the above crude indeed contained Bz-2:Bz-2'-dimethoxy-Bz-1:Bz-1'-dibenzanthronyl with the methoxy groups intact, and therefore affording a good patent example. JLNB-4308, page 139.

Oxidation of Bz-2-Amino-Benzanthrone

This compound failed to give a Bz-1:Bz-1'-dibenzanthronyl when oxidized with manganese dioxide in methyl sulfuric acid, probably due to attack of the amino group by the oxidizing agent, and could therefore not be used as a patent example. JLNB-4308, page 141.

Table 6

Wave Length Milli-microns	Optical Densities of Solutions in 96% Sulfuric Acid (0.01 mg. per cc. in 1 cm. Cell) Bz-1:Bz-1'-Dibenzanthronyl	6:6'-Dimethyl-Bz-1:Bz-1'-Dibenzanthronyl	6:6'-Dichloro-Bz-1:Bz-1'-Dibenzanthronyl
400	.2443	.2588	.3408
410	.2631	.2782	.3212
420	.3095	.3272	.3574
428	.3465	.3628	
430	.3418	.3568	.4204
432			.4224
440	.2391	.2478	.3427
450	.1610	.1721	.1839
460	.1641	.1746	.1321
470	.1945	.2051	.1411
480	.2398	.2524	.1655
490	.3042	.3181	.2002
500	.3806	.3951	.2487
510	.4520	.4703	.3051
520	.5486	.5471	
530	.6124	.6295	.4213
540	.6649	.6841	.4801
542	.6675	.6861	
550	.6376	.6537	.5284
556			.5387
560	.5432	.5576	.5358
570	.4166	.4311	.4893
580	.2862	.3019	.4155
590	.1687	.1850	.3006
600	.0860	.0981	.1954
610	.0366	.0473	.1093
620	.0128	.0226	.0531
630	.0044	.0111	.0236
640	.0013	.0071	.0098
650		.0053	.0036
660		.0049	.0017

JLNB-4212, page 94; JLNB-4308, page 181.

It will be noted from the plotted results (Figure 2) that the dimethyl derivative is very close in its optical properties to those of the parent dibenzanthronyl, whereas the curve of the dichloro derivative is shifted toward the red end of the spectrum. This is noticeable visually also where the latter has a more bluish red appearance (in sulfuric acid solution) than that of dibenzanthronyl

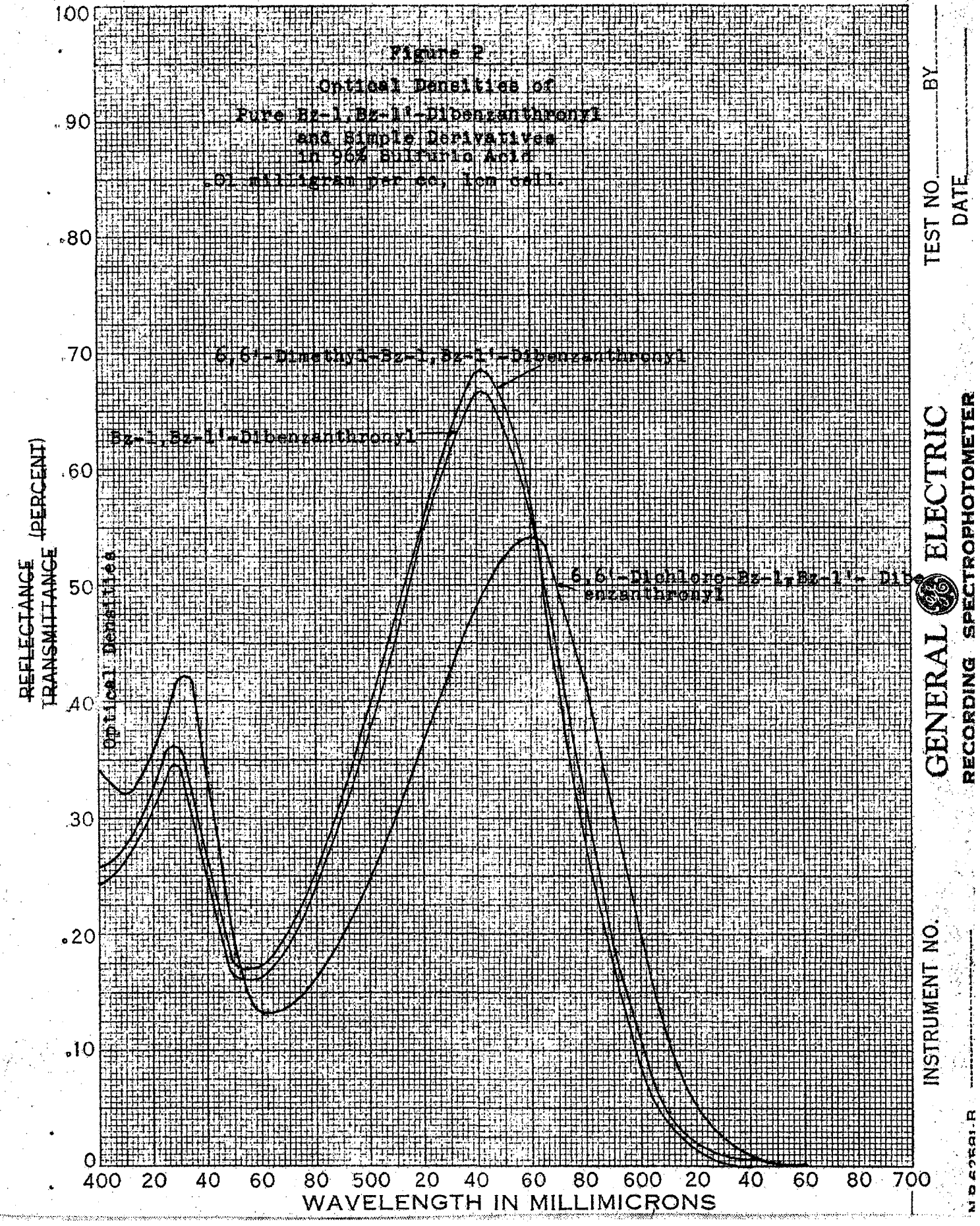
itself. The solution of the dichloro derivative lacks the fluorescence of the parent compound, although this does not show in the spectral absorption curve. It will also be observed that, in the case of the dichloro derivative, the amplitude of the minor maximum (at 432 millimicrons) is considerably enhanced in spite of the principal maximum being lower than that of the parent compound.

Table 7

Wave Length Milli-microns	Optical Densities of Solutions in Mono-Chloro-Benzene 0.01 Milligram per cc.; 1 cm. cell		
	Bz-1:Bz-1' Dibenzanthronyl	6:6'-Dimethyl-Bz-1:Bz-1'-Dibenzanthronyl	6:6'-Dichloro-Bz-1:Bz-1'-Dibenzanthronyl
400	.5929	.5625	.4420
410	.6574	.6226	.4961
415	.6798		
416		.6366	
420	.6402	.6065	.5587
422			.5624
430	.4429	.4172	.4971
440	.2400	.2242	.3129
450	.1075	.1025	.1566
460	.0410	.0381	.0664
470	.0111	.0123	.0232
480	.0026	.0039	.0069
500	.0009	.0011	.0019

JLNB-4214, pages 179, 183 - JLNB-4308, pages 32, 158.

In the plotted curves (Figure 3) the dimethyl derivative is again very similar to that of dibenzanthronyl itself. The maximum is shifted by 1 millimicron toward the red, whereas the dichloro derivative is shifted 7 millimicrons at its maximum.



DUP050041240

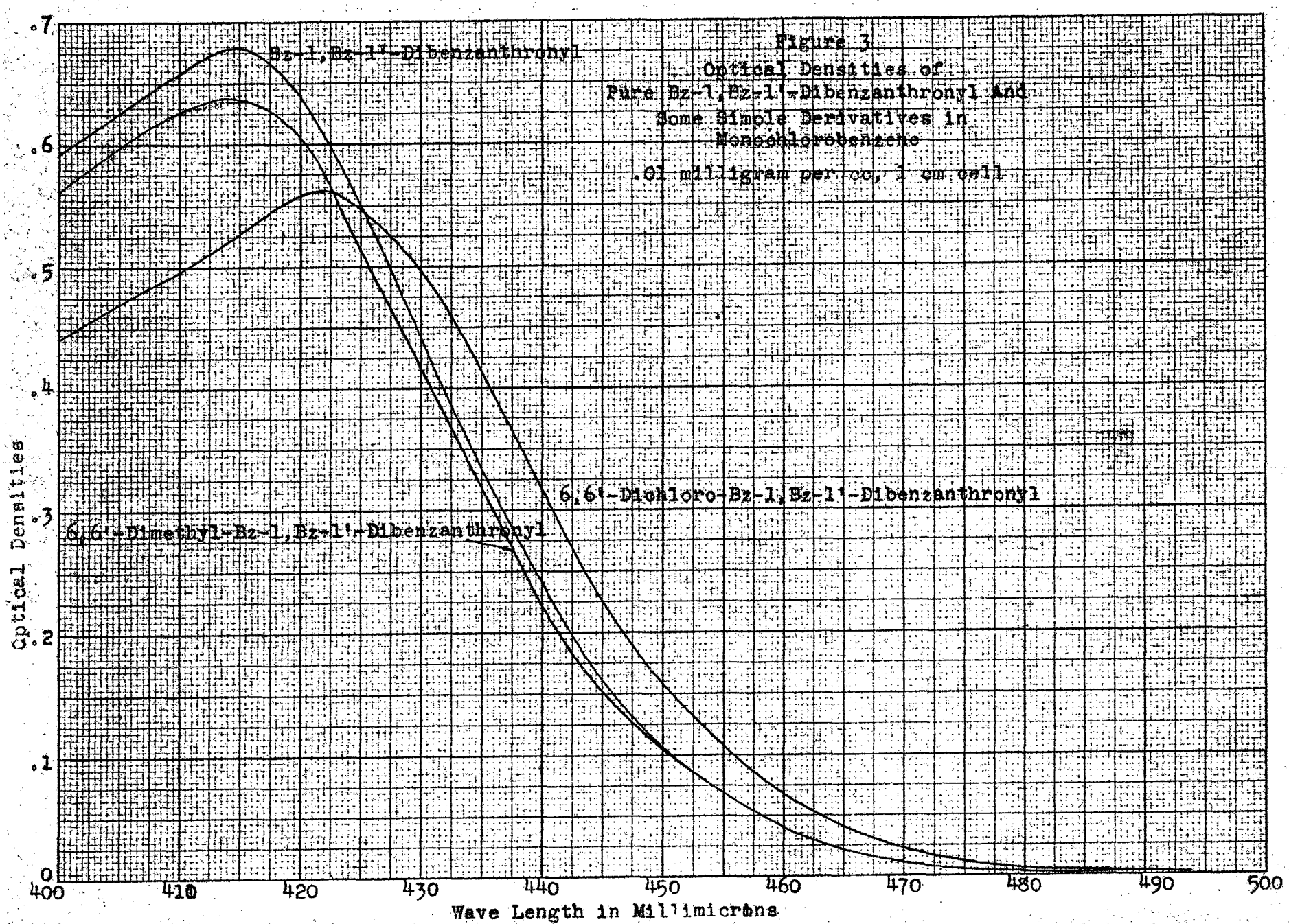


Figure 3
Optical Densities of
Pure Bz-1,Bz-1'-Dibenzanthronyl And
Some Simple Derivatives in
Monochlorobenzene
.01 milligram per cc., 1 cm cell

Kind of Oxidizing Agent

One other kind in addition to manganese dioxide was tried, namely, chromic oxide, CrO_3. The use of this agent had been previously disclosed in connection with the oxidation of benzanthrone in 72% sulfuric acid (D. 431,774, I.G., 1922). Its use in the present case was carried out as follows: 25 Grams of purified benzanthrone was dissolved in 187.5 grams of methyl sulfuric acid containing about 5% of sulfuric acid. The solution was cooled to 2° and was treated during a period of 4-5 hours at 2-5° with 21.5 grams of chromic oxide. The mass was stirred 16 hours at 2-4°, poured into 1000 cc. of water, treated with 25 grams of sodium bisulfite, boiled, filtered, washed acid-free and dried.

Yield dry crude - 25 grams
Analysis: Dibenzanthronyl - 19.0%
Benzanthrone 27.3%
Ash .94%
Oxy Bodies 52.8%

Yield of pure dibenzanthronyl - 4.75 grams
% of initial benzanthrone 19.0%

In Table 8 are shown the results compared with those obtained by the former disclosure.

Table 8

Reference	% of Initial Benzanthrone		
	Dibenzanthronyl	Benzanthrone	Oxy Bodies
D. 431,774	9.0	25.4	57.8
JLNB-4308-133	19.0	27.3	52.8

Thus the use of chromic oxide with methyl sulfuric acid gave more than twice the yield of dibenzanthronyl compared with the former disclosure. This is further support for the patent application.

Submitted for typing
July 12, 1944

Typed
July 14, 1944
emh