Summary

1. *o*-Cresol-tetrachlorophthalein, its diacetate and dibenzoate have been prepared. As these are *colorless* compounds they have the *lactoid* structure. In alkaline solutions the phthalein dissolves with the development of a *reddish-purple color* due to the formation of *quinoid* salts.

2. Dibromo-*o*-cresol-tetrachlorophthalein, its diacetate and dibenzoate and the dimethyl and diethyl ethers have been prepared. These are all *colorless* and have the *lactoid* structure. The dibromo-*o*-cresol-tetrachlorophthalein forms an unstable diammonium salt and a disilver salt. These salts are *blue* and are derived from the *quinoid* form of the dibromophthalein.

3. Dinitro-*o*-cresol-tetrachlorophthalein has been made. As in the case of the dibromo compound, it is probable that the two substituting groups take the *ortho* positions to the hydroxyl groups. The action of ammonia on the dinitro compound has also been studied. When acetylated the dinitro derivative gives a diacetate, which loses a molecule of water at 140°. This would seem to indicate that the diacetate has the carbinol carboxylic acid structure.

4. An isomer of *o*-cresol-tetrachlorophthalein has been made by first making 2′-hydroxy-3′-methyl-benzoyl-3,4,5,6-tetrachloro-2-benzoic acid by the condensation of *o*-cresol with tetrachlorophthalic acid anhydride and then condensing this acid with *o*-cresol. From the method of formation of this isomer, one hydroxyl group must be in the *ortho* position and the other in the *para* position to the methane carbon atom, while in the *o*-cresol-tetrachlorophthalein both the hydroxyl groups are in the *para* positions.

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VAPOR PRESSURES AND BOILING POINTS OF MONO- AND DIMETHYLANILINES AND MONO- AND DIETHYLANILINES

BY O. A. NELSON AND H. WALES

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There has been an ever-increasing demand for physical constants of organic compounds, particularly intermediates for dyes. The vapor pressures and boiling points of many of these compounds have been determined in the past by methods which afterwards were shown to be unreliable,[1] and the results obtained on the same compounds by different workers show in many cases considerable variations. The National Research Council, accordingly, requested that the vapor pressures and boiling

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[1] Smith and Menzies, THIS JOURNAL, **32**, 1416 (1910).

points of many of these compounds be redetermined by the more accurate methods now in use. Monomethylaniline, dimethylaniline, monoethylaniline, and diethylaniline, and the results obtained with them are here reported and discussed.

The method used was that devised by Smith and Menzies[2] and used in the Color Laboratory in the determination of vapor pressures and boiling points of naphthalene, anthracene, phenanthrene, anthraquinone and carbazole[3] and by many other investigators working with different substances. This method is perhaps the most reliable thus far devised and has the additional advantage of being quite rapid. A series of determinations with it can be completed in a single day.

The bath was heated electrically, connections being made to either 220- or 110-volt lines. No difficulty was experienced in keeping the bath liquid at constant temperature long enough to enable the apparatus to come to equilibrium. A copper-constantan thermocouple was used for measuring temperature. Standardized Anschütz thermometers also were suspended in the bath in order to obtain checks. The constant-boiling liquids used in calibrating the thermocouple were water for 100°, naphthalene for 217.95° and benzophenone for 305.9°.

Purification of Materials

The most common impurities in the substituted anilines are other alkylated anilines and free aniline and, in old samples, a red material formed by the action of light. Aniline invariably turns red when exposed to light, as do some of the substituted compounds.

The monomethylaniline was purified in the following manner. A concentrated hydrochloric acid solution of the bases was treated with sodium nitrite, care being taken to keep the temperature between 5° and 10°. Nitrosomethylaniline was formed as an oil, while the diazobenzene hydrochloride and dimethylaniline hydrochloride remained in solution. The nitrosomethylaniline was extracted with ether and converted into methylaniline by treatment with tin and hydrochloric acid. The compound thus obtained was further purified by steam distillation and then fractionated, the fraction distilling between 195.6° and 195.8° being used for vapor-pressure determination. Other samples obtained by redistilling under reduced pressures were used to check the results already obtained, with perfect agreement.

Commercial dimethylaniline was carefully distilled, and the fraction distilling between 193° and 195° was taken for further purification. The dimethylaniline thus obtained was treated with an excess of acetic anhydride and left overnight (about 17 hours), after which it was distilled.

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[2] Ref. 1, p. 1420.

[3] Nelson and Senseman, *J. Ind. Eng. Chem.*, **14**, 58 (1922). Senseman and Nelson, *ibid.*, **15**, 382 (1923).

The fraction boiling between 193° and 194° was washed with dil. sodium hydroxide solution and water, dried and redistilled. The whole process was then repeated, but this time acetylation was accomplished by refluxing the acetic anhydride-dimethylaniline mixture for five or six hours. This treatment should remove all traces of primary and secondary amines and give very pure dimethylaniline. A portion of the product obtained from the final acetylation was redistilled, and a vapor-pressure determination was made on a sample thus obtained. Another sample was then obtained by redistilling in a vacuum, with results that agreed perfectly with those obtained from the first distillation. The mono- and diethylanilines were purified in the same manner as were the mono- and dimethylanilines.

Results

Vapor-pressure determinations were made on mono- and dimethylanilines and mono- and diethylanilines from about 50° to temperatures a few degrees above their boiling points. The pressures were read directly from a manometer with the aid of magnifying glasses. With this device it was possible to read the pressures to within ± 0.2 mm. The temperatures could be determined to within ± 0.01°. It should be noted that the percentage error in reading pressure was necessarily much greater at the lower temperatures where the pressures were small. For these points a Toepler mercury pump was necessary to obtain sufficiently low pressures. Ordinary standardized Anschütz mercury thermometers were used in most determinations up to 80°. This is permissible, as thus it is possible to read the temperatures to within ± 0.1°, and the change in pressure due to this difference in temperature is negligible.

Tables I, II, III and IV give the values observed with the four compounds.

TABLE I

MONOMETHYLANILINE

Boiling point, 195.70°

Temp., °C	50.0	60.0	70.0	80.0	90.10	99.66	103.53	111.96	122.08
Press., mm	3.4	5.2	7.3	13.0	22.1	31.7	37.6	53.5	77.6
Temp., °C	134.18	135.25	141.68	146.84	149.92	154.77	164.21	171.32	175.79
Press., mm	121.0	124.7	158.0	185.1	206.5	248.4	325.1	397.9	444.8
Temp., °C	181.28	183.83	188.09	190.74	190.96	194.49	195.72	199.61	
Press., mm	518.5	555.0	623.6	665.5	671.5	733.6	761.3	834.7	

TABLE II

DIMETHYLANILINE

Boiling point, 193.50°

Temp., °C.	40.0	50.0	60.0	68.5	71.02	80.75	91.67	95.89	101.80	114.89
Press., mm.	2.4	3.9	6.5	9.7	10.9	16.3	26.0	31.5	39.9	67.2
Temp., °C.	118.50	128.61	134.95	140.51	143.91	152.09	156.22	162.86	166.16	168.37
Press., mm.	77.7	110.6	138.0	166.8	185.7	240.7	273.2	333.4	364.6	388.6
Temp., °C.	171.87	174.10	179.42	182.01	190.30	190.91	193.98	195.40	196.78	
Press., mm.	430.1	456.3	528.6	566.5	700.9	711.5	764.9	796.3	821.7	

TABLE III

MONO-ETHYLANILINE

Boiling point, 204.72°

Temp., °C.	50.0	60.0	70.0	81.0	91.55	101.52	107.42	110.66
Press., mm	2.4	4.0	6.1	10.3	16.9	24.2	32.0	38.5
Temp., °C	116.58	122.99	128.88	134.42	135.08	143.47	146.58	152.11
Press., mm	46.5	60.2	74.6	91.9	92.5	126.7	141.6	167.5
Temp., °C	156.34	159.26	162.66	169.97	172.67	182.41	184.08	189.06
Press., mm	194.0	215.2	235.7	295.8	319.9	424.3	439.8	509.0
Temp., °C	190.30	194.60	197.00	200.69	200.90	203.85	205.20	206.70
Press., mm	521.9	586.1	624.0	685.5	688.8	745.7	769.3	795.8

TABLE IV

DIETHYLANILINE

Boiling point, 216.27°

Temp., °C.	50.0	60.0	70.0	79.0	81.6	86.93	96.49	100.93	112.92	123.96
Press., mm.	1.6	2.7	4.2	5.9	6.4	9.7	13.8	17.4	28.8	43.2
Temp., °C.	134.16	140.40	146.76	154.53	162.60	164.08	175.40	182.10	184.23	189.40
Press., mm.	64.7	81.1	101.5	133.8	167.8	183.1	254.4	308.0	328.9	381.2
Temp., °C.	199.30	205.19	207.10	212.20	213.46	215.62	216.30	217.22	217.52	218.40
Press., mm.	493.4	576.1	604.4	686.0	710.8	747.2	761.2	778.6	786.0	799.2

The results obtained were plotted on coördinate paper, 20 dm. square, and the pressures were read from the curves. The pressures at 5° intervals are given in Table V. Using the pressures thus observed, the latent heats of vaporization were computed from the equation, $L = (\log P_2 - \log P_1)T_1T_2\frac{(2.303\ R)}{(T_2 - T_1)}$, where L is the latent heat of vaporization and P_1 and P_2 are pressures corresponding to temperatures T_1 and T_2 on the absolute scale. This equation is derived from the Clapeyron equation of state, $\mathrm{d}P/\mathrm{d}T = L/(RT^2/P)$ as is also the equation[4] for the vapor pressures of these compounds: $\log P = C - \frac{a}{4.5795\ T} - \frac{b}{1.9885} \log T$.

These equations, however, cannot be used to calculate pressures much above those here recorded. The reason for this is that while the latent heat of vaporization can be expressed by a straight-line equation over the relatively short range of temperature and pressure investigated, nevertheless, if L were plotted against temperature, the curve would become steeper as the temperature increased and at the critical temperature it would be almost perpendicular to the temperature axis. It is obvious, therefore, that the equation for L, given for each of these compounds, will not hold much above the temperature recorded in the tables and as the vapor-pressure equations are based on the latent heat of vaporization they are necessarily limited to the same range.

The boiling points of these compounds as determined by different workers vary considerably. A search through the literature showed the following

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[4] *Ind. Eng. Chem.*, **15**, 621 (1923).

TABLE V

VAPOR PRESSURES

Monomethylaniline: $L = 17369.0 - 12.933\ T$.
$\text{Log}\ P = 28.1580 - (3706.4/T) - 6.504 \log T$.
Dimethylaniline: $L = 12953.0 - 4.62\ T$.
$\text{Log}\ P = 15.14437 - (2828.5/T) - 2.3234 \log T$.
Monoethylaniline: $L = 13248.0 - 3.9\ T$.
$\text{Log}\ P = 14.1910 - (2892.9/T) - 1.9613 \log T$.
Diethylaniline: $L = 1412.6 - 5.3081\ T$.
$\text{Log}\ P = 16.40076 - (3102.3/T) - 2.6693 \log T$.

Temperature °C.	Monomethylaniline A[a] mm.	Monomethylaniline B[b] mm.	Dimethylaniline A mm.	Dimethylaniline B mm.	Monoethylaniline A mm.	Monoethylaniline B mm.	Diethylaniline A mm.	Diethylaniline B mm.
40	1.0	1.2	2.5	2.1	1.1	1.1	...	...
45	1.6	...	3.3	...	1.8	...	...	...
50	2.5	2.3	4.1	3.6	2.4	2.1	1.6	1.3
55	3.0	...	5.4	...	3.2	...	2.0	...
60	4.4	4.2	6.8	6.2	4.0	3.6	2.7	2.3
65	6.0	...	8.2	...	5.0	...	3.3	...
70	7.5	7.3	10.0	10.2	6.1	6.1	4.2	3.9
75	9.7	...	12.4	...	7.9	...	5.0	...
80	12.1	12.2	15.4	16.3	10.0	10.0	6.8	6.5
85	15.4	...	19.1	...	12.8	...	8.2	...
90	19.6	19.9	24.3	25.4	16.0	18.3	10.0	10.5
95	25.3	...	30.4	...	19.2	...	12.6	...
100	31.5	31.3	37.9	38.6	24.0	24.6	16.2	16.6
105	40.0	...	46.5	...	29.5	...	20.4	...
110	49.3	47.9	56.8	57.2	36.4	37.3	25.1	25.4
115	60.3	...	68.3	...	45.0	...	31.0	...
120	72.8	71.4	81.8	83.1	54.5	55.2	38.2	38.2
125	87.1	...	97.4	...	65.8	...	46.1	...
130	104.0	103.8	116.2	118.2	79.0	79.5	56.2	55.9
135	124.1	...	138.5	...	93.7	...	67.3	...
140	147.6	148.0	163.9	165.1	112.0	113.0	80.6	80.6
145	175.0	...	193.5	...	132.9	...	95.9	...
150	207.1	206.3	227.1	226.8	158.0	158.9	113.5	113.9
155	244.4	...	265.6	...	186.0	...	134.9	...
160	286.0	288.5	307.0	306.6	218.8	218.3	158.0	157.9
165	330.3	...	354.7	...	256.2	...	185.2	...
170	380.9	379.7	408.1	408.1	296.0	295.2	216.0	215.5
175	437.8	...	468.9	...	342.6	...	252.0	...
180	502.6	502.6	536.0	536.3	394.2	394.0	291.7	289.9
185	572.4	...	611.8	...	450.1	...	337.2	...
190	654.5	654.0	695.4	695.0	518.0	518.6	386.9	384.7
195	745.5	...	787.5	...	590.5	...	443.2	...
200	843.5	841.4	...	911.5	674.4	674.6	504.0	504.2
205	...	...	...	...	765.5	765.4	572.5	...
210	...	...	...	...	867.0	866.4	651.0	651.0
215	...	...	...	...	...	...	738.5	736.4
220	...	...	...	...	...	...	837.0	837.3

[a] Col. A: pressure observed from curve.
[b] Col. B: calculated pressure.

temperatures: for monomethylaniline, 192° at 754 mm.,[5] 193.5° at 760 mm.,[6] 195.5°,[7] and 193.8° at 760 mm.;[8] for dimethylaniline 192.0°,[9]

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[5] Reinhardt, *Ber.*, **16**, 29 (1883).

[6] Pictet and Crépieux, *Ber.*, **21**, 1111 (1888).

[7] The Chemical Rubber Co., "Handbook of Chemistry and Physics," **1918**.

[8] Kahlbaum, *Z. physik. Chem.*, **26**, 606 (1898).

[9] Hofmann, *Ber.*, **5**, 705 (1872).

192.6° to 192.7° at 738.4 mm.,[10] 195° at 767 mm.,[11] 194.0°[7] and 193.1°;[8] for monoethylaniline, 206.0° at 760 mm.;[6] 205.0°[7] and 204.0°;[8] and for diethylaniline, 216° to 217° at 769.5 mm.,[11] 216.0°[7] and 215.5°.[8]

Kahlbaum[8] appears to be the only one who has determined the vapor pressures of these compounds. The methods he used and the results he obtained on these and other compounds have been fully discussed by Smith and Menzies[1] and by Schmidt.[12] These discussions or criticisms direct attention to several facts about his method, which show it to be at fault for the accurate determination of vapor pressures.

Summary

The vapor pressures and boiling points of mono- and dimethylanilines and mono- and diethylanilines have been redetermined by the method devised by Smith and Menzies. The boiling points found for the mono- and dimethyl- and mono- and diethylanilines were 195.70°, 193.50°, 204.72° and 216.27°, respectively, at 760 mm.

[Contribution from the Polarimetry Section of the Bureau of Standards, United States Department of Commerce[1]]

RELATIONS BETWEEN ROTATORY POWER AND STRUCTURE IN THE SUGAR GROUP. IX.[2] THE ROTATION OF THE ALPHA FORM OF METHYL GENTIOBIOSIDE RECENTLY SYNTHESIZED BY HELFERICH AND BECKER

By C. S. Hudson

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In 1917 Hudson and Johnson[3] showed that the rotations of several derivatives of gentiobiose could be calculated, including the alpha and beta forms of methyl gentiobioside, the hepta-acetates of these glycosides, and the alpha form of gentiobiose octa-acetate. They prepared for the first time three of these five substances and found a good agreement between the calculated and observed rotations, as follows: α-gentiobiose octa-acetate, obs. +52° (in chloroform), calcd. +52°; β-methyl gentiobioside, obs. —36° (in water), calcd. —38°; β-methyl gentiobioside hepta-acetate, obs. —19° (in chloroform), calcd. —17°. The alpha form of methyl gentiobioside and its hepta-acetate were unknown and were not prepared because of the lack of a suitable method of synthesis for this alpha glycoside,

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[10] Brühl, *Ann.*, **235**, 14 (1886).

[11] Schiff, *Z. physik. Chem.*, **1**, 383 (1887).

[12] Schmidt, *ibid.*, **8**, 629 (1891).

[1] Published by permission of the Director of the Bureau of Standards.

[2] Part VIII was published in This Journal, **47**, 537 (1925).

[3] *Ibid.*, **39**, 1271 (1917).