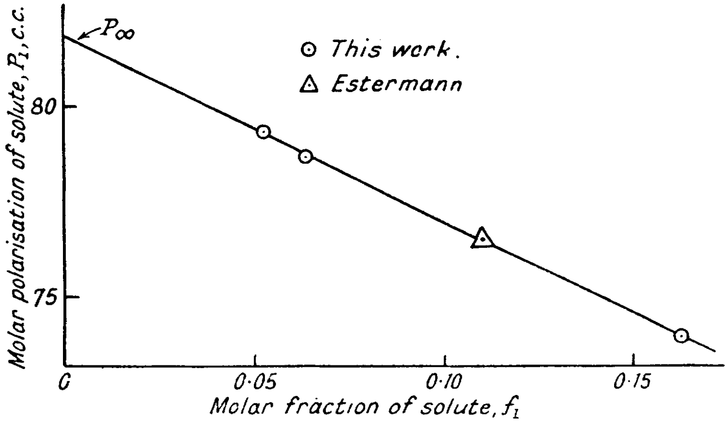
NOTES.

The Molar Polarisation of Solutions of Aniline in Benzene. By H. G. EMBLEM and C. A. McDOWELL.

THE molar polarisation of solutions of aniline in benzene has been measured by Estermann (*Z. physikal. Chem.*, 1928, *B*, **1**, 134), Höjendahl (*Physikal. Z.*, 1929, **30**, 319), Hassel and Uhl (*Z. physikal. Chem.*, 1929, *B*, **8**, 187), Tiganik (*ibid.*, 1931, *B*, **14**, 135), and Le Fèvre and Le Fèvre (J., 1936, 1135), but there are slight discrepancies between the results. Hassel and Uhl, and Le Fèvre and Le Fèvre, report a slight increase of the molar polarisation with dilution, whereas Tiganik's measurements show practically no dependence on concentration. Estermann's work cannot be compared with these as he only measured the temperature variation of the molar polarisation of a single solution. We had occasion to measure accurately the polarisation of solutions of aniline in benzene and our results show a fairly definite increase in the molar polarisation with dilution. In the figure we have plotted the values for the molar polarisation of aniline in benzene solution at 20° against the molar concentration of the solution and have included the value obtained by Estermann at the same temperature; it will be seen that this is in good agreement with our results. The value of the molar polarisation at infinite dilution ($P_{\infty} = 81{\cdot}91$ c.c.), calculated from our measurements by the method of least squares, is in excellent agreement with the value ($P_{\infty} = 81{\cdot}6$ c.c.) obtained by Hassel and Uhl, and is slightly higher than other recorded values. From this value of P_{∞}, we have computed the dipole moment of aniline after allowing for the atomic polarisation,



Molar polarisation of aniline in benzene at 20°.

P_A, in the manner suggested by Sugden and Groves (J., 1937, 1779, 1782), who showed that the atomic polarisation of aniline is approximately 5% of the electronic polarisation P_E; since P_E is 30·66 c.c., we get P_{E+A} = 32·2 c.c., and as $P_\infty = P_A + P_E + P_O$, we find P_O, the orientation polarisation, to be 49·7 c.c., yielding for the dipole moment of aniline in benzene solution at 20°, the value $1{\cdot}54 \times 10^{-18}$ E.S.U. In the following table we summarize the various published values for the molar polarisation and dipole moment of aniline in benzene solution.

Molar polarisation and dipole moment of aniline in benzene solution.

Temp.	P_∞ (c.c.).	$\mu \times 10^{18}$ (E.S.U.).	Authors.	Temp.	P_∞ (c.c.).	$\mu \times 10^{18}$ (E.S.U.).	Authors.
18°	81·6	1·55	Hassel and Uhl.	20°	79·7	1·52	Tiganik.
20	—	1·51	Höjendahl.	25	78·4	1·51	Le Fèvre and Le Fèvre.
20—50	—	1·60	Estermann.	20	81·91	1·54	This work.

Apparatus.—The capacities were measured by means of a Muirhead Type 3A heterodyne capacity set which had been calibrated at the National Physical Laboratory. Calibrated cells of the Sayce–Briscoe pattern as modified by Sugden (J., 1933, 770) were employed. All measurements were made with the dielectric cell in an oil thermostat.

Calculation of Molar Polarisations.—The dielectric constants of the solutions were calculated from their measured capacities by Miller's method (*J. Amer. Chem. Soc.*, 1942, **64**, 117), and the molar polarisations of the aniline from the usual mixture formula.

Densities.—The densities of the solutions were determined in double capillary-necked pycnometers of a special design. All measurements were made in a thermostat controlled to 0·01°.

Materials.—*Aniline.* A sample of "AnalaR" aniline was carefully purified by Knowles's procedure (*Ind. Eng. Chem.*, 1920, **12**, 881), and then distilled several times in a vacuum; the final product had $n_D^{20°}$ 1·5860, $d_{4°}^{20°}$ 1·0214.

Benzene. "AnalaR" Benzene was washed with concentrated sulphuric acid, dried over sodium, distilled, and frozen three times to remove homologues. A sample was refluxed over phosphoric oxide for 10 hours, stored over this reagent, and distilled from it immediately before use. The final product had $n_D^{20{\cdot}5°}$ 1·5006.

Results.—In the following table, ϵ = dielectric constant, f_1 = molar fraction of aniline, $d_{4°}^{20°}$ = density of solution, P_1 = molar polarisation of aniline in benzene solution, all at 20°.

Molar polarisation of solutions of aniline in benzene.

f_1.	ε.	$d_{4°}^{20°}$.	P_1, c.c.	f_1.	ε.	$d_{4°}^{20°}$.	P_1, c.c.	f_1.	ε.	$d_{4°}^{20°}$.	P_1, c.c.
0·0519	2·480	0·8865	79·38	0·0626	2·512	0·8873	78·75	0·1604	2·872	0·9042	73·94

$$P_{E+A} = 32{\cdot}2 \text{ c.c.};\quad P_\infty = 81{\cdot}91 \text{ c.c.};\quad \mu = 1{\cdot}54 \times 10^{-18} \text{ E.S.U.}$$

We wish to express our thanks to Dr. E. A. Moelwyn-Hughes, whose efforts made this work possible, and to Dr. G. H. Whiting, for help of various kinds. We are also indebted to the Chief Scientific Officer, Ministry of Supply, for permission to publish this note.—THE UNIVERSITY, LIVERPOOL 3. [*Received, December 18th*, 1945.]

The Fries Reaction. Part II. On the Nature of the Substance described as 2-Hydroxy-1-benzoylnaphthalene (m. p. 175°).*

By ALEXANDER SCHÖNBERG and AHMED MUSTAFA.

HOUBEN and FISCHER (*Ber.*, 1927, **60**, 1777) directed attention to the fact that two different substances, m. p. 142° and m. p. 175°, are described as being 1-benzoyl-2-naphthol and, without carrying out experiments, they suggested that the latter substance is 3-benzoyl-2-naphthol. According to our observations, however, it is 6-benzoyl-2-naphthol, because on alkaline fusion we obtained 6-carboxy-2-naphthol, previously obtained by Butler and Royle (*J.*, 1923, **123**, 1654). In agreement with the new formula, the substance (m. p. 175°) couples with benzenediazonium chloride and is readily converted into a *methyl ether* by either diazomethane or methyl sulphate.

The formation of 6-benzoyl-2-naphthol is believed to be due to a Fries reaction: $C_{10}H_7{\cdot}OH(2) + CPhCl_3 \longrightarrow C_{10}H_7{\cdot}O{\cdot}CPhCl_2(2) \longrightarrow (6)CPhCl_2{\cdot}C_{10}H_6{\cdot}OH(2) \longrightarrow (6)\ Ph{\cdot}CO{\cdot}C_{10}H_6{\cdot}OH(2)$. Since, as a result of a Fries rearrangement, 2-naphthyl acetate gives 6-acetoxy-2-naphthol, but in only 5% yield (Witt and Braun, *Ber.*, 1914, **47**, 3231; cf. Fries and Schimmelschmidt, *Ber.*, 1925, **58**, 2837), whereas that of 6-benzoyl-2-naphthol is 70%, the latter is a suitable starting material for derivatives of 2-naphthol substituted in position 6.

6-*Benzoyl*-2-*naphthol.*—This substance was prepared according to Gesellschaft für Chemische Industrie in Basle, D.-R.P. 378,908 (cf. Friedlaender, "Fortschritte der Teerfarbenfabrikation," Bd. XIV, 1921—1925, p. 469), in almost colourless crystals, m. p. 175°. It is readily soluble in aqueous sodium hydroxide with an intense yellow colour and its alcoholic solution gives no colour with ferric chloride solution [Found: C, 82·1; H, 4·8; *M* (Rast), 231. Calc. for $C_{17}H_{12}O_2$: C, 82·2; H, 4·8%; *M*, 248]. Its solution in aqueous sodium hydroxide, when treated with a cold acid aqueous solution of benzenediazonium chloride, gives a bright red precipitate.

Fusion of 6-*Benzoyl*-2-*naphthol with Potassium Hydroxide.*—6-Benzoyl-2-naphthol (1 g.) was mixed with powdered potassium hydroxide (8 g.) in a nickel crucible and heated for 15 mins. at 240° (bath temp.); the temperature was raised to 280° and kept there for 5 mins. After cooling, the solid contents were dissolved in water (10 c.c.), and the solution was filtered, acidified with ice-cold dilute hydrochloric acid, and extracted with ether. The ethereal extract was washed with aqueous sodium carbonate and on evaporation gave 2-naphthol (identified by mixed m. p.). The aqueous sodium carbonate washings were acidified and extracted with ether; on evaporation colourless crystals were obtained which, on recrystallisation from water, proved to be 6-carboxy-2-naphthol, m. p. 245° (Butler and Royle, *loc. cit.*, give 241°). 6-Carboxy-2-naphthol is soluble in alcohol but difficultly soluble in benzene. Its alcoholic solution, when treated with ferric chloride in aqueous alcohol, gives an orange coloration as described by Butler and Royle (Found: C, 69·8; H, 4·4. Calc. for $C_{11}H_8O_3$: C, 70·2; H, 4·2%). The acetyl derivative, crystallised from water, had m. p. 220—221° (Butler and Royle give 221—223°).

2-*Methoxy*-6-*benzoylnaphthalene* was obtained by the action of methyl sulphate or of ethereal diazomethane solution on 6-benzoyl-2-naphthol. It crystallised readily from light petroleum (b. p. 80—90°), dissolved in hot ethyl alcohol, and was insoluble in aqueous sodium hydroxide. Its alcoholic solution did not give a colour with aqueous ferric chloride (Found: C, 82·4; H, 5·3; OMe, 11·5. $C_{18}H_{14}O_2$ requires C, 82·4; H, 5·3; OMe, 11·8%).—FOUAD 1ST UNIVERSITY, FACULTY OF SCIENCE, ABBASSIA, CAIRO, EGYPT. [*Received, January 2nd*, 1946.]

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* Schönberg and (Miss) Akila Mustafa, *J.*, 1943, 79, is regarded as Part I.