114. *Substituted Benzidines and Related Compounds as Reagents in Analytical Chemistry. Part I. Solubilities of the Sulphates.*

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An examination has been made of the reactions of substituted benzidines and related compounds with the object of developing new reagents in analytical chemistry. The solubilities of the sulphates of a series of these amines have been determined in an attempt to establish possible fundamental relationships between molecular structure and solubility, and to obtain new reagents for the rapid determination of the sulphate ion.

Benzidine possesses three particular properties which make it a valuable reagent in analytical chemistry: (1) it is easily oxidised, (2) it forms complexes with metallic salts, (3) it forms salts with acids. In some cases, however, *e.g.*, the determination of sulphate, the reagent is not entirely satisfactory, and it seemed to us that compounds of similar structure might have advantages as analytical reagents. Accordingly, we have prepared a number of substituted benzidines and related compounds, and examined their reactions. The present paper describes the sulphate-precipitating properties of these compounds. Subsequent papers will describe further reactions and their analytical applications.

Many examples are known of decrease in solubility of complex compounds with increase in molecular weight (see Feigl, " Specific, Selective, and Sensitive Reactions," Academic Press, 1949, Chap. IX). Since the majority of the substituted benzidines and related compounds we prepared are of higher molecular weight than benzidine itself, it was thought that a weighting effect might exist, resulting in a decrease in solubility of the sulphate.

A survey of the literature revealed that several substituted benzidines and some related compounds formed difficultly soluble sulphates. In only one case, however, were solubility data given, *viz.*, *o*-tolidine sulphate (1·2 g. per l. at room temperature; Van Loon, *Chem. Zent.*, 1908, II, 1169) though naphthidine sulphate was stated to be less soluble than benzidine sulphate (Nietzki and Goll, *Ber.*, 1885, **18**, 3255).

The sulphates of several amines were prepared, and their solubilities in water determined (see table); ultimate analysis showed that in every case the normal sulphate had been obtained, but none of the sulphates examined was less soluble than benzidine sulphate. However, the following general observations can be made: (1) No weighting effect is evident; *i.e.*, increase in the weight of the molecule does not result in a decrease in solubility; some other factor may be opposing any weighting effect. (2) In general, separation of the rings in such a way that resonance between them is stopped results in a greatly increased sulphate solubility; with 4 : 4′-diaminostilbene, where resonance between the rings is maintained, a marked decrease in sulphate solubility is found. (3) Monomethylation of one of the amino-groups of benzidine results in an increase in sulphate solubility. This loss of sulphate-precipitating properties with methyl blocking is confirmed by the behaviour of *NN*′-dimethylbenzidine, which is stated by Willstätter and Kalk (*Ber.*, 1904, **37**, 3773) to have a very soluble sulphate. On the other hand, it is known that monoacetylated and monobenzoylated benzidines will give precipitates with sulphates (Hovorka, *Chem. Listy*, 1942, **36**, 113), though no solubility data are available. *NN*′-Diacetylbenzidine is described as giving only a faint precipitate under the same conditions, and it may be assumed that the sulphate of this compound is more soluble than that of monoacetylbenzidine.

Vanillylidenebenzidine has been used in the volumetric determination of sulphate (*idem, ibid.*), but from the experimental details given it would seem that the sulphate of this compound is more soluble than that of benzidine. Other mono- and di-methines derived from benzidine have been prepared (*idem, ibid.*) and these all give precipitates with sulphate. It may be concluded that condensation in this way restores the sulphate-precipitating properties of benzidine, but no solubility data are available.

	Analysis of sulphate.									
	Found, %.				Calc., %.				Solubility of sulphate,	
Amine.	C.	H.	N.	S.	C.	H.	N.	S.	g./l. at 25°.	Ref.
Benzidine	51·0	4·8	10·0	11·1	51·1	5·0	9·9	11·3	0·098	1
2-Methylbenzidine	52·8	5·4	9·2	10·5	52·7	5·4	9·5	10·8	0·342	2
3-Methylbenzidine	52·6	5·2	9·5	10·7	52·7	5·4	9·5	10·8	0·448	3
2 : 2′-Dimethylbenzidine	54·2	5·8	9·2	10·0	54·2	5·9	9·0	10·3	8·907	4
2 : 3′-Dimethylbenzidine	54·0	6·0	8·9	10·2	54·2	5·9	9·0	10·3	0·488	5
3 : 3′-Diethylbenzidine	56·7	6·7	8·3	9·4	56·8	6·6	8·3	9·5	0·429	6
3 : 3′-Diaminobenzidine	35·3	4·5	13·5	15·6	35·1	4·4	13·7	15·6	1·121	7
2-Aminodiphenyl	65·7	5·7	6·4	7·0	66·0	5·6	6·4	7·3	0·264	8
4-Aminodiphenyl	66·0	5·7	6·4	7·0	66·0	5·6	6·4	7·3	0·130	9
4-Amino-1-*p*-aminophenylnaphthalene	57·9	4·7	8·7	9·3	57·8	4·9	8·5	9·6	0·205	10
4 : 4′-Diamino-1 : 1′-dinaphthyl	62·9	4·4	7·5	8·4	62·8	4·7	7·3	8·4	0·101	11
4 : 4′-Diamino-3 : 3′-dimethyl-1 : 1′-dinaphthyl	64·6	5·2	6·6	7·7	64·4	5·4	6·8	7·8	0·162	12
2 : 7-Diaminofluorene	53·1	4·6	9·2	10·7	53·1	4·8	9·5	10·9	0·175	13
2 : 7-Diaminodiphenylene oxide	48·6	4·0	9·8	10·6	48·6	4·1	9·5	10·8	0·218	14
4 : 4′-Diaminodiphenylmethane	52·6	5·4	9·4	10·6	52·7	5·4	9·5	10·8	>10	15
4 : 4′-Diaminostilbene	54·6	5·4	8·8	10·4	54·5	5·2	9·1	10·4	0·132	16
4 : 4′-Diaminodiphenylamine	48·5	5·3	14·4	10·7	48·5	5·1	14·1	10·8	4·248	17
2-Aminodiphenylamine	61·5	5·4	11·8	6·7	61·8	5·6	12·0	6·9	1·452	18
4-Aminodiphenylamine	61·6	5·6	12·1	6·9	61·8	5·6	12·0	6·9	1·352	19
4-Aminobenzophenone	63·6	4·6	5·7	6·2	63·4	4·9	5·7	6·5	2·652	20
4 : 4′-Diaminoarsenobenzene	33·6	3·1	6·7	7·4	33·4	3·3	6·5	7·4	1·347	21
Naphthylene-1 : 2-diamine	46·9	4·5	10·8	12·2	46·9	4·7	10·9	12·5	5·516	22
Naphthylene-1 : 8-diamine	46·6	4·8	10·7	12·4	46·9	4·7	10·9	12·5	0·222	23
N-Methylbenzidine	63·3	6·2	11·5	6·2	63·1	6·1	11·3	6·5	>10	24

[1] Cf. Bisson and Christie, *Ind. Eng. Chem.*, 1920, **12**, 485 (0·096—0·098 g./l.). [2] Jacobson, *Ber.*, 1895, **28**, 2549. [3] *Idem, ibid.*, p. 2544. [4] Schultz and Rohde, *Chem. Zent.*, 1902, II, 1447. [5] Schultz, *Ber.*, 1884, **17**, 469. [6] Schultz and Flachsländer, *J. pr. Chem.*, 1902, **66**, 163. [7] Brunner and Witt, *Ber.*, 1887, **20**, 1025. [8] Fichter and Sulzberger, *Ber.*, 1904, **37**, 879. [9] *Idem, ibid.*, p. 881. [10] Bucherer and Sonnenburg, *J. pr. Chem.*, 1910, **81**, 19. [11] Cohen and Oesper, *Ind. Eng. Chem. Anal.*, 1936, **8**, 306. [12] Fries and Lohmann, *Ber.*, 1921, **54**, 2922. [13] Morgan and Thomason, *J.*, 1926, 2694. [14] Bayer, D.R.-P. 48,709. [15] King, *J.*, 1920, 992. [16] Elbs and Hoermann, *J. pr. Chem.*, 1889, **39**, 502. [17] Barbier and Sisley, *Bull. Soc. chim.*, 1905, **33**, 1233. [18] Kehrmann and Havas, *Ber.*, 1913, **46**, 342. [19] Meyer, *Ber.*, 1920, **53**, 1273. [20] Chattaway, *J.*, 1904, 395. [21] Ehrlich and Bertheim, *Ber.*, 1911, **44**, 1266. [22] Lawson, *Ber.*, 1885, **18**, 2427. [23] Hodgson and Whitehurst, *J.*, 1945, 203. [24] Rassow and Berger, *J. pr. Chem.*, 1911, **84**, 273.

Apart from the above observations, no relation between structure and solubility can be shown yet, but we hope to continue this work later.

Experimental.—The solubilities were determined as follows: The finely powdered amine sulphate was suspended in 200 ml. of distilled water, contained in a 250-ml. conical flask immersed in a thermostat at 25° ($\pm$0·1°). The contents of the flask were stirred for 72 hours by an electrically driven, rotating, glass stirrer, and then 100 ml. of the solution were filtered off and evaporated to dryness in a platinum basin on a steam-bath, and the residue was weighed.

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