274. *Substituted Benzidines and Related Compounds as Reagents in Analytical Chemistry. Part XII.* Reagents for the Precipitation of Sulphate.*

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The sulphates of the 4-amino-4′-halogenodiphenyls have been prepared, and their solubilities in water determined. The values obtained are considerably less than those for 4-amino- and 4 : 4′-diamino-diphenyl. One compound, 4-amino-4′-chlorodiphenyl, has the least soluble sulphate and has been developed as a new reagent for the rapid and accurate alkalimetric determination of the sulphate ion. Interferences are few; in particular, the nitrate ion has no effect. The reagent is simply prepared and is readily and completely recovered after use.

The solubility of benzidine sulphate has been determined by several workers. Recently, Belcher and Nutten (*J.*, 1951, 544) showed that none of the sulphates of several nuclear-substituted 4 : 4′-diaminodiphenyls is less soluble than benzidine sulphate. The solubility of 4-aminodiphenyl sulphate is comparable with that of benzidine sulphate (*loc. cit.*), and it is evident that the diamino-structure of benzidine is not an essential cause of insolubility of sulphates. The presence of one amino-group is sufficient provided it occupies one of the available *para*-positions in the diphenyl nucleus: the sulphates of both 2 : 4′-diaminodiphenyl (diphenyline) and 2-aminodiphenyl are more soluble than those of the corresponding *para*-substituted bases.

Belcher and Nutten had shown (*loc. cit.*) that no simple weighting effect was apparent from their examination of alkylbenzidines. The properties of 4-aminodiphenyl are similar in precipitation reactions to those of 4 : 4′-diaminodiphenyl (benzidine). The former has the 4′-position available for substitution, and it was decided to examine the effect of halogen in this position because its introduction would appreciably increase the molecular weight. It was thought that sulphates less soluble than that of 4-aminodiphenyl would be obtained, the solubility decreasing with increase in molecular weight. Accordingly, 4-amino-4′-chloro- and -4′-bromo-diphenyl were prepared, and the solubilities of their sulphates, determined by Belcher and Nutten's method (*loc. cit.*), were much less than those of benzidine or 4-aminodiphenyl and were, moreover, in the reverse of the order, Br $<$ Cl, to be expected from a weighting effect.

This reversal appeared to indicate that an electronic effect was exerting an influence on the lattice energy of the sulphate crystal which, in turn, influenced its solubility. The crystals of the 4-aminodiphenyl sulphates under investigation may be considered to be built of units of $X\cdot C_6H_4\cdot C_6H_4\cdot\overset{+}{N}H_3\cdot\overset{--}{SO_4}\cdot\overset{+}{N}H_3\cdot C_6H_4\cdot C_6H_4X$, where $X =$ hydrogen or halogen. The lattice energy of such a crystal will be affected by any alteration of the electrostatic forces binding the sulphate ion, and the van der Waals forces binding adjacent units. The inductive and mesomeric effects which arise when halogen is introduced into the molecule must affect these forces in the crystal structure and may result in a considerable alteration of the lattice energy for the different substituents. Thus, the inductive effect should result in an increase in lattice energy by increasing the electrostatic forces binding the sulphate ion and so should decrease the solubility, whilst the mesomeric effect, acting in opposition, should cause an increase in solubility. The van der Waals forces are much weaker than the electrostatic forces and may be ignored, as it is evident that the inductive and mesomeric effects also contribute greatly to the binding of adjacent units.

The solubilities of the sulphates of 4-aminodiphenyl and its four 4′-halogeno-derivatives appear to depend on the relative values of the inductive and mesomeric effects, and an examination of these values for hydrogen and the halogens should indicate the order of these solubilities. However, no values which would allow the comparison of their magnitudes have been recorded, although various expressions have been proposed for each effect, separately.

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* Part XI, *J.*, 1952, 2438.

The solubilities found for all four halogeno-base sulphates were less than that of the 4-amino-sulphate, the salt of 4-amino-4'-chlorodiphenyl being the least soluble; the order was: Cl<Br<F<I<H. However, van Hove (*Bull. Sci. Acad. roy. Belg.*, 1922, **2**, 524) has reported the solubility of 4-amino-4'-fluorodiphenyl sulphate to be 200 mg./l., *i.e.*, much greater than that of 4-aminodiphenyl; in the absence of details of van Hove's work, this discrepancy cannot be explained. The following Table lists the solubilities (S, in mg./l. at 25°) of the various sulphates. The analytical data show that only the normal sulphates were examined; van Hove may have obtained an acid sulphate of higher solubility. The amounts of sulphate left in solution are included for comparison.

Analyses and solubilities of sulphates.

	Found, %				Calc., %					
4-Aminodiphenyl	C	H	N	S	C	H	N	S	S	SO$_4^{2-}$ left in soln., mg./l.
(Unsubstituted)	(See Belcher and Nutten, *loc. cit.*)								130	28·6
4'-Amino-									98	33·4
4'-Iodo-	42·1	3·1	4·1	4·6	42·0	3·2	4·1	4·7	110	15·3
4'-Fluoro-	61·1	4·6	6·0	8·1 *	61·0	4·7	5·9	8·0 *	55	11·2
4'-Bromo-	48·6	3·7	4·8	5·2	48·5	3·7	4·7	5·4	35	5·7
4'-Chloro-	57·0	4·3	5·4	6·2	57·0	4·4	5·6	6·3	15	2·9

* Values for F (not S).

These results indicate that all four halogeno-derivatives should prove useful reagents for the precipitation of sulphate. However, the salts formed by the iodo-base with all the common acids were too insoluble to enable them to be used as reagents and this substance was not examined further. The sensitivity of the other three bases towards the sulphate ion decreased in the order of increasing sulphate solubility: that of the chloro-substituted base was comparable with that of barium chloride. The hydrochloride of 4-amino-4'-chlorodiphenyl is the most soluble of the halogeno-amines (*ca.* 0·35%), and as this amine also has the best sulphate-precipitating properties, it alone was examined as a possible reagent.

Preliminary experiments had shown that a boiling, saturated, aqueous solution of 4-amino-4'-chlorodiphenyl was alkaline towards phenolphthalein. Samples of its sulphate, freshly precipitated and also after various periods of storage, were readily titrated with alkali although the end-points with phenolphthalein were difficult to discern. Accordingly, a mixed indicator having a lower pH range was used in all subsequent titrations. Actual sulphate determinations were carried out to determine the most suitable conditions for precipitation. It was found that between pH 1 and 2 a two-fold excess of reagent and a standing time of 15—20 minutes gave quantitative recoveries of sulphate. Below pH 1, the hydrochloride of the base tended to be precipitated, and could not readily be washed out of the sulphate. Above pH 2, the precipitate was very finely divided and filtered slowly. It was difficult to dissolve the requisite amount of reagent in solutions of such acidity. Amounts of sulphate of 2·5—25 mg. and 25—100 mg. were rapidly and accurately determined under these conditions, a more concentrated reagent solution being used for the larger amounts of sulphate. Results are given in the following table.

Recoveries from pure sulphate solutions at pH 1·3—1·5.

SO$_4^{2-}$ taken (mg.)	0·04775N-NaOH reqd., ml.	Vol. of 0·2% reagent (ml.)	SO$_4^{2-}$ found (mg.)	SO$_4^{2-}$ taken (mg.)	0·1256N-NaOH reqd., ml.	Vol. of 0·4% reagent (ml.)	SO$_4^{2-}$ found (mg.)
2·53	1·10	20	2·53	25·33	4·20	80	25·31
5·07	2·21	30	5·08	38·00	6·30	120	37·94
10·15	4·42	60	10·15	50·66	8·41	160	50·62
10·47	4·52	75	10·47	63·33	10·52	200	63·33
15·20	6·61	90	15·17	75·99	12·62	240	75·99
20·26	8·82	120	20·25	88·66	14·71	280	88·55
22·91	9·98	150	22·88	101·32	16·82	320	101·30
25·33	11·03	150	25·32				

The effect of foreign ions on the recovery of 25 mg. of sulphate was examined. Of the common anions, chloride, bromide, iodide, nitrate, acetate, citrate, and tartrate did not interfere when present in 20-fold amounts (the maximum examined). Oxidising agents except hydrogen peroxide interfered by decomposing the reagent; 5 ml. of 30% peroxide had no effect on the sulphate recovery. Zinc, copper, and magnesium formed soluble complexes with the reagent, but the results were not impaired when these elements were present in 10-fold amounts. Iron(III), chromium(III), calcium, and the alkali metals did not interfere when present in 20-fold amounts (the maximum examined). Aluminium seriously interfered by forming an insoluble complex salt containing neutral sulphate, but this was avoided by use of tartaric acid. Phosphate, tellurite, selenate, and oxalate interfered by forming insoluble salts with the reagent. Interference by phosphate was the only disadvantage in the use of this reagent, but this could be eliminated by prior removal as calcium phosphate or, with zinc oxide, as zinc phosphate.

EXPERIMENTAL

A. *Preparation of 4-Amino-4′-halogenodiphenyls and Their Sulphates.*—(i) *4-Amino-4′-chlorodiphenyl.* 4-Chloro-4′-nitrodiphenyl (69 g.) (prepared in 65% yield by Turner and Le Fèvre's method, *J.*, 1928, 253) was reduced with pure electrolytic iron and hydrochloric acid in 90% ethanol (cf. Gray, Hartley, and Jones, *J.*, 1952, 1959). Pure 4-amino-4′-chlorodiphenyl was obtained in colourless (or faintly yellow) shimmering plates on recrystallisation from light petroleum (b. p. 80—100°) (yield 95%; m. p. 128°, unchanged by vacuum-sublimation).

(ii) *4-Amino-4′-bromodiphenyl.* 4-Bromo-4′-nitrodiphenyl, obtained in 60—65% yield by Turner and Le Fèvre's method (*J.*, 1926, 2045), was reduced as for (i). Pure 4-amino-4-bromodiphenyl was obtained in pale yellow plates (yield 95%), m. p. 146°, unchanged by vacuum-sublimation.

(iii) *4-Amino-4′-iododiphenyl.* 4 : 4′-Dinitrodiphenyl (10 g.) was suspended in 50% ethanol (600 ml.) with vigorous stirring, and the mixture boiled under reflux. A solution of sodium sulphide nonahydrate (16 g.) and sulphur (4·2 g.) in water (60 ml.) was added during 15 min., and the mixture refluxed for a further ½ hr. After cooling, 4-amino-4′-nitrodiphenyl was filtered off and recrystallised from acetone; this gave 8 g. (90%) of orange-red, shimmering plates, m. p. 198°. This base (8 g.) was dissolved in glacial acetic acid (50 ml.), and the solution cooled to 10°. Solid sodium nitrate (2·5 g.) was gradually added (10 min.) to the vigorously stirred solution, which was then stirred for a further 15 min. The diazonium solution was decomposed with potassium iodide (4 g.) in water (15 ml.) and warmed on a water-bath until evolution of nitrogen had ceased. The mixture was diluted with water (250 ml.), and sulphur dioxide passed in for 1—2 min. The precipitated 4-iodo-4′-nitrodiphenyl was filtered off, washed well with water, and recrystallised from glacial acetic acid, giving 11 g. of yellow-brown needles, m. p. 204° (cf. Angeletti, *Giorn. Farm. Chim.*, 1926, **75**, 261). 4-Iodo-4′-nitrodiphenyl (10 g.) was refluxed with ethanol (100 ml.) containing concentrated hydrochloric acid (5 ml.); zinc dust (8·5 g.) was added in small portions (10 min.), and the solution refluxed for a further ½ hr., then filtered, and the ethanol removed by distillation. The residue was made alkaline and extracted by ether. The extract was evaporated, and the residual pale yellow solid recrystallised from light petroleum (b. p. 80—100°), giving pale yellow plates (6 g.), m. p. 165°.

(iv) *4-Amino-4′-fluorodiphenyl.* 4-Fluorodiphenyl was prepared by a modification of Schiemann and Roselius's method (*Ber.*, 1929, **62**, 1805). Diphenyl-4-diazonium chloride was treated with a solution of sodium borofluoride (cf. Adams, "Organic Reactions," 1949, Vol. V, p. 193). A quantitative yield of diphenyl-4-diazonium borofluoride was obtained, which was readily decomposed to give 4-fluorodiphenyl in 95% yield (cf. *op. cit.*). 4-Fluorodiphenyl (20 g.) was nitrated, and the 4-fluoro-4′-nitrodiphenyl reduced with zinc dust and hydrochloric acid (Van Hove, *loc. cit.*, p. 219). 4-Amino-4′-fluorodiphenyl was obtained as colourless plates from light petroleum (b. p. 80—100°) (yield 15 g.; m. p. 120°).

(v) *Preparation of sulphates.* 5 G. of each base were dissolved in sufficient 50% aqueous acetone and a solution of sulphuric acid in acetone was added until precipitation was complete. The sulphates were filtered off, washed with ether, and dried.

B. *Determination of Sulphate Solubilities.*—Belcher and Nutten's procedure (*loc. cit.*) was used.

C. *Determination of Sulphate.*—*Solutions required.* 4-Amino-4′-chlorodiphenyl hydrochloride, 0·24 and 0·48%* in 0·05N-hydrochloric acid. These solutions were prepared by dissolving with warming 2·4 g. and 4·8 g., respectively, of the hydrochloride in *ca.* 800 ml. of distilled water containing 50 ml. of N-hydrochloric acid. The solutions were filtered hot and diluted to

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* Approximately equivalent to 0·2 and 0·4% solutions of free base.

1 l. On storage, the stronger solution precipitated some hydrochloride; accordingly, warm freshly prepared reagent was used.

Sodium sulphate, 0·052M. Approx. 7·34 g. of anhydrous sodium sulphate were dissolved in distilled water and the solution diluted to 1 l. This solution, containing approx. 5 mg. of SO_4^{2-} per ml., was standardised gravimetrically.

Sodium hydroxide, 0·1 and 0·05N.

Mixed indicator solution. 0·04% Aqueous phenol-red (sodium salt) and 0·04% aqueous bromothymol-blue (sodium salt), 3 : 2 by vol.

Procedure. (a) 2·5—25 Mg. of SO_4^{2-}. The sulphate solution (1—10 ml., pH 1—7) contained in a conical beaker was treated with a small amount of filter-paper slurry and sufficient tartaric acid was added to form a complex with any aluminium present (5 mg. of tartaric acid/1 mg. of Al). Sufficient 0·24% reagent solution was added to give a 2-fold excess (6 ml./1 mg. of SO_4^{2-}), and the mixture set aside for 15—20 min. (The acidity of the reagent ensured a final pH of 1—2 for precipitation.)

(b) 25—100 Mg. of SO_4^{2-}. This was effected as in (a), but with 5—25 ml. of sulphate solution, sufficient warm (40°) 0·48% reagent solution (3 ml./1 mg. of SO_4^{2-}), and 30 min. storage.

The subsequent procedure was identical for (a) and (b). The precipitate was filtered on a pulp filter, prepared as follows. A conical glass filter-funnel (diam. 3″) was three-quarters filled with water, the end of the stem being closed with one finger. A Witt plate (diam. 1″) was securely placed in the funnel, care being taken to remove any air bubbles trapped beneath it. A slurry of Whatman No. 41 filter-paper fibre was added, and the liquid allowed to drain from the stem. The layer of pulp (about ½″ deep) was gently and evenly pressed down, and the finger was replaced on the end of the stem. More slurry was added until, on draining, an amount equal to, or slightly less than that in the first layer, was obtained. The surface of the pad was gently tamped down, and the filter and pad washed with water. An unbroken column of water extended from the base of the plate to the end of the stem.

When all the precipitate had been filtered off, 5—10 ml. of the mother-liquor were returned to the precipitation vessel and used to transfer any appreciable amounts of precipitate which might have remained on the walls. The vessel was then washed well with two or three 5-ml. amounts of distilled water, the filter being allowed to drain before each addition of wash liquid. The precipitate was then washed with distilled water until the washings were chloride-free, and the filter drained under gentle suction. The upper layer of pulp was removed by a stainless-steel spatula and transferred to the precipitation vessel. The lower layer was used to transfer particles of precipitate adhering to the wall of the funnel.

The pulp slurry was then vigorously stirred to break up aggregates of precipitate. (This is essential for rapid and accurate titrations, because the sodium hydroxide reacts very slowly with the precipitate unless it is finely divided.) The filter-funnel was then washed with distilled water directly into the vessel. The contents of the vessel (40—50 ml.) were boiled for 1 min., 3 or 4 drops of indicator added, and the solution titrated with standard alkali (0·05N for 2·5—25 mg., 0·1N for 25—100 mg. of SO_4^{2-}) to the first purple colour in the solution. The solution was then re-heated, and the titration continued until the first permanent purple tinge was obtained. (The pulp retains a small amount of precipitate and the first end-point is false, although it is an excellent guide to the nearness of the true end-point.)

Recovery of reagent. When about 5 l. of filtration and titration liquors had accumulated, they were made alkaline and filtered on a Buchner funnel. The pulp residue was washed well with water, drained, and transferred to a 600-ml. beaker. The pulp was stirred with warm methanol (150 ml.), filtered, and washed with ether (200—300 ml.) in several portions. The ether and about 50 ml. of methanol were removed by distillation, and the distillate was retained for future recoveries of reagent. The methanolic solution of 4-amino-4′-chlorodiphenyl was treated with 50 ml. of 6N-hydrochloric acid, and the precipitated hydrochloride was dissolved by boiling, more methanol being added if necessary. On cooling, the hydrochloride crystallised in colourless leaves which were filtered off and dried. A further yield was obtained by concentrating the filtrate. The recovery of the reagent was almost quantitative.

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