767. *Bisquaternary Ammonium Salts. Part II.* Salts of 4 : 4′-Diaminostilbene-2 : 2′-disulphonic Acid.*†

By W. G. Leeds and R. Slack.

4 : 4′-Diaminostilbene-2 : 2′-disulphonic acid forms sparingly water-soluble, highly crystalline salts with a wide variety of bisquaternary ammonium bases. These salts provide convenient intermediates for the conversion of one soluble salt into another since they are quantitatively decomposed by treatment with appropriate mineral or organic acids.

Several methods are available for the conversion of a water-soluble salt B^+X^- into a salt B^+Y^- of comparable or greater solubility, but where the base concerned is a bisquaternary ammonium derivative many of the procedures are difficult or inapplicable and an alternative method involving insoluble salts of 2 : 2′-dihydroxy-1 : 1′-dinaphthylmethane-3 : 3′-dicarboxylic acid has recently been described.[1]

This acid exhibits a high degree of specificity in salt formation and for the development of maximum insolubility the cationic component must possess, amongst other things, a minimum chain-length of 8—9 Å. In contrast, it has been found that 4 : 4′-diaminostilbene-2 : 2′-disulphonic acid forms sparingly soluble salts (stoicheiometry 1 : 1) with a

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* The paper by Libman, Pain, and Slack, *J.*, 1952, 2305, should be regarded as Part I of this series.

† Some of this work is described in B.P. 748,224.

[1] Barber and Gaimster, *J. Appl. Chem.*, 1952, **2**, 565.

wide variety of bisquaternary ammonium bases and can be used with advantage for the isolation and purification of many such compounds. Thus, although the dicarboxylic acid salts of tetramethylene-1 : 4-bis- and 4-ethylbenzene-1 : ω-bis-trialkylammonium hydroxides are either too soluble or too ill-defined to permit isolation, the corresponding stilbenedisulphonates are relatively insoluble and crystallise well. Most salts of the new series have solubilities between 0·1 and 0·5% in water at 20°. Again, certain mono-acid bases, and diacid bases which contain only one strongly basic group, form similar highly crystalline salts (stoicheiometry 2 : 1); examples of these are given in the Table. All the disulphonates described (see Table) have been prepared by treating an aqueous solution of a soluble quaternary salt with the appropriate amount of disodium or diammonium 4 : 4′-diaminostilbene-2 : 2′-disulphonate in water. The high solubility of the sodium and ammonium salts precludes inorganic contamination of the products. The salts are easily recrystallised from water and some of them separate with varying amounts of water of crystallisation. Vacuum-drying at 100° gives the anhydrous salt which are hygroscopic. The stilbenedisulphonates, the solubilities of which increase greatly with increasing temperature, can be converted into soluble quaternary salts by dissolution or suspension in water and precipitation of the insoluble 4 : 4′-diaminostilbene-2 : 2′-disulphonic acid by addition of the calculated amount of acid corresponding to the desired anion, preferably

4 : 4′-*Diaminostilbene*-2 : 2′-*disulphonates of various quaternary ammonium bases.*

Cation	Formula	Water content (mol.)	Found (%), followed by Required (%) †			
			C	H	N	S
Hexamethylene-1 : 6-bistrimethylammonium	$C_{26}H_{42}O_6N_4S_2$	—	54·2	7·6	9·3	11·3
			54·7	7·4	9·8	11·2
Hexamethylene-1 : 6-bis-1′-methylpyrrolidinium [a]	$C_{30}H_{46}O_6N_4S_2$	—	—	—	9·0	10·4
					9·0	10·3
Pentamethylene-1 : 5-bis-1′-methylpyrrolidinium [a]	$C_{29}H_{44}O_6N_4S_2$	3·50	51·8	7·8	8·2	—
			51·9	7·6	8·4	—
		5·00 *	50·0	7·5	7·9	—
			49·9	7·7	8·0	—
4-Ethylbenzene-1 : ω-bistrimethylammonium [b]	$C_{28}H_{38}O_6N_4S_2$	4·00	50·9	7·3	8·4	—
			50·8	7·0	8·5	—
		5·00 *	49·5	6·9	8·5	—
			49·4	7·1	8·2	—
4-Pentylbenzene-1 : ω-bisdimethylethylammonium [b]	$C_{33}H_{48}O_6N_4S_2$	1·20	58·0	7·6	—	9·6
			58·1	7·4	—	9·4
4-Pentylbenzene-1 : ω-bisdiethylmethylammonium [b]	$C_{35}H_{52}O_6N_4S_2$	0·31	60·8	7·8	7·9	—
			60·6	7·6	8·1	—
4-Ethyl*cyclo*hexane-1 : ω-bistrimethylammonium (α-form) [b]	$C_{28}H_{44}O_6N_4S_2$	4·86	49·3	8·0	—	—
			49·2	7·9	—	—
		5·04 *	48·7	7·6	8·5	—
			48·9	7·9	8·2	—
4-Ethyl*cyclo*hexane-1 : ω-bistrimethylammonium (β-form) [b]	$C_{28}H_{44}O_6N_4S_2$	3·64	50·7	7·9	8·2	—
			50·8	7·8	8·5	—
Tetramethylene-1 : 4-bisdiethylmethylammonium [c]	$C_{28}H_{46}O_6N_4S_2$	—	—	—	9·2	10·5
					9·4	10·7
2 : 4-Dichlorophenoxymethyldimethyloctylammonium [d]	$C_{48}H_{68}O_8N_4Cl_4S_2$	0·64	55·7	6·7	5·4	—
			55·1	6·6	5·4	—
ω-*p*-Aminophenoxyhexyltrimethylammonium	$C_{44}H_{66}O_8N_6S_2$	3·42	57·2	8·1	9·1	—
			56·8	7·8	9·0	—
4-Hexyloxybenzene-1 : ω-bistriethylammonium [e]	$C_{38}H_{58}O_7N_4S_2$	2·54	57·7	8·0	7·2	—
			57·6	8·0	7·1	—

* Alternative values for different samples exhibiting varying degrees of hydration. † Calculated values for hydrated material where necessary.

[a] Di-iodide described by Libman, Pain, and Slack.[2] [b] Ashley and Leeds.[3] [c] Prepared by K. Gaimster (see Barber and Gaimster [1] for other salts). [d] Chloride described by Barber and Green.[4] [e] Atkinson, Heywood, and Leeds.[5]

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[2] Libman, Pain, and Slack, *J.*, 1952, 2305.

[3] Ashley and Leeds, unpublished work.

[4] Barber and Green, *J. Appl. Chem.*, 1954, **4**, 115.

[5] Atkinson, Heywood, and Leeds, unpublished work.

below 60°. Quantitative decomposition occurs even with relatively weak acids such as tartaric.

4 : 4′-Diaminostilbene-2 : 2′-disulphonic acid is readily available commercially and has been used for many years in the dyestuffs industry. For the present purpose, however, the use of pure acid is important since crude commercial samples—particularly those which give deep red solutions in aqueous ammonia—often yield highly coloured derivatives. Occasional slight discoloration (presumably photo-instability) of diamino-disulphonates prepared from the pure acid has also been observed but this does not lead to difficulties during subsequent decompositions nor does it appear to affect analytical figures. Pure reagent can easily be obtained by acid decomposition of a *recrystallised* sample of a suitable quaternary ammonium salt, *e.g.*, hexamethylene-1 : 6-bis(trimethylammonium) 4 : 4′-diaminostilbene-2 : 2′-disulphonate.

EXPERIMENTAL

Examples given in detail illustrate general techniques. Other 4 : 4′-diaminostilbene-2 : 2′-disulphonates are prepared similarly.

Hexamethylene-1 : 6-*bistrimethylammonium* 4 : 4′-*Diaminostilbene*-2 : 2′-*disulphonate*.—Hexamethylene-1 : 6-bistrimethylammonium bromide (3·62 g.) in water (15 c.c.) was added to a solution of disodium 4 : 4′-diaminostilbene-2 : 2′-disulphonate (4·14 g.) in water (10 c.c.) at 50°. The pale yellow salt (5·34 g.) was collected after 12 hr. at 2° and was recrystallised from water, to give the pure compound (4·7 g.), m. p. 280° (decomp.), which contains water of crystallisation. Prolonged drying at 100° *in vacuo* over phosphoric oxide gave the *anhydrous salt*, m. p. 293—294° (decomp.). The solubility of the salt in water at 12° is approx. 0·4%.

Hexamethylene-1 : 6-*bis*-1′-*methylpyrroldinium* 4 : 4′-*diaminostilbene*-2 : 2′-*disulphonate*, m. p. 285—290° (decomp.), was prepared in a similar manner (solubility at 12° approx. 0·15%).

Hexamethylene-1 : 6-bis(trimethylammonium hydrogen tartrate) was prepared from the 4 : 4′-diaminostilbene-2 : 2′-disulphonate (5·7 g.) in water (15 c.c.) at 35—40° by treatment with (+)-tartaric acid (3·0 g.) in water (10 c.c.). The 4 : 4′-diaminostilbene-2 : 2′-disulphonic acid was collected and washed with cold water, and the combined filtrates were evaporated to dryness. The resulting syrup, after being treated with cold alcohol, gave the hydrogen tartrate (4·45 g.), m. p. 180—182° after recrystallisation from methanol (Barber and Gaimster[2] give m. p. 180—185°).

Pentamethylene-1 : 5-*bis*-1′-*methylpyrrolidinium* 4 : 4′-*Diaminostilbene*-2 : 2′-*disulphonate*.—The corresponding dibromide, a highly deliquescent, colourless, crystalline solid (4 g., from pentamethylene dibromide and 1-methylpyrrolidine in methanol), in water (10 c.c.) was added to a warm filtered solution of 4 : 4′-diaminostilbene-2 : 2′-disulphonic acid (4 g.) in water (15 c.c.) and aqueous ammonia (*d* 0·88; 5 c.c.). The pale yellow *salt* (4·6 g.) was collected after 3 hr. at 2°, washed with water, and dried in air. It slowly developed a pale red colour on the crystal surfaces but remained analytically pure, m. p. 305° (decomp.).

4-Ethylbenzene-1 : ω-bistrimethylammonium 4 : 4′-diaminostilbene-2 : 2′-disulphonate, m. p. >230° (decomp.), was prepared similarly from 4-ethylbenzene-1 : ω-bis(trimethylammonium iodide) and was converted into the corresponding dihydrogen phosphate by treating an aqueous suspension [1·812 kg., 2·71 moles of anhydrous salt in water (21 l.)] with phosphoric acid (100% recovery) and was filtered off and washed with water. The combined filtrates were filtered (charcoal) and concentrated under reduced pressure to 2 l. After being filtered (charcoal), the solution was added to methanol (4 l.) and acetone (4 l.), to give the colourless microcrystalline *dihydrogen phosphate tetrahydrate* (1·86 kg., 90%), m. p. 199° (decomp.) (Found: N, 5·8; P, 12·7; H_2O, 14·7. $C_{14}H_{30}O_8N_2P_2,4H_2O$ requires N, 5·7; P, 12·7; H_2O, 14·7%).

4-*Ethyl*cyclo*hexane*-1 : ω-*bistrimethylammonium* 4 : 4′-*diaminostilbene*-2 : 2′-*disulphonate*.—Sodium hydroxide (486 g.) in water (1 l.) was added gradually to a stirred solution of 2-(4-amino*cyclo*hexyl)ethylamine dihydrochloride[3] (α-form) (323 g.), and dimethyl sulphate (1·31 kg.) was added dropwise at 50° during 45 min. (external cooling). After a further hour at 50°, the filtered solution was added to 4 : 4′-diaminostilbene-2 : 2′-disulphonic acid (635 g.) in water (3·2 l.) and ammonia (*d* 0·88; 550 c.c.). The highly crystalline, pinkish-yellow 4 : 4′-diaminostilbene-2 : 2′-disulphonate (973 g.) separated immediately. Dehydration at 50° gave a primrose-yellow product which reverted to a stable hydrate, m. p. 290° (decomp.), in moist air.

The corresponding chloride was prepared from the 4 : 4′-diaminostilbene-2 : 2′-disulphonate (1·925 kg.) by treatment in aqueous suspension at 20° with 5·8N-hydrochloric acid (982 c.c.).

Recrystallisation from ethanol–acetone gave the *chloride trihydrate* (770 g., 77%), m. p. 317° (decomp.) (Found: C, 48·0; H, 10·8; N, 7·7; Cl, 20·5; H_2O, 15·0. $C_{14}H_{32}N_2Cl_2,3H_2O$ requires C, 47·6; H, 10·8; N, 7·9; Cl, 20·1; H_2O, 15·3%).

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RESEARCH LABORATORIES, MAY & BAKER LTD.,
DAGENHAM, ESSEX.

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