

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

PARA-TOLUENE SULFONATES AS DERIVATIVES FOR THE IDENTIFICATION OF AROMATIC AMINES

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Forster and Keyworth have made a systematic investigation of the amine salts of benzene sulfonic acid,^{1c} *m*-nitrobenzene sulfonic acid,^{1d} *o*- and *p*-nitrotoluene sulfonic acids,^{1e} α - and β -naphthalene sulfonic acids,^{1b} and the 2,6- and 2,7-naphthalene disulfonic acids,^{1a} and have pointed out the advantages of these salts over other derivatives for identifying aromatic amines. Because of the ready availability of *p*-toluene sulfonic acid and the possibility that it might yield lower melting derivatives than any of the other sulfonic acids, we have prepared and determined the melting points of the *p*-toluene sulfonates of a number of the more common amino compounds. The results are summarized in the table.

On comparing our results with those of Forster and Keyworth, we find that the *p*-toluene sulfonates are in general lower melting than the previously described sulfonates with the exception of the α -naphthalene sulfonates, where out of fifteen cases in which a comparison can be made, in eight cases the α -naphthalene sulfonates are lower melting. The melting points of these compounds are listed in the table for comparison. The ready availability of *p*-toluene sulfonic acid would seem to give its use a slight advantage over α -naphthalene sulfonic acid.

Three salts, namely, those of *p*-chloro- and *p*-bromoaniline, and *p*-aminobenzoic acid, were found difficult to prepare with a sharp melting point although analysis indicated them to be pure. In a number of cases great difficulty was found in causing the salts to crystallize and these have been reported as oils even though in a few cases the compounds have previously been isolated as solids. It was felt that if any special care was necessary in order to get crystalline products, the salt was not a satisfactory one for identification purposes. The failure to crystallize is the chief reason that the sulfonates are unsatisfactory derivatives for aliphatic amines.

Quite a few of the salts listed have been prepared before but in most such cases our preparations show a higher melting point. We have found that considerable care in drying the samples is necessary and traces of moisture may account for the lower melting points of other investigators. The previously recorded melting point and reference are also listed in the table.

¹ (a) Forster and Keyworth, *J. Soc. Chem. Ind.*, **43**, 165T (1924); (b) *ibid.*, **43**, 299T (1924); (c) Keyworth, *ibid.*, **43**, 341T (1924); (d) *ibid.*, **46**, 20T (1927); (e) *ibid.*, **46**, 397T (1927). References to other work on the sulfonates of amines will be found in these papers.

TABLE I
 PARA-TOLUENE SULFONATES OF AMINES^a

| Amine | Recryst. | Melting point, °C. | | Previously recorded m. p., °C. | Neut. equiv. | | Nitrogen | | M. p. o α -naphthalene sulfonate, ^b °C. |
|--------------------------------------|----------|--------------------|-------------|--|--------------|-------|----------|-------|---|
| | | Obs. | Corr. | | Calcd. | Found | Calcd. | Found | |
| Aniline | 2 | 232.0 | 238.4 | 223, ³ 235-235.5, ⁴ 230-231, ⁵ 216 ⁶ | 265.2 | 265.4 | 5.28 | 5.31 | 183 |
| <i>o</i> -Toluidine | 2 | 185.5-186.2 | 189.7-190.5 | 180 ³ | 279.2 | 278.0 | 5.02 | 4.97 | 237 |
| <i>m</i> -Toluidine | 2 | 171-172.5 | 174.6-176.1 | 161 ⁷ | 279.2 | 277.4 | 5.02 | 5.00 | 195-196 |
| <i>p</i> -Toluidine | 3 | 193-194.5 | 197.7-199.2 | ... | 279.2 | 278.7 | 5.02 | 4.94 | 181 |
| 4-Amino-1,3-dimethylbenzene | 3 | 176.6-177.5 | 180.4-181.3 | ... | 293.2 | 291.7 | 4.78 | 4.71 | ... |
| <i>o</i> -Chloroaniline ^b | 3 | 188.5-189.2 | 192.9-193.6 | 198 ⁶ | 299.6 | 297.0 | 4.67 | 4.47 | 237 |
| <i>m</i> -Chloroaniline ^b | 2 | 204.7-205.2 | 209.8-210.3 | ... | 299.6 | 299.1 | 4.67 | 4.56 | 176 |
| <i>p</i> -Chloroaniline ^b | 4 | 207-225 | 213-231 | 225-226 ⁸ | 299.6 | 299.3 | 4.67 | 4.68 | 231 |
| <i>o</i> -Bromoaniline ^b | 2 | 201-201.5 | 206.1-206.6 | ... | 344.1 | 341.3 | 4.07 | 3.96 | ... |
| <i>m</i> -Bromoaniline ^b | 2 | 199.1-200 | 204.1-205.0 | ... | 344.1 | 344.0 | 4.07 | 3.99 | 168 |
| <i>p</i> -Bromoaniline ^b | 2 | 208-228 | 214.2-234.2 | ... | 344.1 | 343.9 | 4.07 | 4.05 | 224 |
| <i>o</i> -Nitroaniline | .. | Oil | ... | ... | ... | ... | ... | ... | ... |
| <i>m</i> -Nitroaniline | 2 | 208-209.5 | 213.5-215.0 | ... | 310.2 | 310.2 | 9.03 | 9.02 | 261 |
| <i>p</i> -Nitroaniline ^c | 2 | 226-228.5 | 232.2-234.7 | ... | 310.2 | 308.0 | 9.03 | 8.55 | 241 |
| <i>o</i> -Aminophenol ^d | 2 | 219-220.5 | 224.7-226.2 | ... | 281.2 | ... | 4.98 | 5.09 | ... |
| <i>m</i> -Aminophenol ^d | .. | Oil | ... | ... | ... | ... | ... | ... | 200 |
| <i>p</i> -Aminophenol ^d | 2 | 245-246.5 | 252.1-253.6 | 220-245(d.) ⁴ | 281.2 | 280.0 | 4.98 | 4.95 | ... |
| <i>o</i> -Aminobenzoic acid | 2 | 218.5-219.0 | 224.1-224.6 | ... | 154.6 | 154.7 | 4.52 | 4.57 | ... |
| <i>m</i> -Aminobenzoic acid | 3 | 248.4-249.0 | 255.9-256.5 | ... | 154.6 | 154.7 | 4.52 | 4.52 | ... |
| <i>p</i> -Aminobenzoic acid | 3 | 230-235 | 236.5-241.5 | ... | 154.6 | 156.7 | 4.52 | 4.52 | ... |
| <i>p</i> -Aminoacetophenone | 3 | 174-175.5 | 177.8-179.3 | ... | 307.2 | 314.1 | 4.55 | 4.50 | ... |
| α -Naphthylamine | 3 | 241.5-243.0 | 248.4-249.9 | 239 ³ | 315.2 | 314.2 | 4.45 | 4.43 | 229 |
| β -Naphthylamine ^b | 3 | 212-213.8 | 217.3-219.1 | 219 ⁹ | 315.2 | 317.8 | 4.45 | 4.45 | 200-201 |
| <i>o</i> -Aminodiphenyl ^c | 3 | 189.5-189.1 | 194.1-195.6 | ... | 341.2 | 340.8 | 4.11 | 4.20 | ... |
| <i>p</i> -Aminodiphenyl ^b | 2 | 246.5-247.6 | 253.8-254.9 | ... | 341.2 | 342.8 | 4.11 | 4.14 | ... |

TABLE I (Concluded)

| Amine | Recryst. | Melting point, °C. | | Previously recorded m. p., °C. | Neut. equiv. | | Nitrogen | | M. p. of naphthalene sulfonate, ^b °C. |
|-----------------------------|----------|--------------------|-------------|--------------------------------|--------------|-------|----------|-------|--|
| | | Obs. | Corr. | | Calcd. | Found | Calcd. | Found | |
| Benzylamine | 2 | 180.5-181.5 | 184.5-185.5 | 180 ¹⁰ | 279.2 | ... | 5.02 | 5.04 | ... |
| Dibenzylamine | 2 | 155.5-156.5 | 158.3-159.3 | | 369.3 | 369.8 | 3.79 | 3.75 | ... |
| Tribenzylamine ^c | 2 | 200-202.5 | 205.2-207.7 | | 459.3 | 455.6 | 3.05 | 3.11 | ... |
| Benzylaniline | | 146-146.5 | 148.3-148.8 | | 355.2 | 356.0 | 3.94 | 3.94 | ... |
| Dibenzylaniline | | Oil | ... | | ... | ... | ... | ... | ... |
| <i>o</i> -Phenylenediamine | 2 | 259-260.5 | 267.3-268.8 | | 226.2 | 226.3 | 6.19 | 6.19 | ... |
| <i>m</i> -Phenylenediamine | 3 | 287-288 | 296.8-297.8 | | 226.2 | 226.4 | 6.19 | 6.27 | ... |
| <i>p</i> -Phenylenediamine | 3 | > 340 | ... | | 226.2 | 226.4 | 6.19 | 6.10 | 330 |
| 2,4-Diaminotoluene | 3 | 262.5-263.0 | 270.8-271.3 | | 233.2 | 236.4 | 6.00 | 6.04 | ... |

^a In addition to the salts listed in the table, unsuccessful attempts were made to prepare a number of others. Methylaniline, ethylaniline, dimethylaniline, diethylaniline, *p*-aminodimethylaniline, *i*-amylamine, di-*n*-propylamine, tri-*i*-amylamine, pyridine and quinoline gave oils which could not be readily crystallized. α - and β -aminoanthraquinone did not react with the sulfonic acid, or gave salts which were quite insoluble in water. ^b A large volume of water is necessary for recrystallizing the salts of β -naphthylamine, *p*-aminodiphenyl, *o*-chloroaniline, and *o*-bromoaniline. ^c A large excess of sulfonic acid must be used in preparing the salts of *o*-aminodiphenyl, *p*-nitroaniline, and tribenzylamine. Dilute hydrochloric acid (1 concd.:1 water) must be used in washing the salts of the last two compounds. ^d Benzylamine is too basic to titrate the *p*-toluene sulfonate, and the color of a solution of the salt of *o*-aminophenol is too deep to determine the end-point of the titration. ³ Norton and Otten, *Am. Chem. J.*, **10**, 140 (1888). ⁴ Bamberger and Rising, *Ber.*, **34**, 252 (1901). ⁵ Curtius and Kraemer, *J. prakt. Chem.*, [2] **125**, 323 (1930). ⁶ Heiduschka and Langkammerer, *ibid.*, [2] **88**, 425 (1913). ⁷ Meyer and Meyer, *ibid.*, [2] **68**, 290 (1903). ⁸ Halberkann, *Ber.*, **54**, 1833 (1921). ⁹ Slotta and Franks, *ibid.*, **63**, 678 (1930). ¹⁰ Neber and Uber, *Ann.*, **467**, 52 (1928).

Experimental

Aqueous solutions of *p*-toluene sulfonic acid were prepared by refluxing a weighed quantity of *p*-toluene sulfonyl chloride, m. p. 64–66°, with distilled water until a homogeneous solution resulted. This was diluted with water to a volume such that the concentration of *p*-toluene sulfonic acid was 2.5 molar. No attempt was made to remove the hydrochloric acid formed on hydrolysis as it does not interfere with and, in some cases, even aids the formation of the amine sulfonate.

To form the salts, 20 cc. of the above solution was added to an equivalent amount of amine, *i. e.*, 0.05 mole of monoamines and 0.025 mole of diamines. The mixture was heated to boiling until a clear solution resulted, a small amount of decolorizing carbon added, the solution filtered hot and then cooled in an ice-bath. In some cases it was necessary to add more water while in others the solution had to be evaporated in order to get the optimum concentration for crystallization. The products were recrystallized to constant melting point. The salts were air dried or dried in a vacuum desiccator, and then dried at 110°.

The neutral equivalents were determined according to the procedure of Perkin and Sewell² using phenolphthalein as an indicator and heating to boiling toward the end of the titration. Nitrogen was determined by a modified Kjeldahl procedure.

Summary

The *p*-toluene sulfonates of aromatic amines can, in general, be readily prepared in a pure state and are quite satisfactory derivatives for identification purposes.

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² Perkin and Sewell, *J. Soc. Chem. Ind.*, **42**, 27T (1923).