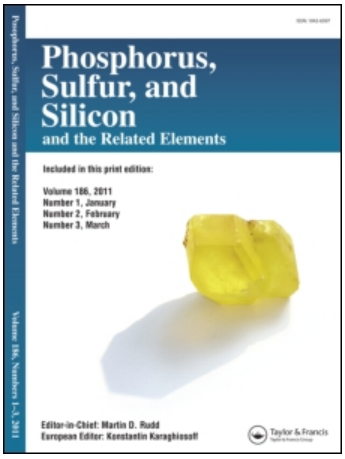

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SYNTHESIS OF SULFONATED 1,2-DICYANOBENZENES

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SYNTHESIS OF SULFONATED 1,2-DICYANOBENZENES

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Employing the corresponding halogen or amino (via the diazonium salts) substituted 1,2-dicyanobenzenes as starting materials 2,3- and 3,4-dicyanobenzenesulfonic acids (**3**) and (**4**) are synthesized. Several intermediates useful for the preparation of the sulfonic acids (**3**) and (**4**) are also obtained: 3- and 4-mercapto-1,2-dicyanobenzenes (**5**), (**16**), 2,3- and 3,4-dicyanobenzenesulfonyl chlorides (**10**), (**11**)), bis(2,3-dicyanophenyl)- and bis(3,4-dicyanophenyl)-disulfides (**14**), (**15**), and several sulfonamides (**17**)–(**24**) (from the sulfochlorides (**10**), (**11**). In addition, the synthesis of 4-(4-phonoxy-1,2-dicarbonitrile)benzenesulfonic acid (**26**) is described.

Key words: Dicyanobenzenesulfonic acids, 1,2-dicyanobenzene substituted, phthalodinitrile substituted.

INTRODUCTION

This paper describes the preparation of various 1,2-dicyanobenzenes bearing sulfur containing substituents. Most interesting are sulfonic acid groups due to their hydrophilic character and sulfonyl chlorides and mercapto groups due to their reactivity. Substituted 1,2-dicyanobenzenes are suitable starting materials for macrocyclic and heterocyclic compounds like phthalocyanines, isoindoles and triazines. For example sulfonated phthalocyanines are prepared either by the reaction of 3,4-dicarboxybenzenesulfonic acid derivatives in the presence of urea and a metal salt at high temperature or by direct sulfonation (or sulfochlorination) of unsubstituted phthalocyanines with statistic substitution.[1–6] The use of sulfonated 1,2-dicyanobenzenes would allow milder reaction conditions for the preparation of different reaction products such as phthalocyanines. Surprisingly up to now only few sulfonamides of 1,2-dicyanobenzenes are mentioned by one of us.[7] Therefore it seemed of interest to describe in this paper possibilities for the preparation of the sulfur containing derivatives employing known substituted 1,2-dicyanobenzenes.

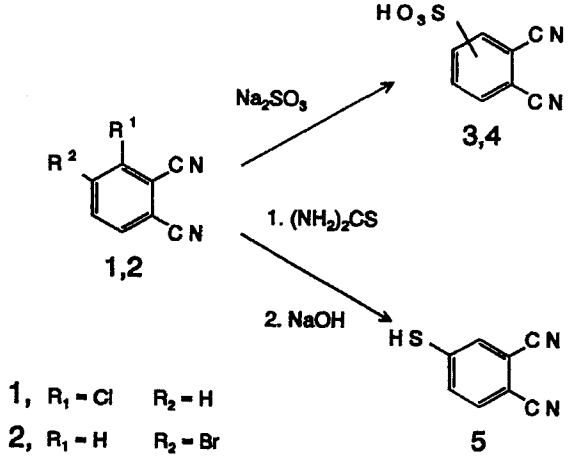
RESULTS AND DISCUSSION

For the synthesis of 1,2-dicyanobenzenes containing a directly connected sulfonic acid group at positions 3 or 4 in the benzene ring, two routes were examined:

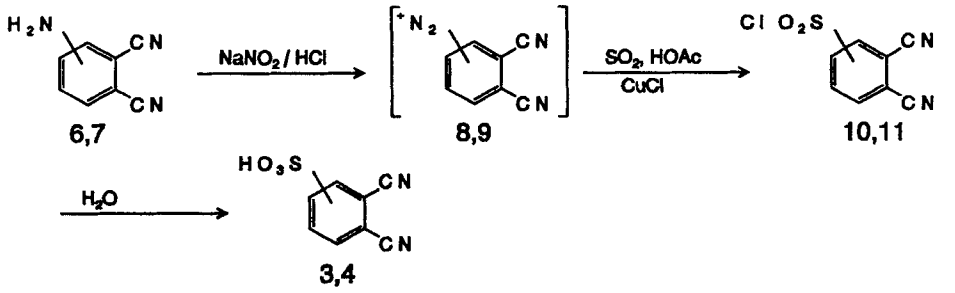
nucleophilic substitution of a halogen substituent in halogenated 1,2-dicyanobenzenes or substitution of a diazonium group employing amino substituted 1,2-dicyanobenzenes.

It is well known that the reaction of arylhalogenides with sodium sulfite in aqueous solution or in a water-dioxane mixture in the presence of cupric salts results in the substitution of the halogen substituent with formation of aromatic sulfonic acids.[8] It is expected that the presence of cyano groups may favor the nucleophilic substitution.[9] Surprisingly however, 2,3- and 3,4-dicyanobenzenesulfonic acids (**3**) and (**4**) employing the halogenated compounds (**1**) and (**2**) (Scheme I) are obtained in yields of only 5–18%. Also the introduction of a mercapto group by the reaction of 4-bromo-1,2-dicyanobenzene (**2**) with thiourea via the isothiouroniumsalt in analogy to References 10 and 11 leads only in a yield of 10% to 4-mercapto-1,2-dicyanobenzene (**5**) (Scheme I).

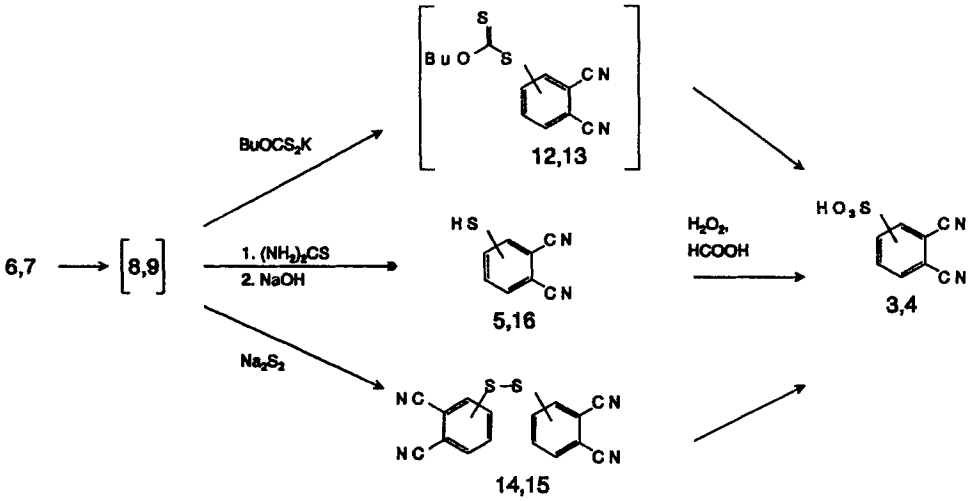
The second route uses the reaction of the diazonium salts (**8**, **9**) (from 3- and 4-amino-1,2-dicyanobenzenes (**6**, **7**) with SO_2 in acetic acid similar to a method described in References 12 and 13 with formation of the sulfochlorides (**10**, **11**). They are readily converted in water into the corresponding sulfonic acids (**3**, **4**) in high yields. Beside the sulfochlorides (**10**, **11**) several other intermediates are obtained by the reaction of the diazonium salts (**8**, **9**) with sulfur nucleophiles. By treatment of the diazonium salts with potassium butylxanthogenate, sodium disulfide or thiourea using procedures described in References 14 and 15 the dicyanophenyl-*o*-butyldithiocarbonates (**12**, **13**), the dicyanophenyldisulfides (**14**, **15**) and the mercaptodicyanobenzenes (**5**, **16**) are available. With the exception of 3-mercapto-1,2-dicyanobenzene (**16**), which was synthesized in a yield of only 7%, the other dinitriles are obtained in high yields. All these dinitriles are converted by oxidation with a solution of hydrogen peroxide in formic acid to the sulfonic acids (**3**) and (**4**) in yields of around 80%. The before mentioned sulfochlorides



SCHEME I Synthesis of 2,3- and 3,4-dicyanobenzenesulfonic acids (**3**, **4**) and 4-mercapto-1,2-dicyanobenzene (**5**) from halogenated 1,2-dicyanobenzenes (**1**, **2**). Substituents in compounds (**1**) (R = Cl), (**3**) are in the position 3 and in compound (**2**) (R = Br), (**4**) in position 4 of the benzene ring.



SCHEME II Synthesis of 2,3- and 3,4-dicyanobenzenesulfonic acids (**3**, **4**) from aminosubstituted 1,2-dicyanobenzenes (**6**), (**7**). Substituents in compounds (**3**), (**6**), (**8**), (**10**) are in the position 3 and in compounds (**4**), (**7**), (**9**), (**11**) in position 4 of the benzene ring.

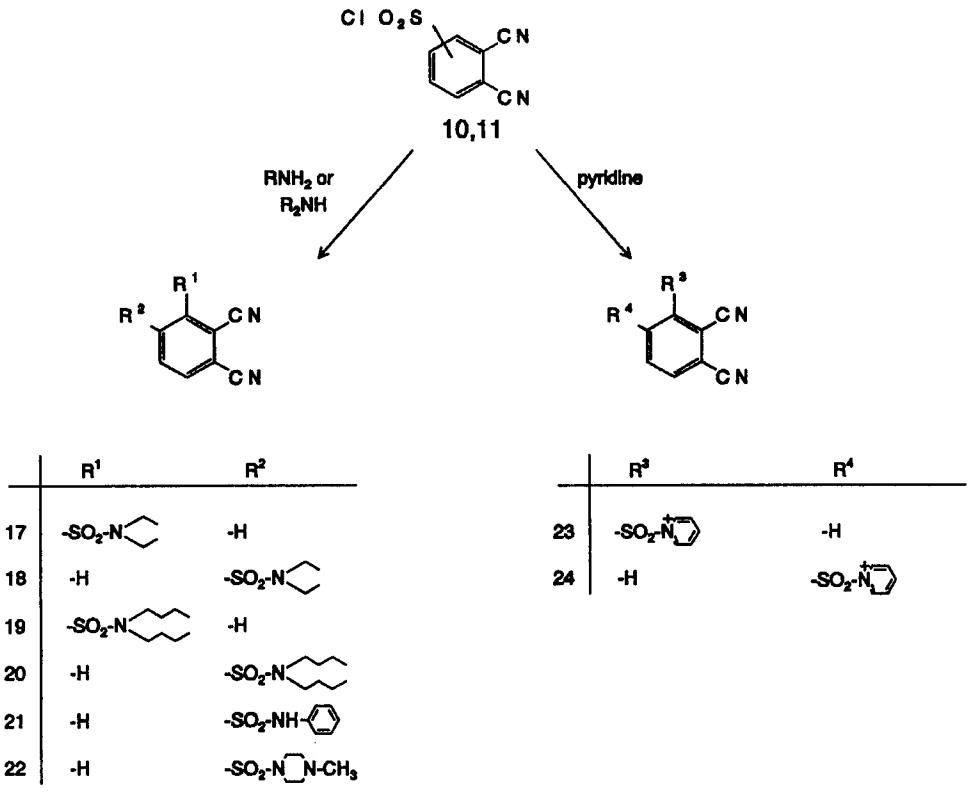


SCHEME III Reaction of the diazonium salts (**8**, **9**) with different sulfur nucleophiles and the oxidation of the reaction products to the sulfonic acids (**3**, **4**). Substituents in compounds (**3**), (**6**), (**8**), (**12**), (**14**), (**16**) are in the position 3 and in compounds (**4**), (**5**), (**7**), (**9**), (**13**), (**15**) in position 4 of the benzene ring.

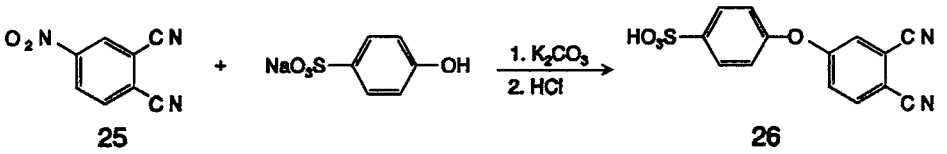
(**10**, **11**) can be obtained also by treatment of the corresponding sulfonic acids (**3**, **4**) in DMF. The replacement of the amino group via the diazonium salts is a more convenient method for the introduction of the sulfonic acid group in 1,2-dicyanobenzenes compared to the halogen substitution method (Schemes II and III).

The compounds (**10**) and (**11**) are valuable starting materials for the synthesis of various sulfonylamido-substituted dicyanobenzenes. Treatment with different amines affords in high yields the corresponding 3- and 4-sulphamoyl substituted 1,2-dicyanobenzenes (**17**–**22**). Reaction with pyridine yields the water soluble 3- and 4-pyridinosulfonyl substituted 1,2-dicyanobenzenes (**23**, **24**) (Scheme IV).

4-(4-phonoxy-1,2-dicarbonitrile)benzenesulfonic acid (**26**) is prepared in high yields by a nitro displacement reaction[16] of 4-nitro-1,2-dicyanobenzene (**25**) with 4-hydroxybenzenesulfonic acid (Scheme V).



SCHEME IV Preparation of various sulfonylamido substituted 1,2-dicyanobenzenes from the sulfonylchlorides (**10**, **11**).



SCHEME V Preparation of the sulfophenoxy-substituted 1,2-dicyanobenzene (**26**).

EXPERIMENTAL

IR: FT/IR spectrometer Biorad SPC-3200.—^{1}H NMR: Bruker WH 360 (Aspect 3000).—MS: EI and FAB Finnigan MAT 8222.—Elemental analysis: Beller, Göttingen, Germany.—Melting points: Kofler apparatus (Reichert, Vienna, Austria).—3-Chloro- and 4-bromo-1,2-dicyanobenzene (**1**), (**2**) were prepared as described.[17,18] These compounds are also obtained by dehydration of the corresponding diamides in high yields by a method described by one of us.[19] 3- and 4-amino-1,2-dicyanobenzene (**6**), (**7**) are synthesized by reduction of the corresponding nitro derivatives.[20]

2,3-Dicyanobenzenesulfonic acid (**3**), *method A*: A solution of the diazonium salt (**8**), prepared from 1.43 g (0.01 mol) of 3-amino-1,2-dicyanobenzene (**6**) and 0.74 g (0.01 mol) of sodium nitrite in 40 ml of 20% hydrochloric acid was added to a solution of 2.7 g (0.015 mol) of potassium butylxanthogenate in 200 ml of water. The yellow precipitate was washed with water and dried to give 3.35 g (nearly 100%) of (2,3-dicyanophenyl)-O-butyldithiocarbonate (**12**). This intermediate was not further characterized. The dithiocarbonate (**12**) (1.0 g, 4 mmol) was dissolved in 20 ml of formic acid, and 6.4 ml

of 30% hydrogen peroxide was added dropwise at 60–70°C. Heating was continued for 0.5 h, the solvent was removed in the vacuum, and the residue was washed with ethanol. The nitrile (**3**) was obtained in 80.5% yield (0.67 g), m.p. > 300°C. Oxidation of 3-mercapto-1,2-dicyanobenzene (**16**) under the same condition yields quantitatively 2,3-dicyanobenzenesulfonic acids. Anal. Calcd. for $C_8H_4N_2O_3S \cdot H_2O$ (226.2): C 42.58, H 2.67, S 14.17. Found C 43.18, H 2.89, S 14.11.—IR (KBr): ν = 3258–3225 cm^{-1}, 2236, 1414, 1245, 1188.—FAB-MS, m/z (%): 207 (100) $[M^+-H]$.—^1H NMR (DMSO-d_6): δ 7.87 (1H, 5-H), 8.00 (1H, 6-H), 8.30 (1H, 4-H).

(**3**), *method B*: To a solution of 0.64 g (0.002 mol) of bis(2,3-dicyanophenyl)-disulfide (**14**) in 10 ml of chloroform was added a mixture of 5 ml of formic acid and 6.4 ml of 30% hydrogen peroxide. The reaction mixture was refluxed for 2 h, the solvent was removed in the vacuum to give, after washing with ethanol 0.65 g (80%) of the same dinitrile.

(**3**), *method C*: A suspension of 0.81 g (0.005 mol) of 3-chloro-1,2-dicyanobenzene (**1**), 0.80 g (0.006 mol) of sodium sulfite and 0.10 g of copper sulfate in 30 ml of 50% aqueous dioxane was refluxed for 3 h, cooled and filtered. The residue after removal of the solvents was dissolved in 10 ml of water, diluted with 30 ml of ethanol, the insoluble inorganic salts filtered and the solvent evaporated to give 0.05 g (5%) of the same product.

3, *method D*: An identical product was prepared in quantitative yield by refluxing 2,3-dicyanobenzenesulfonyl chloride (**10**) with a tenfold amount of water with subsequent evaporation of the solvent.

3,4-Dicyanobenzenesulfonic acid (**4**), *method A*: By oxidation of the intermediate bis(3,4-dicyanophenyl)-O-butyldithiocarbonate (**13**) (in quantitative yield from 4-amino-1,2-dicyanobenzene (**7**) in analogy to the 3-isomer) or of 4-mercapto-1,2-dicyanobenzene (**5**) (as in the case of 2,3-dicyanobenzenesulfonic acid) (method A) the title compound was obtained in quantitative yield in the form of a colorless, hygroscopic, transparent glass, m.p. > 320°C. Anal. Calcd. for $C_8H_4N_2O_3S \cdot H_2O$ (226.2): C 42.58, H 2.67, S 14.17. Found C 42.13, H 2.96, S 13.98.—FAB-MS: m/z (%) = 207 (93) $[M^+-H]$, 159 (100) $[C_8H_3N_2S^+]$.—IR (KBr): ν = 3273–3039 cm^{-1}, 2241, 1473, 1212, 1195, 1040.

(**4**), *method B*: the same product was prepared in quantitative yield by oxidation of bis(3,4-dicyanophenyl)disulphide (**15**) as in the case of the corresponding 3-isomer (method B).

(**4**), *method C*: The same product was obtained in a yield of 18% by interaction of 4-bromo-1,2-dicyanobenzene (**2**) with sodium sulphite as in the case of the 3-isomer (method C).

(**4**), *method D*: In analogy to the 3-isomer, compound (**4**) was obtained in quantitative yield by refluxing 3,4-dicyanobenzenesulphonyl chloride (**11**) with a small amount of water, with subsequent evaporation of water.

4-Mercapto-1,2-dicyanobenzene (**5**), *method A*: To the solution of 2.30 g (0.03 mol) of thiourea in 100 ml of water was added at 50–60°C a solution of the diazonium salt (**9**), prepared from 2.86 g (0.02 mol) of 4-amino-1,2-dicyanobenzene (**7**) in 45 ml of 20% hydrochloric acid. The pH of the reaction mixture was adjusted to 10–12 using 20% sodium hydroxide. The mixture was heated to reflux, then cooled to room temperature, filtered and acidified to pH 3–4. The precipitate was washed with water. After recrystallization from ethanol 1.35 g (41.5%) of (**5**) was obtained, m.p. 105–106°C. Anal. Calcd. for $C_8H_4N_2S$ (160.2): C 59.98, H 2.52, N 17.49. Found C 59.73, H 2.58, N 17.19.—MS (EI, 70 eV): m/z (%) = 160 (100) $[M^+]$, 133 (21) $[M^+-HCN]$, 127 (19) $[M^+-SH]$.

(**5**), *method B*: A suspension of 1.04 g (0.005 mol) of 4-bromo-1,2-dicyanobenzene (**2**) and 0.4 g (0.005 mol) of thiourea was refluxed 3 h in 25 ml of ethanol. A solution of 0.6 g (0.015 mol) of sodium hydroxide in 5 ml of water was added, the mixture was refluxed for 1 h and was then added to 50 ml of water. After filtration the filtrate was acidified and extracted with chloroform. After removal of the solvent the residue was recrystallized from ethanol to give 0.08 g (10%) of the same product.

3-Mercapto-1,2-dicyanobenzene (**16**): This compound was prepared analogously to (**5**) (method A) employing the diazonium salt (**8**) obtained from (**6**). Yield 7%, m.p. 87–90°C. Anal. Calcd. for $C_8H_4N_2S$ (160.2): C 59.98, H 2.52, N 17.49. Found C 59.61, H 2.83, N 17.13.

2,3-Dicyanobenzenesulfonyl chloride (**10**): A solution of the diazonium salt (**8**) (from 2.86 g (0.020 mol) of 3-amino-1,2-dicyanobenzene (**6**) in 15 ml 35% HCl) was quickly added with intensive stirring at 10°C to a mixture of 10 ml of sulphur dioxide, 20 ml of acetic acid and a catalytic amount of cuprous chloride. After 10 min the reaction mixture was extracted with chloroform and purified by chromatography in silica yielding 2.03 g (45%) of 2,3- (**10**), m.p. 72–74°C. Anal. Calcd. for $C_8H_3ClN_2O_2S$ (226.6): C 42.40, H 1.33, Cl 15.46, N 12.36, S 14.15. Found C 42.01, H 1.32, Cl 15.38, N 11.91, S 14.01.—MS (EI, 70 eV): m/z (%) = 226 (25) $[M^+]$, 191 (88) $[M^+-Cl]$, 127 (100) $[M^+-SO_2Cl]$, 100 (38) $[C_7H_2N^+]$.

3,4-Dicyanobenzenesulfonyl chloride (**11**): This compound was obtained in a yield of 75% analogously to the 3-isomer starting from 4-amino-1,2-dicyanobenzene (**7**); m.p. 84–85°C (from benzene-hexane = 1:1). Anal. Calcd. for $C_8H_3ClN_2O_2S$ (226.6): C 42.40, H 1.33, Cl 15.46, N 12.36, S 14.15. Found C 42.05, H 1.27, Cl 15.73, N 11.75, S 14.12.—IR (KBr): υ = 2242 cm^{-1}, 1383, 1191.—^1H NMR (DMSO-d_6): δ 8.32 (1H, 6-H), 8.54 (1H, 5-H), 8.78 (1H, 3-H).

Bis(3,4-dicyanophenyl)disulfide (**15**): 0.3 g (0.01 mol) of sulfur was dissolved in mixture of 2.4 g (0.01 mol) of sodium sulfide · H_2O and 100 ml of water at 50–60°C. A solution of the diazonium salt (**9**) was added, prepared from 2.86 g (0.02 mol) of 4-amino-1,2-dicyanobenzene (**7**) in 20% hydrochloric acid as described before. The resulting precipitate was isolated by filtration, extracted with refluxing ethanol and the solvent was removed. The residue was purified by chromatography on silica. After recyrstallization from ethanol 1.68 g (52%) of the title product was obtained, m.p. 117–119°C. Anal. Calcd. for $C_{16}H_6N_4S_2$ (318.4): C 69.36, H 1.90, N 17.60, S 20.14. Found C 69.63, H 1.74, N 17.66, S 20.41.—MS (EI, 70 eV): m/z (%) = 318 (100) [M^+], 159 (64) [M^+-$C_8H_3N_2S$], 132 (11) [$C_7H_2NS^+$].

Bis(2,3-dicyanophenyl)disulfide (**14**): was obtained from 3-amino-1,2-dicyanobenzene (**6**) similarly in a yield of 49% and was used further without additional purification (caution: the dry product is explosive by contact!).

3-(N,N-Diethylsulfamoyl)-1,2-dicyanobenzene (**17**): To a solution of 0.45 g (0.0020 mol) of the sulfochloride (**10**) in 5 ml of acetone 0.43 ml (0.31 g, 0.0042 mol) of diethylamine was added dropwise. The reaction mixture was boiled for 5 min, diethylamine hydrochloride was filtered off and washed with 5 ml of acetone. The acetone solutions were combined, evaporated and the residue chromatographed on silica with chloroform. Yield of nitrile (**17**) was 0.46 g (87%), m.p. 108–108.5°C (from benzene-hexane = 1:1). Anal. Calcd. for $C_{12}H_{13}N_3O_2S$ (263.3): C 54.74, H 4.98, N 15.96, S 12.18. Found C 54.54, H 5.04, N 15.66, S 12.35. Analogously by interaction of the sulfochlorides (**10**) and (**11**) with diethylamine, dibutylamine and anilines the sulfamoyl compounds (18) to (21) were obtained.

-4-(N,N-Diethylsulfamoyl)-1,2-dicyanobenzene (**18**): Yield 90%, m.p. 114.5–115.5°C from benzene (Reference 7, m.p. 112–113°C).

-3-(N,N-Dibutylsulfamoyl)-1,2-dicyanobenzene (**19**): Yield 77%, m.p. 77.5–78°C (from benzene-heptane). Anal. Calcd. for $C_{16}H_{21}N_3O_2S$ (319.4): C 60.16, H 6.63, N 13.16, S 10.04. Found C 60.32, H 6.29, N 13.52, S 10.80.

-4-(N,N-Dibutylsulfamoyl)-1,2-dicyanobenzene (**20**): Yield 72%, m.p. 86.5–87.5°C from hexane-benzene (Reference 7, m.p. 89–90°C). Anal. Calcd. for $C_{16}H_{21}N_3O_2S$ (319.4): C 60.16, H 6.63, N 13.16, S 10.04. Found C 59.78, H 6.19, N 13.21, S 10.40.

-4-(N-Phenylsulfamoyl)-1,2-dicyanobenzene (**21**): Yield 55% (after recrystallization from benzene), m.p. 134.5–135.5°C (from ethanol). Anal. Calcd. for $C_{14}H_9N_3O_2S$ (283.3): C 59.35, H 3.20, N 14.83, S 11.32. Found C 59.18, H 3.04, N 14.35, S 11.42.

4-(4-Methylpiperazinosulfonyl)-1,2-dicyanobenzene (**22**): To a solution of 2.04 g (0.0090 mol) of **11** in 10 ml of acetone was added dropwise 1.0 ml (0.9 g, 0.09 mol) of N-methylpiperazine. The reaction mixture was boiled for 5 min, the precipitate was filtered off, washed with acetone giving 2.91 g (99%) of the hydrochloride (**22**). To it's solution in 100 ml of water 10 ml of 5% sodium hydroxide was added, (**22**) was filtered off and washed with water. Yield of the nitrile (**22**) 2.37 g (91%), m.p. 160.5–161°C. Anal. Calcd. for $C_{13}H_{14}N_4O_2S$ (290.3): C 53.78, H 4.86, N 19.13, S 11.04. Found C 54.05, H 4.97, N 19.37, S 11.19.

3-(Pyridinosulfonyl)-1,2-dicyanobenzene hydroxide (**23**): To a solution of 0.45 g (0.0020 mol) of nitrile (**10**) in 3 ml of acetone was added 1.0 ml of pyridine, the mixture was stirred for 20 min, the solvent was evaporated, and the remaining solid was recrystallized from ethanol. Yield of (**23**) 0.50 g (87%), m.p. 206–210°C. Anal. Calcd. for $C_{13}H_9N_3O_3S$ (287.3): N 14.63, S 11.16. Found N 14.77, S 11.85.—MS (EI, 70 eV): m/z (%) = 209 (70) [M^+-Py], 144 (25) [M^+-Py-SO_2], 79 (100) [Py^+].—^1H NMR (DMSO-d_6): δ 7.88 (1H, 5-H), 8.01 (1H, 6-H), 8.13 (2H, β-H), 8.30 (1H, 4-H), 8.68 (1H, γ-H), 8.89 (2H, α-H).

4-(Pyridinosulfonyl)-1,2-dicyanobenzene (**24**): This compound was analogously prepared employing (**11**). Yield 89%, m.p. 175–177°C. Anal. Calcd. for $C_{13}H_9N_3O_3S$ (287.3): C 54.35, H 3.16, N 14.63, S 11.16. Found C 54.94, H 3.36, N 14.36, S 11.16.—IR (KBr): υ = 3091 cm^{-1}, 2242, 1255, 1210, 1058.—MS (EI, 70 eV): m/z (%) = 209 (75) [M^+-Py], 144 (30) [M^+-Py-SO_2], 79 (100) [Py^+].—^1H NMR (DMSO-d_6): δ 8.04 (1H, 6-H), 8.13 (2H, β-H), 8.19 (1H, 5-H), 8.27 (1H, 3-H), 8.68 (1H, γ-H), 8.88 (2H, α-H).

4-(4-phonoxy-1,2-dicarbonitrile)benzenesulfonic acid (**26**): Dried potassium carbonate (3.17 g, 22.97 mmol) was suspended in dried DMSO (23 ml) under a nitrogen atmosphere. 2 g (11.56 mmol) of 4-nitro-1,2-dicyanobenzene (**25**) and 3.35 g (17.1 mmol) of 4-hydroxybenzenesulfonic acid[21] were added. After 4 h and again after 24 h 3.14 g of potassium carbonate were added to the mixture. The suspension was stirred for 4 days at room temperature. The light-brown precipitate was dissolved in water (150 ml) and the pH was adjusted to 0 using hydrochloric acid. The product precipitated by evaporation of the solvent. It was washed with ethanol and dried in the vacuum at room temperature. Yield 2.81 g (80%), m.p. > 290°C.—IR (KBr): υ = 3442 cm^{-1} (s, SO_3H), 3090 (w, C-H), 2233 (s, CN), 1649 (w, C=C), 1587 (s), 1251 (s, C—O—C), 1209 (s, S=O asym.st.), 1129 (s, SO_3H), 1042 (s, S=O sym.st.).—FAB-MS: m/z (%) = 299 (100) [M^+], 219 (8) [M^+-SO_3H], 143 (21) [$C_8H_3N_2O^+$], 127 (10) [$C_8H_3N_2^+$], 91 (21) [$C_6H_4O^+$].—^{1}H NMR (DMSO-d_6): δ 7.13 (d; 2H, 2-H, 6-H), 7.4 (d d; 1H, 5'-H), 7.71 (d; 2H, 3-H, 5-H), 7.83 (d; 1H, 3'-H), 8.1 (d; 1H, 6'-H).

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