Synthesis of Polyfunctional Aromatic Imines with Zwitterionic Character

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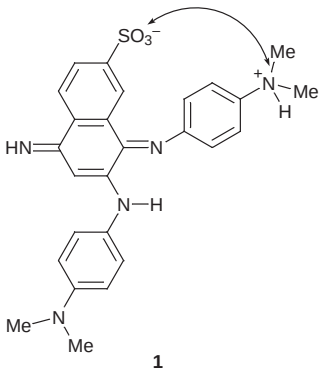
Polyfunctional aromatic imines with a zwitterionic character involving sulfonic acid and *N,N*-dimethylamino functionalities are synthesized by oxidative condensation of 5-aminonaphthalene-2-sulfonic acid (Cleve's β-acid) and *N,N*-dimethyl-*p*-phenylenediamine.

The synthesis of organic ferromagnets has been considered since the 1960s.[1] Ferromagnetic properties have been observed in organic compounds such as nitroxyl derivatives[2] and poly(*m*-phenylenecarbenes).[3] However, this ferromagnetic character is more often observed at very low temperatures (< 100 K). In 1995, Galaj *et al.*[4] synthesized a copolymer of aniline and Cleve's β-acid, 'Marcoussis polymer' for which ferromagnetic behaviour was observed at temperatures higher than 300 K. According to the authors, a 'bended zwitterionic' structure, resulting from internal acid–base interactions between amino and adjacent sulfonic acid groups, induces an ordering of the magnetic moments. To further this phenomenon, zwitterionic polyfunctional oligomeric imines have been synthesized. *N,N*-dimethyl-*p*-phenylenediamine was used instead of aniline, in order to avoid polymerization and increase the basicity of the amino group involved in the intramolecular strain. In 1996, Wei *et al.*[7] developed a one-step method to synthesize *N,N*′-bis(4′-aminophenyl)-1,4-quinonediimine and several derivatives, by oxidative condensation of *p*-phenylenediamine with aniline or a substituted aniline in acidic aqueous medium. Adopting this method, four polyfunctional aromatic imines have been successfully prepared from Cleve's β-acid and *N,N*-dimethyl-*p*-phenylenediamine.

Compound **1** results from a stoichiometric reaction of Cleve's β-acid and *N,N*-dimethyl-*p*-phenylenediamine in DMSO. Compounds **2** and **3** were obtained from a stoichiometric reaction of 5-aminonaphthalene-2-triethylammonium sulfonate and *N,N*-dimethyl-*p*-phenylenediamine dihydrochloride in acidic aqueous medium. The structure of the compound **2** was deduced from its ^{1}NMR spectrum. The mass spectrum shows singly and doubly charged molecular ions ($M^- = 711$ u and $M^{2-} = 355.5$ u) resulting from the presence of two sulfonic acid groups. Isomers **1** and **3** were distinguished by ^{1}H NMR, according to the different chemical shifts of the protons in α position relative to an imino or (*N,N*-dimethyl *p*-aminophenyl)imino group.

Compound **4** was formed when 5-aminonaphthalene-2-triethylammonium sulfonate is used in excess relative to *N,N*-dimethyl-*p*-phenylenediamine dihydrochloride.



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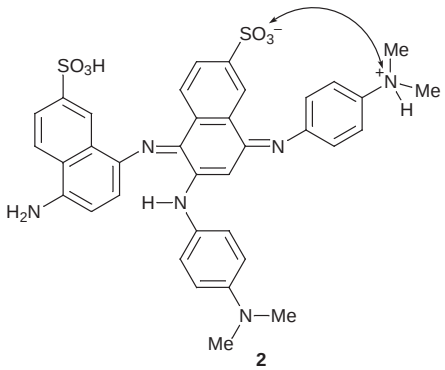

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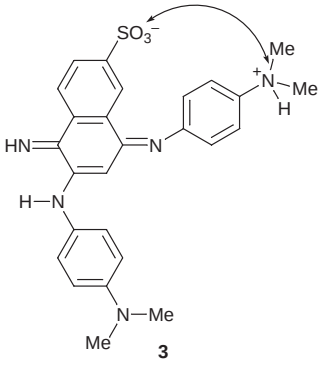

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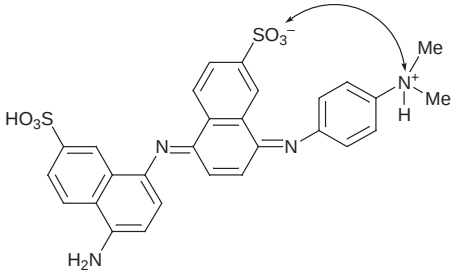

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Compounds **1**–**4** can be dissolved in DMSO or basic media and their melting points are $> 300\,^\circ$C.

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This study confirms that polyfunctional aromatic imines can easily be obtained in good yields by a one-step oxidative condensation.

The magnetic susceptibilities values of compounds **1**–**4**, measured at 20 °C on a Faraday balance, are in the range −0.5 to −0.8 and so are diamagnetic. The spatial organization of these oligomers and the resulting geometrical strains are presently being studied using conformational energy calculations.

Experimental

7-[(N,N-*Dimethyl*-p-*aminophenyl*)*amino*]-8-[(N,N-*dimethyl*-p-*aminophenyl*)*imino*]-*5-imino-naphthalene*-2-*sulfonic Acid* **1**.—MS: *m/z* 490 (M^-) ($C_{26}H_{27}N_5O_3S$). Yield 75% (crude product), blue–black solid.

6-[(N,N-*Dimethyl*-p-*aminophenyl*)*amino*]-8-[(N,N-*dimethyl*-p-*aminophenyl*)*imino*]-*5-(4-amino*-7-*sulfonaphthyl*)*iminonaphthalene*-2-*sulfonic Acid* **2**.—MS: *m/z* 711 (M^-) and 355.5 (M^{2-}) ($C_{36}H_{34}N_6O_6S_2$). Yield 41%, blue–black solid.

6-[(N,N-*Dimethyl*-p-*aminophenyl*)*amino*]-8-[(N,N-*dimethyl*-p-*aminophenyl*)*imino*]-5-*iminonaphthalene*-2-*sulfonic Acid* **3**.—MS: *m/z* 490 (M^-) ($C_{26}H_{27}N_5O_3S$). Yield 32%, blue–black solid.

8-[(N,N-*Dimethyl*-p-*aminophenyl*)*imino*]-5-[(4-*amino*-7-*sulfonaphthyl*)*iminonaphthalene*-2-*sulfonic Acid* **4**.—MS: *m/z* 576 (M^-), 288 (M^{2-}) ($C_{28}H_{24}N_4O_6S_2$). Yield 90%, (crude product), blue–black solid.

Techniques used: ^{1}H NMR, ^{13}C NMR, FTIR, MS.

References: 9

Tables: 2

Schemes: 5

Figures: 1

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