Syntheses and Spectral Properties of New Dicyanopyrazine-related Heterocycles from Diaminomaleonitrile

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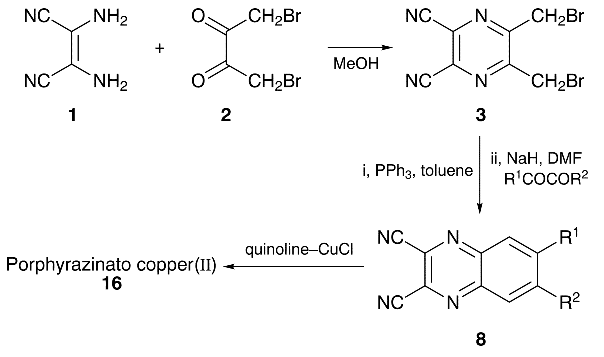
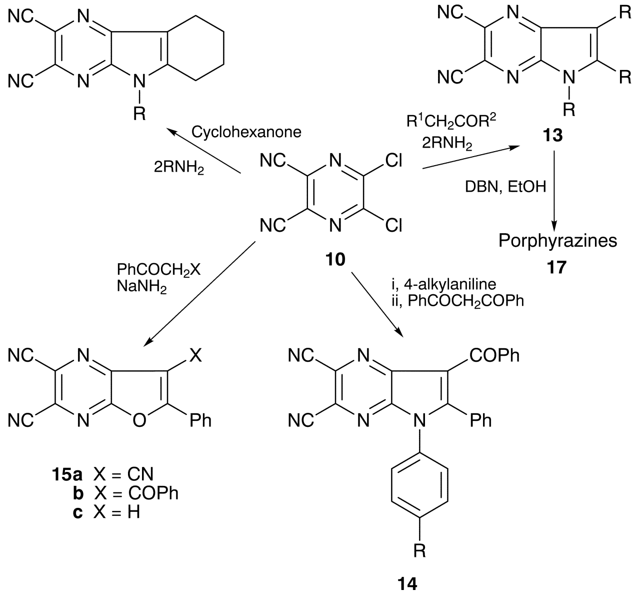
A series of new dicyanopyrazine-related heterocycles are synthesized and their spectral properties correlated with their structures.

2,3-Dicyanopyrazine derivatives derived from diaminomaleonitrile and 1,2-dicarbonyl compounds have been applied to synthesize a wide variety of heterocycles useful as bioactive substances and as coloring materials. We are interested in the substituent effects of pyrazine chromophores on their chemical, electronic and physical properties.[4,5] Pyrazine chromophores have large dipole moments and a strong fluorescence even in the solid state and are of interest with respect to functional dye materials. We report the correlation of their structures with their functionalities from the points of view of their intermolecular interactions.

We report the syntheses of new dicyanopyrazine-related heterocycles including pyrazinoporphyrazines. Their absorption and fluorescence properties were correlated with their chemical structures.



Scheme 1



Scheme 2

2,3-Dicyanoquinoxalines **8** were conventionally prepared by the Wittig reaction of 2,3-bis(bromomethyl)-5,6-dicyanopyrazine **3** with 1,2-dicarbonyl compounds.

The 2,3-dicyanopyrrolo[2,3-*b*]pyrazines **13** and their furo analogues **15** were synthesized by the cyclization of 2,3-dichloro-5,6-dicyanopyrazine **10** with carbonyl compounds and enamines, respectively. Compound **14**, the N-aryl analogue of **13** could be prepared alternatively by the cyclization of 2-arylamino-3-chloro-5,6-dicyanopyrazine with the appropriate diarylketone in the presence of sodium hydride. Pyrazinoporphyrazines **16** and **17** were easily synthesized from the corresponding dicyanopyrazine derivatives **8** and **13**, respectively. Dye **16** is insoluble in almost all organic solvents and absorbs at 840 nm in concentrated sulfuric acid. On the contrary, dye **17**, having long alkyl substituents, is readily soluble in cyclohexane and chloroform. They absorb at around 712 nm and fluoresce at 719 nm. A very small Stokes' shift of 7 nm was observed. It is very useful that dye **17** showed a red fluorescence even in the solid state which makes it suitable as an emitter for an electroluminescence device. Dye **17** showed a crystal morphology affected by intermolecular hydrophobic interactions of the alkyl sub-

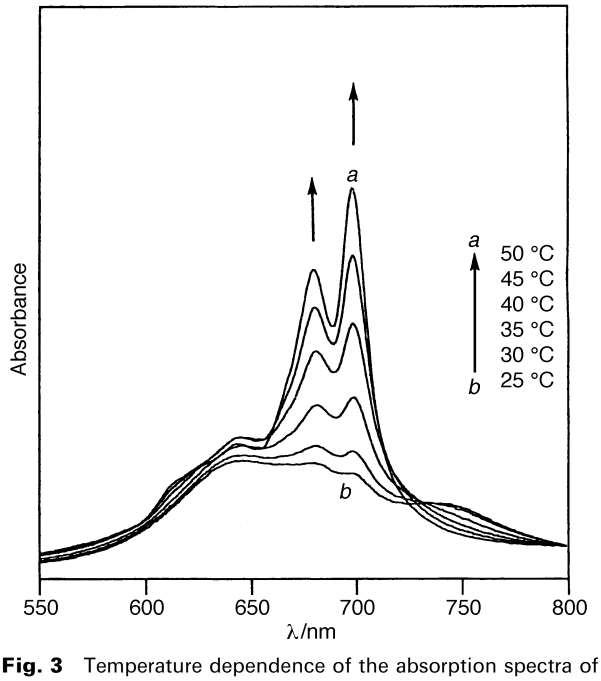


Fig. 3 Temperature dependence of the absorption spectra of **17a** in cyclohexane

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stituents. They showed reversible spectral changes depending on the polarity of solvent and temperature (Fig. 3).

Techniques used: ^{1}H NMR spectroscopy, mass spectrometry, UV–VIS, fluorescence spectrophotometry, elemental analysis

Table 1: Reaction of **6** with 1,2-dicarbonyl compounds

Table 2: Syntheses of pyrrolopyrazines and furopyrazines

Table 3: Syntheses of quinoxalinoporphyrazines and pyrrolopyrazinoporphyrazines

Table 4: Visible and fluorescence spectra of **7** and 2,3-dicyanoquinoxalines **8**

Table 5: Visible and fluorescence spectra of **13**, **14** and **15**

Table 6: Visible and fluorescence spectra of **16** and **17**

Schemes: 7

References: 12

Fig. 1: The effects of solvent polarity on the absorption spectra of **17a**

Fig. 2: Spectral changes of **17a** in cyclohexane by the addition of chloroform

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