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Fischer's base as an electron donor for new penta- and heptamethines

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Abstract

Asymmetric cyanine dyes (penta- and heptamethines) prepared by coupling Fischer's base or Fischer's aldehyde with malononitrile dimer or analogous compounds are described. Dye characteristics are given and structure-color correlations are discussed.

Keywords: Fischer's base; Fischer's aldehyde; Malononitrile; Malononitrile dimer; Polymethines; Dimethylformamide–dimethylacetale (DMF–DMA)

1. Introduction

Technical polymethine dyes and some groups of natural dyes contain electron donor and electron acceptor groups at opposite ends of the methine chain. A wide choice of donor and acceptor substituents are used in the syntheses of polymethines, but there are relatively few major synthetic methods.

While trimethines can be obtained easily by the reaction of two (heterocyclic) quarternary salts, if one of them contains a methyl group in the α-position to the heteroatom, the syntheses of longer methine chains afford additional C-fragments between the electron donor and electron acceptor moieties [1].

Fischer's base (1,3,3-trimethyl-2-methylene-indoline, F.B., [2]) is a compound which has been frequently used in dye chemistry and represents a donor with excellent properties. The reactive methylene group is able to react with other CH-acidic compounds and orthoesters in three component reactions [3]. Malononitrile (**1a**) and malononitrile dimer (2-amino-1,1,3-tricyano-1-propene, **2a**, [4]) are both excellent electron acceptors because of their nitrile groups and powerful methylene active compounds. Therefore, they were used in numerous reactions [5, 6].

In this paper we describe pentamethines and heptamethines, which formally consist of F.B. as electron donor, malononitrile (**1a**) or analogous compounds as electron acceptors, and a C-1 fragment connecting them.

In principle there are three ways to build up the chromophoric system, viz.

1. Three component reaction of the CH-acidic compound with ethyl orthoformate and F.B. (Scheme 1).
2. Reaction of the CH-acidic compound with dimethylformamide–dimethylacetale (DMF–DMA) yielding an aminomethylene derivative in the first step and subsequent condensation (elimination of dimethylamine) with F.B. (Scheme 2).

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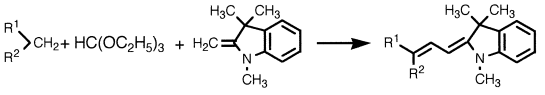
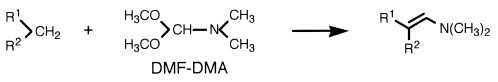
3. Vilsmaier formylation of F.B. to yield Fischer's aldehyde (1,3,3-trimethyl-2-formyl-methylene-indoline F.A., [7]), followed by a Knoevenagel condensation with the CH-acidic compound (Scheme 3).

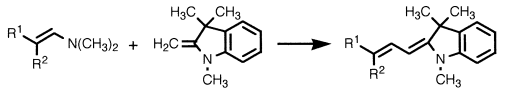
All three methods applied to synthesize the polymethines are described in this paper. The use of **1a** or **2a** to introduce the electron acceptors gave the polymethines **3a, 4a**, respectively. According to the concept of Dähne [8, 9] the amino group in both compounds should disturb the colored system. Electrophilic substitutions at the amino group with DMF-DMA, chloroformic acid ethylester and succinic anhydride were expected to yield products with higher longwave absorptions **(5a–c)**.

Other methylene active compounds, like ω-cyanoacetophenone (**1b**) [10–13], 3-amino-2-cyanocrotononitrile (**2b**) [14], 1-phenylethylidene-malononitrile (**2c**) [15,16] and 3-aminocrotononitrile (**2d**) (Scheme 4) were also reacted with orthoformate and F.B.

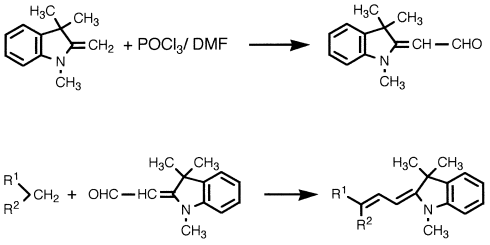


Scheme 1.





Scheme 2.



Scheme 3.

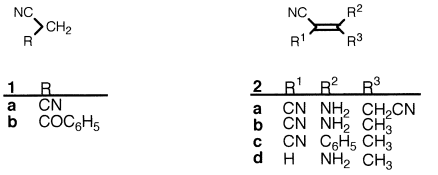
The change in reactivity as well as the positions of the maximum absorption wavelengths were examined.

Reactions of the CH-acidic compounds with DMF–DMA gave yellow aminomethylene products **7a, b** and **8a–c** (Scheme 5), which were combined with F.B. in order to obtain the corresponding polymethines with elimination of dimethylamine [3].

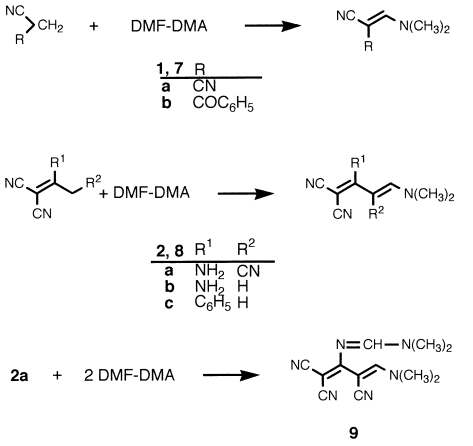
F.A. (obtained from F.B. [7]) was combined with **1a, b** and **2a–d** to give the pentamethines **3a, b, 6** and heptamethines **4a, b** (Scheme 6).

2. Results and discussion

All three methods described above could be applied to synthesize **3a**. Three component reaction of malononitrile (**1a**) with orthoformate and F.B., according to method 1 gave **3a** in 24% yield. Reaction of **1a** with DMF-DMA (first step of method 2) gave only 20% of the aminomethylene compound **7a**. Condensation of **7a** with F.B. gave **3a** in 25% yield. Maximum yield of **3a** was



Scheme 4.



Scheme 5.

obtained by method 3. Although the formylation of F.B. gave only 39% F.A., subsequent condensation with **1a** proceeded smoothly, thus giving an overall yield of 34%.

3b could also be synthesized by all three methods. The maximum yield was obtained by the three component reaction, which yielded 64%. The use of orthoacetate instead of orthoformate led to **3c** with even higher (88%) yield.

Three component reaction was the best way to obtain the heptamethine **4a**. It could also be obtained via F.A. (method 3), but in lower yield. Method 2 was not successful: although **2a** gave **8a** with DMF–DMA, **8a** could not be reacted with F.B. **8a** was obtained in 46% yield. With a surplus of DMF–DMA, a second condensation occured at the amino group of **2a** and 2-[(dimethylamino methylene)amino]-4-dimethylamino-1,3-butadiene-1,1,3-tricarbonitrile (**9**, Scheme 5) was obtained [17, 18].

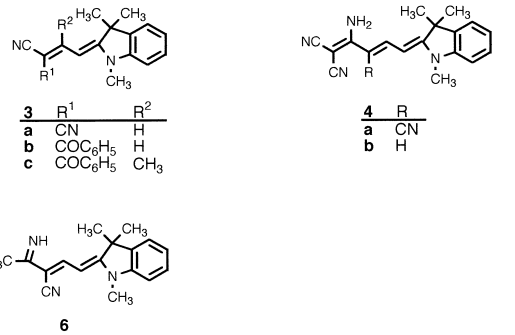
4b could only be obtained via F.A. (method 3), but also in this case the yield was low.

The only reasonable way to obtain the pentamethine **6** was method 3 (23% overall yield based on F.B.). Method 1 gave only 8%. Method 2 was not successful as **2d** could not be reacted with DMF-DMA. The ^{1}H NMR spectrum of **2d** showed the signals of 3-aminocrotononitrile (enamino form) as well as of 3-iminobutyronitrile (imino form). The imino tautomer turned out to be the reactive one. The attack of orthoformate in the three component reaction was observed at the methylene and not at the methyl group and **6** was formed.

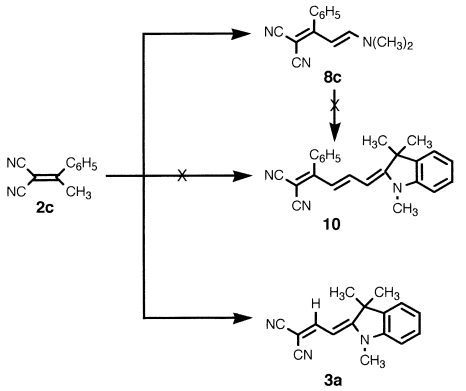
10 could not be obtained by any of the methods mentioned above. **2c** gave no product in the three component reaction. With DMF–DMA (method 2) the aminomethylene compound **8c** was obtained, which could not be reacted with F.B. **2c** and F.A. (method 3) gave **3a** instead of **10**. This was somewhat surprising as reactions of **2c** with other aldehydes have been observed earlier [19]. TLC indicated, that **2c** decomposed in a first step, giving rise to the formation of **1a**. Subsequent condensation of **1a** with F.A. gave **3a** (Scheme 7).

Electronic spectra data of pentamethines **3a–c, 6** and heptamethines **4a, b, 5a–c** are given in Table 1.

3a shows a long wave absorption of 433 nm, which is remarkably high for a pentamethine dye and should result from the fact that the symmetric dicyano methylene group is an excellent electron acceptor. **3b** and **3c** contain a benzoyl group instead of the second cyano group. This shifts the long wave absorption to 471 nm and 474 nm for **3b** and **3c**, respectively. Compared to **3a**, the pentamethine **6** contains an 1-iminoethyl group instead of the second cyano group, resulting in a hypsochromic shift of the maximum absorption wavelength.



Scheme 6.



Scheme 7.

Table 1
Electronic spectra data of pentamethines **3a–c**, **6** and heptamethines **4a**, **b**, **5a–c** (spectra taken in acetone)

	λ_{max} (nm)	log ε		λ_{max} (nm)	log ε
3a	433	4.795	**4b**	463	4.753
3b	451	4.742	**4b**	446	4.569
	471	4.774	**5a**	488	4.677
3c	474	3.830	**5b**	531	4.893
6	< 340		**5c**	532	4.784

The amino groups in **4a** and **4b** are electron donating substituents in the "wrong" positions [8, 9] and consequently the maximum absorption wavelengths of 463 nm (**4a**) and 446 nm (**4b**) are low for heptamethine dyes, compared e.g. to the pentamethine **3a**, the maximum absorption wavelength of which can be found at 433 nm. Electron withdrawing substituents at the nitrogen of the amino group shifted the maximum absorption to longer wavelengths:

Electrophilic substitution at the amino group of **4a** with dimethylformamide-dimethylacetale (DMF–DMA), chloroformic acid ethylester and succinic anhydride gave **5a–c** (Scheme 8) with maximum absorption wavelengths between 488 and 532 nm. Yields and reaction times depended on the base [20].

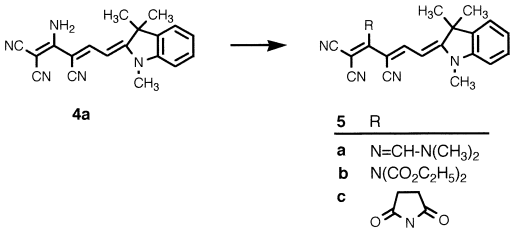
3. Experimental

3.1. General

All melting points are uncorrected. Spectral data were recorded with the following instruments: IR spectra: Perkin–Elmer 500 Spectrophotometer (KBr); ^{1}H NMR spectra: Varian Gemini 200 (spectra are referenced to tetramethylsilane); UV-Vis spectra: Hitachi U-3501 spectrophotometer (quartz cuvettes); Elemental analyses were performed on a C, H, N — Automat Carlo Erba 1106.

3.2. 1-Phenylethylidene–malononitrile **2c**

3.00 g (25 mmol) acetophenone was heated with 1.65 g (25 mmol) malononitrile **1a** and 3 drops of piperidine/acetic acid (1:5) in 25 ml abs. ethanol to 60°C for 6 h. Further 0.82 g (13 mmol) **1a** were added and the mixture was stirred for an additional 16 h at 60°C. After evaporating the solvent in vacuo, a small amount of petroleum ether was added and the precipitate was allowed to crystallize on an ice bath. **2c** was filtered and washed with petroleum ether giving colorless prisms, 1.70 g (40%), mp 95°C (94°C [15, 16]). IR: 2220, 1585, 1565 cm^{-1}.



Scheme 8.

$C_{11}H_8N_2$	Calcd.: C78.58,	H4.76,	N16.66.
(168.13)	Found: C78.52,	H4.94,	N16.33.

3.3. 3-(1,3,3-Trimethyl-2,3-dihydro-1H-indol-2-ylidene)-1-pentene-1,1-dicarbonitrile **3a**

3.3.1. Method 1

A mixture of 6.61 g (100 mmol) **1a**, 1.48 g (10 mmol) triethyl orthoformate and 1.73 g (10 mmol) F.B. was refluxed in 3 ml acetic acid for 3 h. After cooling to room temperature and filtering, the product was washed with methanol, giving orange crystals, 0.60 g (24%), mp 270°C. IR: 2980, 2920, 2200, 1620, 1550 cm^{-1}. ^{1}H NMR (d_6-DMSO): δ 1.57 (s, 6H, CH_3), 3.47 (s, 3H, N–CH3), 6.75–6.81 (d, 1H, CH), 7.14–7.55 (m, 4H, aromatic protons), 8.15–8.22 (d, 1H, CH) ppm. UV/Vis (acetone): λ_{max}: 433 nm, log ε: 4.795.

$C_{16}H_{15}N_3$	Calcd.: C77.12,	H6.02,	N16.86.
(249.20)	Found: C77.32,	H6.27,	N16.51.

3.3.2. Method 2

1.21 g (10 mmol) **8a** and 3.46 g (20 mmol) F.B. were refluxed for 3 h. On cooling to room temperature **3a** crystallized. The solid was filtered and washed with cold methanol to give orange crystals. 0.50 g (20%), mp 270°C.

$C_{16}H_{15}N_3$	Calcd.: C77.12,	H6.02,	N16.86.
(249.20)	Found: C77.15,	H6.04,	N16.81.

3.3.3. Method 3

0.66 g (10 mmol) **1a**, 1.00 g (5 mmol) F.A. and 0.65 g piperidine acetate were refluxed in 50 ml dry toluene on a Dean and Stark water separator for 20 h. After cooling to room temperature the product was filtered and washed with cold methanol to give orange crystals, 1.10 g (88%), mp 271°C.

$C_{16}H_{15}N_3$	Calcd.: C77.12,	H6.02,	N16.86.
(249.20)	Found: C77.20,	H6.10,	N16.70.

3a could also be obtained by the following procedure: 3.36 g (20 mmol) **2c**, 2.00 g (10 mmol) F.A., 0.30 g ammonium acetate and 0.8 ml acetic acid were refluxed in 75 ml dry toluene on a Dean and Stark water seperator. After 8 h the solution was cooled to give orange crystals, 0.30 g (12%), mp 272°C (dioxane).

$C_{16}H_{15}N_3$	Calcd.: C77.12,	H6.02,	N16.86.
(249.20)	Found: C77.10,	H6.01,	N16.80.

3.4. 1-Oxo-1-phenyl-4-(1,3,3-trimethyl-2,3-dihydro-1H-indol-2-ylidene)-2-butene-2-carbonitrile **3b**

3.4.1. Method 1

A mixture of 1.45 g (10 mmol) **1b** [13], 1.48 g (10 mmol) triethyl orthoformate, 1.73 g (10 mmol) F.B. and 5 ml acetic acid was refluxed for 2 h. The product crystallized at room temperature and was filtered and washed with methanol. 2.10 g (64%), mp 196°C. IR: 2200, 1630, 1605 cm^{-1}. ^1H NMR (d_6-DMSO): δ 1.48 (s, 6H, CH_3), 3.52 (s, 3H, N–CH_3), 5.90–5.98 (d, 1H, CH), 7.15–7.70 (m, 9H, aromatic protons), 8.25–8.31 (d, 1H, CH) ppm. UV/Vis (acetone): λ_{max}: 451 nm; log ε: 4.742; λ_{max}: 471 nm; log ε: 4.774.

$C_{22}H_{20}N_2O$	Calcd.: C80.50,	H6.09,	N8.53.
(328.26)	Found: C80.45,	H5.97,	N8.62.

3.4.2. Method 2

2.00 g (10 mmol) **7b** and 3.46 g (20 mmol) F.B. were refluxed for 2 h. On cooling to room temperature the product crystallized. It was filtered and washed with cold methanol. 2.80 g (85%), mp 196°C.

$C_{22}H_{20}N_2O$	Calcd.: C80.50,	H6.09,	N8.53.
(328.26)	Found: C80.53,	H6.00,	N8.60.

3.4.3. Method 3

A mixture of 0.87 g (6 mmol) **1b** [13], 1.00 g (5 mmol) F.A., 2 drops of piperidine, 2 drops of acetic acid and 10 ml abs. ethanol was refluxed for 3 h. **3b** precipitated in the hot solution; after cooling to room temperature, the precipitate was filtered and washed with cold ethanol to give orange needles. 0.60 g (37%), mp 196°C (ethanol or acetonitrile).

$C_{22}H_{20}N_2O$	Calcd.: C80.50,	H6.09,	N8.53.
(328.26)	Found: C80.45,	H6.12,	N8.48.

3.5. 3-Methyl-1-oxo-1-phenyl-4-(1,3,3-trimethyl-2,3-dihydro-1H-indol-2-ylidene)-2-butene-2-carbonitrile **3c**

3.5.1. Method 1

1.45 g (10 mmol) **1b** [13], 3.24 g (20 mmol) triethyl orthoacetate and 1.73 g (10 mmol) F.B. were refluxed for 3 h, cooled to room temperature, a small amount of methanol was added and the product filtered and washed with methanol to give yellow crystals, 3.00 g (88%), mp 160°C (decomp.) (ethanol). IR: 2964, 2200, 1660, 1610 cm^{-1}. ^1H NMR (d_6-DMSO): δ 1.30 (s, 6H, CH_3), 2.25 (s, 3H, CH_3), 2.90 (s, 3H, N–CH_3), 5.82 (s, 1H, CH), 6.84–7.62 (m, 9H, aromatic protons) ppm. UV/Vis (acetone): λ_{max}: 474 nm; log ε: 3.840.

$C_{23}H_{22}N_2O$	Calcd.: C80.71,	H6.43,	N8.18.
(342.27)	Found: C80.97,	H6.43,	N8.26.

3.6. 1-(2-Amino-1,1,3-tricyano-1-propene-3-ylidene)-2-(1,3,3-trimethyl-2,3-dihydro-1H-indol-2-ylidene) ethane **4a**

3.6.1. Method 1

1.32g (10 mmol) of **2a** [4], 1.48 g (10 mmol) of triethyl orthoformate and 1.73 g (10 mmol) of F.B. were refluxed in 3 ml of acetic acid for 6 h. On cooling to room temperature the product precipitated and was filtered and washed with cold methanol to give orange lustrous crystals, 1.45 g (46%), mp 265°C (acetonitrile). IR: 3400, 3320, 2200, 2180, 1655, 1640 cm^{-1}. ^1H NMR (d_6-DMSO): δ 1.62 (s, 6H, CH3), 3.50 (s, 3H, N–CH_3), 5.79–5.85 (s, 1H, CH), 7.12–7.55 (m, 4H, aromatic protons), 8.01–8.07 (d, 1H, CH), 8.25 (s, 2H, NH_2) ppm. UV/Vis (acetone): λ_{max}: 463 nm; log ε: 4.753.

$C_{19}H_{17}N_5$	Calcd.: C72.39,	H5.39,	N22.22.
(315.24)	Found: C72.19,	H5.47,	N21.98.

3.6.2. Method 3

A mixture of 1.32 g (10 mmol) **2a** [4], 1.00 g (5 mmol) F.A. and 0.65 g piperidine acetate were refluxed in 50 ml dry toluene on a Dean and Stark water separator. The product precipitated in the hot solution; after 3 h the solution was cooled to room temperature and **4a** was filtered and washed with cold methanol to give orange crystals. 1,20 g (76%), mp 264°C.

$C_{19}H_{17}N_5$	Calcd.: C72.39,	H5.39,	N22.22.
(315.24)	Found: C72.20,	H5.45,	N22.35.

*3.7. 2-Amino-5-(1,3,3-trimethyl-2,3-dihydro-1*H*-2-ylidene)-1,3-pentadiene-1,1-dicarbonitrile* **4b**

3.7.1. Method 3

A mixture of 1.40 g (13 mmol) **2b** [14], 1.32 g (6 mmol) F.A., 0.65 g piperidine acetate and 50 ml dry toluene was refluxed on a Dean and Stark water separator for 24 h. Compound **4b** precipitated on cooling to room temperature and was filtered and washed with methanol to give red crystals. 0.60 g (21%), mp 212°C (dimethylformamide/water). IR: 3400, 3340, 3240, 2200 und 2180, 1660 cm^{-1}. ^1H NMR (d_6-DMSO): δ 1.58 (s, 6H, CH_3), 3.28 (s, 3H, N–CH3), 5.60–5.68 (d, 1H, CH), 5.88–5.95 (d, 1H, CH), 6.90–7.38 (m, 4H, aromatic protons), 7.80–7.95 (m, 3H, NH_2, CH) ppm. UV/Vis (acetone): λ_{max}: 446 nm; log ε: 4.569.

$C_{18}H_{18}N_4$	Calcd.: C74.49,	H6.29,	N19.30.
(290.22)	Found: C74.22,	H6.17,	N19.32.

*3.8. 2-[(Dimethylaminomethylene)amino]-5-(1,3,3-trimethyl-2,3-dihydro-1*H*-indol-2-ylidene)-1,3-pentadiene-1,1,3-tricarbonitrile* **5a**

A mixture of 0.75 g (3 mmol) **4a** and 0.60 g (5 mmol) DMF–DMA was refluxed in 10 ml ethanol for 4 h. Compound **5a** precipitated on cooling to room temperature; it was filtered and washed with cold ethanol giving red crystals with a bluish lustre, 0.83 g (93%), mp 183°C (acetonitrile/H_2O). IR: 2200, 1620, 1555 cm^{-1}. ^1H NMR (d_6-DMSO): δ 1.60 (s, 6H, CH_3), 3.10 (s, 3H, N–CH_3), 3.20 (s, 3H, N–CH_3), 3.53 (s, 3H, N–CH_3), 5.87–5.95 (d, 1H, CH), 7.18–7.55 (m, 4H, aromatic protons), 8.17–8.23 (d, 2H, CH) ppm. UV/Vis (acetone): λ_{max}: 488 nm; log ε: 4.677.

$C_{21}H_{22}N_6$	Calcd.: C70.40,	H6.14,	N23.46.
(358.27)	Found: C70.18,	H5.96,	N23.51.

*3.9. 2-[Di(ethoxycarbonyl)]amino-5-(1,3,3-trimethyl-2,3-dihydro-1*H*-indol-2-ylidene)-1,3-pentadiene-1,1,3-tricarbonitrile* **5b**

A mixture of 2.52 g (8 mmol) **4a**, 50 ml dichloromethane and 7.25 ml pyridine was stirred at 0°C, 9.50 g (112 mmol) chloroformic acid ethylester was dropped slowly (temperature not more than 10°C) and stirred for 30 min at room temperature. The dark red reaction mixture was diluted with 50 ml dichloromethane and washed twice with 100 ml 1N HCl, four times with 100 ml saturated sodium chloride solution, once with saturated sodium hydrogencarbonate solution and twice with saturated sodium chloride solution. After drying over magnesium sulfate the solvent was removed in vacuo giving violet crystals, 1.60 g (44%), mp 170°C (ethanol). IR: 2200, 1760, 1740, 1570 cm^{-1}. ^1H NMR (d_6-DMSO): δ 1.25–1.30 (t, 6H, CH_3), 1.65 (s, 6H, CH_3), 3.79 (s, 3H, N–CH_3), 4.28–4.38 (q, 4H, CH_2), 6.25–6.32 (d, 1H, CH), 7.38–7.75 (m, 4H, aromatic protons), 7.62–7.71 (d, 1H, CH) ppm. UV/Vis (acetone): λ_{max}: 531 nm; log ε: 4.893.

$C_{25}H_{25}N_5O_4$	Calcd.: C65.38,	H5.44,	N15.25.
(459.31)	Found: C65.65,	H5.49,	N15.40.

*3.10. 1-[1,1,3-Tricyano-2-(2-(2,5-dioxo-perhydropyrrole-1-yl)-1-propene-3-ylidene]-2-(1,3,3-trimethyl-2,3-dihydro-1*H*-indol-2-ylidene)ethane* **5c**

2.52 g (8 mmol) **4a** was stirred in 40 ml dichloromethane. To this solution 2 ml triethylamine and

6.70 g (67 mmol) succinic anhydride was added and stirred at room temperature for 24 h. After filtration the reaction mixture was diluted with 100 ml ethylacetate, washed with 100 ml of 1N HCl, 100 ml saturated sodium hydrogencarbonate solution and 100 ml saturated sodium chloride solution. After drying the dark red reaction mixture, the solvent was removed in vacuo to give lustrous dark red crystals, 0.80 g (25%), mp 225°C (ethanol). IR: 2200, 2180, 1730, 1660, 1620 cm^{-1}. ^1H NMR (d_6-DMSO): δ 1.68 (s, 6H, CH_3), 3.30 (s, 4H, CH_2), 3.79 (s, 3H, N–CH_3), 6.25–6.32 (d, 1H, CH), 7.40–7.73 (m, 4H, aromatic protons), 8.27–8.35 (d, 1H, CH) ppm. UV/Vis (acetone): λ_{max}: 532 nm; log ε: 4.784.

$C_{23}H_{19}N_5O_2$	Calcd.: C69.50,	H4.78,	N17.63.
(397.29)	Found: C69.54,	H4.90,	N17.53.

3.11. 2-Imino-5-(1,3,3-trimethyl-2,3-dihydro-1H-indol-2-ylidene)-3-pentene-3-carbonitrile **6**

3.11.1. Method 1

A mixture of 1.64 g (20 mmol) **2d**, 2.96 g (20 mmol) triethyl orthoformate, 3.46 g (20 mmol) F.B. and 6 ml acetic acid was refluxed for 2 h. After cooling to room temperature the solution was diluted with a small amount of petroleum ether. After 1 h the precipitate was filtered and washed with cold methanol to give orange crystals. 0.40 g (8%), mp 140°C. IR: 3450, 2990, 2215, 1605 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.70 (s, 6H, CH_3), 2.52 (d, 3H, CH_3), 2.82 (s, 3H, CH_3), 3.35 (d, 1H, NH), 6.55–6.60 (d, 1H, aromatic proton), 6.75–6.82 (t, 1H, aromatic proton), 6.93–6.98 (d, 1H, CH), 7.20–7.25 (t, 1H, aromatic proton), 7.42–7.48 (d, 1H, aromatic proton), 7.62–7.68 (d, 1H, CH) ppm. UV/Vis (acetone) < 340 nm.

$C_{17}H_{19}N_3$	Calcd.: C76.99,	H7.16,	N15.84.
(265.21)	Found: C76.76,	H7.43,	N15.54

3.11.2. Method 3

0.82 g (10 mmol) **2d**, 1.00 g (5 mmol) F.A. and 0.65 g piperidine acetate were refluxed for 7 h in 50 ml dry toluene on a Dean and Stark water separator while the clear yellow solution became dark red. After cooling, the solvent was removed in vacuo and after standing for a long time the product crystallized; it was filtered and washed with acetonitrile; orange crystals, 0.80 g (60%), mp 140°C (acetonitrile/water).

$C_{17}H_{19}N_3$	Calcd.: C76.99,	H7.16,	N15.84.
(265.21)	Found: C76.55,	H7.33,	N15.45.

3.12. 2-Dimethylamino-ethene-1,1-dicarbonitrile **7a**

1.98 g (30 mmol) **1a** was refluxed with 7.14 g (60 mmol) DMF–DMA for 3 h. After cooling to room temperature the reaction mixture was poured onto ice chips and the precipitate was filtered to give colorless crystals. 1.45 g (25%), mp 76°C. IR: 3000, 2200, 1650 cm^{-1}. ^1H NMR (d_6-DMSO): δ3.18 (s, 3H, CH_3), 3.21 (s, 3H, CH_3), 7.68 (s, 1H, CH) ppm.

$C_6H_7N_3$	Calcd: C59.52,	H5.78,	N34.70.
(121.09)	Found: C59.60,	H5.85,	N34.55.

3.13. 1-Dimethylamino-3-oxo-3-phenyl-1-propene-2-carbonitrile **7b**

4.35 g (30 mmol) **1b** [13] were stirred with 7.14 g (60 mmol) DMF–DMA at room temperature; **7b** precipitated immediately. After 1 h a small amount of petroleum ether was added and the liquor filtered to yield yellow crystals. 4.50 g (67%), mp 106–108°C (ethanol). IR: 2200, 1650, 1600 cm^{-1}. ^1H NMR (d_6-DMSO): δ 3.40 (s, 6H, N–CH_3), 7.45–7.69 (m, 5H, aromatic protons), 7.93 (s, 1H, CH) ppm.

$C_{12}H_{12}N_2O$	Calcd.: C72.01,	H6.00,	N14.00.
(200.15)	Found: C72.12,	H5.95,	N13.94.

3.14. 2-Amino-4-dimethylamino-1,3-butadiene-1,1,3-tricarbonitrile **8a**

A mixture of 2.64 g (20 mmol) **2a** [4], 4.76 g (40 mmol) DMF–DMA and 5 ml ethanol was refluxed

for 45 min. After cooling to room temperature the product was filtered and washed with cold ethanol; 1.60 g (43%) yellow crystals, mp 192°C (ethanol). IR: 3340, 3220, 2210, 2190, 1670, 1640 cm^{-1}. ^1H NMR (d_6-DMSO): δ 3.26 (s, 3H, CH_3), 3.31 (s, 3H, CH_3), 7.66 (s, 1H, CH), 7.95 (s, 2H, NH_2) ppm.

$C_9H_9N_5$	Calcd.: C57.77,	H4.81,	N37.42.
(187.13)	Found: C57.83,	H5.07,	N37.41.

3.15. 2-Amino-4-dimethylamino-1,3-butadiene-1,1-dicarbonitrile **8b**

2.72 g (20 mmol) **2b** [14] was refluxed with 4.76 g (40 mmol) DMF–DMA in 5 ml methanol for 30 min. After cooling the reaction mixture was poured onto ice chips and was allowed to stand in the refrigerator overnight. The precipitate was filtered and washed with water giving yellow crystals, 1.74 g (64%), mp 148°C (methanol). IR: 2940, 2200, 2170, 1630 cm^{-1}. ^1H NMR (d_6-DMSO): 2.90 (s, 3H, N–CH_3), 3.15 (s, 3H, N–CH_3), 5.13–5.20 (d, 1H, CH), 7.43-7.50 (d, 1H, CH) ppm; no NH_2-signal was observed.

$C_8H_{10}N_4$	Calcd.: C59.27,	H6.17,	N34.56.
(162.11)	Found: C59.62,	H6.20,	H34.48.

3.16. 4-Dimethylamino-2-phenyl-1,3-butadiene-1,1-dicarbonitrile **8c**

3.36 g (20 mmol) **2c** [15, 16] and 4.76 g (40 mmol) DMF–DMA were refluxed for 45 min. After cooling to room temperature a small amount of toluene was added and the liquor filtered to yield yellow needles, 2.40 g (54%), mp 150°C (acetic acid). IR: 2200, 1620 cm^{-1}, UV/Vis (acetone): λ_{max}: 384 nm; log ε: 4.629.

$C_{14}H_{13}N_3$	Calcd.: C75.35,	H5.83,	N18.82.
(223.17)	Found: C75.35,	H5.77,	H18.78.

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