Dyes and Pigments, Vol. 28, No. 4, pp. 297–315, 1995
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0143-7208/95 $9.50 + 0.00

ELSEVIER 0143-7208(95)00022-4

Syntheses with Nitriles. Part 96: Colorformers Based on Pyrazolomalononitriles—Synthesis, Properties and Structure–Color Relationships*

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(Received 17 January 1995; accepted 23 February 1995)

ABSTRACT

One-component colorformers were obtained from 4-dicyanomethylene pyrazolone derivatives and anilines or tetramethyl-dihydroquinoline in excellent yields. They were transformed into dyes of maximum absorption wavelengths between 527 and 628 nm by thermolysis as well as by photolysis. Different substituents and donor elements (anilines and quinoline) showed a remarkable and partially unexpected influence on the dye properties and they were evaluated using semi-empirical quantum chemical calculations (AM1, CNDO/S-CI).

1 INTRODUCTION

Modern dye chemistry features various kinds of speciality dyes for high technology applications.[1,2] These include colorformers, which are used in papers for thermoprinting and for other thermographic recording processes. To be practically applicable, a colorformer must meet the following requirements: (i) the colorless precursor(s) must react with sufficient speed to yield a dye of good lightfastness; and (ii) these reactions may be induced mechanically (pressure), photochemically (light of different wavelengths) or thermally. Most papers published on colorformers report on systems containing two or more components (the colorformer and at

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* For Part 95 see Deshmukh, M., Mittelbach, M. & Junek, H., *Monatsh. Chem*, **126** (1995) 91.

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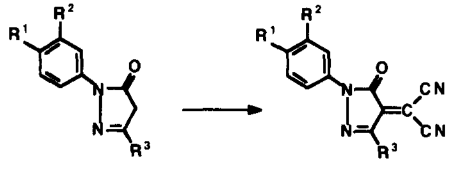


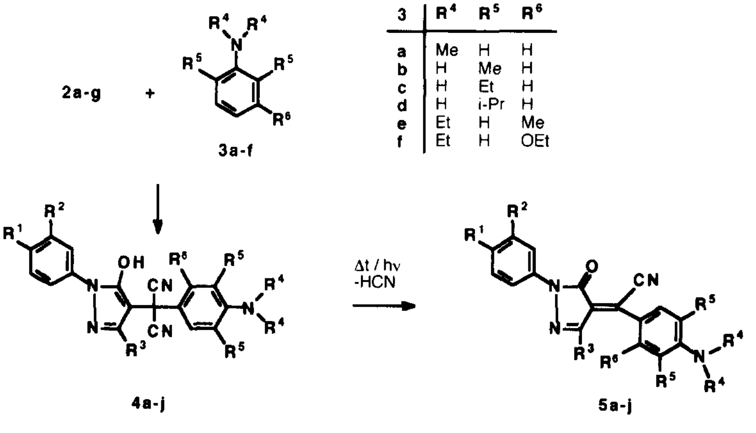
1a-g 2a-g

1, 2	R¹	R²	R³
a	Me	H	Me
b	Cl	H	Me
c	H	Cl	Me
d	H	H	Et
e	H	H	Pr
f	H	H	c-Hex-Et
g	H	H	Me

Scheme 1

least one co-reactant, which are incorporated in microcapsules). A group from Japan recently described intramolecular thermogenesis of dyes based on allyl-aryl ethers, which gave phenol lactones by Claisen rearrangement.[3] Subsequent intramolecular acid–base reaction yielded dyes with maximum longwave absorptions of 530–565 nm and log ε values between 3·46 and 3·99.

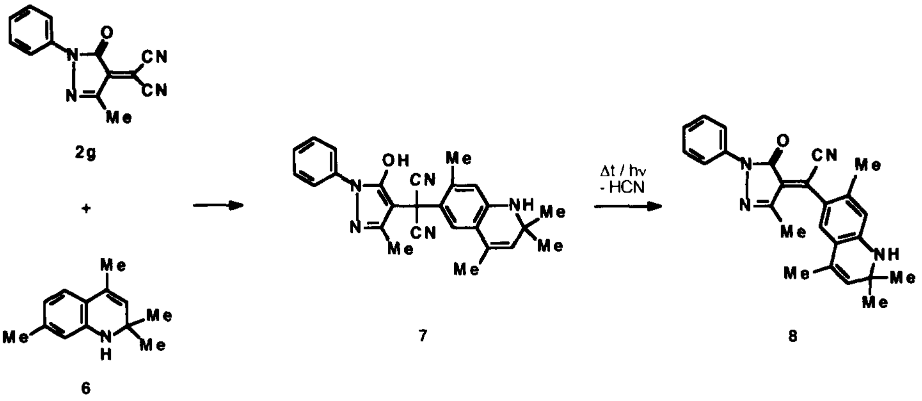
Our investigations have been particularly concerned with one-component colorformers, which are reacted to give dyes in a one-step elimination reaction.[4–7] In this paper we report on the synthesis and the properties of one-component colorformers based on symmetrically and unsymmetrically substituted pyrazoles. Quantum chemical considerations deal with the



3	R⁴	R⁵	R⁶
a	Me	H	H
b	H	Me	H
c	H	Et	H
d	H	i-Pr	H
e	Et	H	Me
f	Et	H	OEt

4, 5	R¹	R²	R³	R⁴	R⁵	R⁶
a	Me	H	Me	Me	H	H
b	Cl	H	Me	Me	H	H
c	H	H	Et	Me	H	H
d	H	H	Pr	Me	H	H
e	H	H	c-Hex-Et	Me	H	H
f	H	H	Me	H	Et	H
g	H	H	Me	H	i-Pr	H
h	H	Cl	Me	H	Me	H
i	H	H	Me	Et	H	Me
j	H	H	Me	Et	H	OEt

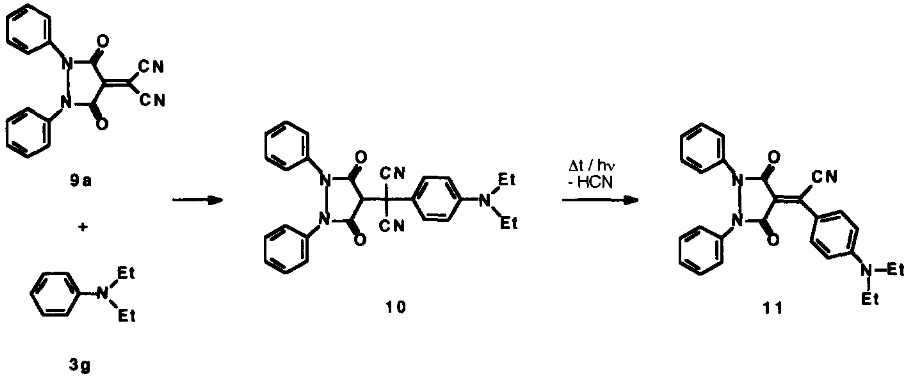
Scheme 2



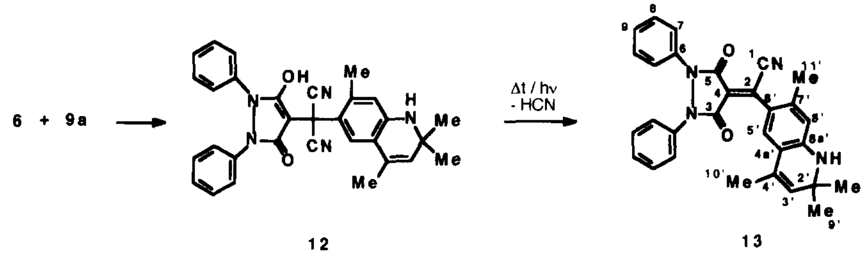
Scheme 3

influence of the substitution patterns and the symmetry on the dye properties.

Pyrazoles **1a–g** were reacted with tetracyanoethylene (TCNE) to yield the corresponding dicyanomethylene compounds **2a–g** (Scheme 1). Analogously, **9a** was obtained from 1,2-diphenylpyrazol-3,5-dione. When **2a–g** and **9a** were reacted with anilines **3a–g** or quinoline **6**, off-white colorformers (disubstituted malononitriles) **4a-j** (Scheme 2), **7** (Scheme 3), **10** (Scheme 4) and **12** (Scheme 5) were formed in excellent yields. The colorformers gave dyes **5a-j**, **8**, **11** and **13** by thermal or photochemical elimination of hydrocyanic acid. Dye formation started immediately, as is necessary for applications in e.g. thermoprinting or photo-recording processes. For the preparation of dyes **5a-j**, **8**, **11** and **13**, photolysis was the method of choice since the yields were much better than for thermolysis and fewer by-products were formed. Compound **11** can also be obtained by reaction of



Scheme 4



Scheme 5

anilinobenzaldehyde with diphenylpyrazoledione and subsequent cyanation of the condensation product; it can be used in thermal dye transfer systems.[8]

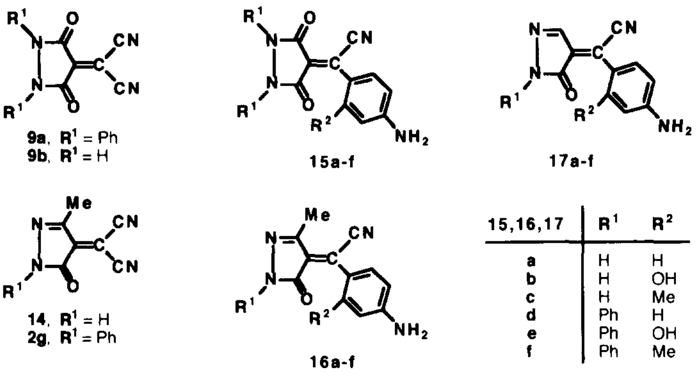
Dyes **5a-j**, which contain an asymmetric pyrazolone and a substituted aniline moiety, show absorptions between 527 nm (**5f**) and 546 nm (**5b**). Substituents R^1 and R^2 (in the pyrazolone part of the molecule) as well as R^4 (in the aniline part) have little influence on the maximum absorption wavelength; R^5 in the *ortho* position of the aniline is more important. This is considered in detail in the quantum chemical calculations. Compound **11**, which is derived from a symmetrical pyrazole, shows a long wavelength absorption of 570 nm and in compounds **8** and **13**, both of which contain a tetramethyl-dihydroquinoline as electron donor, the maximum absorption wavelengths were shifted to 613 nm (**8**) and 628 nm (**13**). For some of the anilino dyes (**5f-h**) which contain primary amino groups (R^4 = H), two isomers were found: one is as represented by the structure given for **5a-j** in Scheme 2, and in the other, the positions of the anilino group and the nitrile group are reversed. As the three compounds gave normal visible spectra, no attempt was made to separate the isomers. Dyes **8** and **13**, which contain a quinoline moiety, gave only one isomer.

2 QUANTUM CHEMICAL CALCULATIONS

With respect to the UV/Vis properties of the compounds, the experimental results can be summarized as follows.

(i) Dyes derived from the symmetrical dicyanomethylene-1,2-diphenyl pyrazol-3,5-dione (**11**, **13**) absorb at somewhat longer wavelengths than those obtained from the unsymmetrical dicyanomethylene-3-methyl-1-phenylpyrazol-5-one (**5a-j**, **8**).

(ii) A methyl group in the *ortho* position of the aniline ring (**5i**) leads to a bathochromic shift, while an ethoxy group (**5i**) leads to a hypsochromic shift of the longest wavelength absorption band.



9a, R^1 = Ph
9b, R^1 = H

15a-f

17a-f

14, R^1 = H
2g, R^1 = Ph

16a-f

15,16,17	R^1	R^2
a	H	H
b	H	OH
c	H	Me
d	Ph	H
e	Ph	OH
f	Ph	Me

Scheme 6

(iii) The effect of substituents is more pronounced in the series of dyes derived from dicyanomethylene-1,2-diphenylpyrazol-3,5-dione.

The most surprising result is the opposite effect of a methyl versus an ethoxy group. If one applies the polymethine concept[9,10] to these dyes, a hypsochromic shift would be expected in both cases (donor substituent at an even position of the polymethine chain). The observed effect of the ethoxy group clearly conforms to this empirical rule, whereas that of the methyl group is at variance with it. To obtain some further insight into the UV/Vis properties, quantum chemical calculations were performed on a series of model compounds (the structures of which are given in Scheme 6). First, geometries were fully optimized without any restrictions (PRECISE option) by the AM1 method.[11] Using these structures, electronic excitation energies were calculated by the CNDO/S-CI method taking into account 250 singly excited configurations.[12] Due to size limitations, not all compounds shown in Scheme 6 could be treated by CNDO/S. Therefore, a limited CI was also used, involving single and double excitations from the five highest occupied and five lowest virtual orbitals, respectively (76 configurations) with the aid of the AM1 method as implemented in the VAMP package.[13] For the compounds of series **16a-f** and **17a-f**, besides the *E*-conformations shown in Scheme 6, the corresponding *Z*-isomers were also considered. The results of the calculations are collected in Table 1. As had been found previously for compound **9b**[11] CNDO/S calculations predict two rather weak longest wavelength transitions of the n–π^* type for model compound **9b**. The third transition of compound **14** can be assigned to a π–π^* absorption dominated almost exclusively by the HOMO–LUMO single excitation (93%). The two orbitals involved in this transition are depicted in Fig. 1. From their shapes, this transition might be termed an intramolecular charge transfer excitation.[4] According to

TABLE 1
Calculated (AM1) Heats of Formation ΔH_f (kcal mol^{-1}), Wavenumbers ν (cm^{-1}) and Oscillator Strengths f of Electronic Transitions (CNDO/S-CI, AM1)

Compound	*AM1*	*CNDO/S*		*AM1*	
	ΔH_f *(kcal mol^{-1})*	$\nu \times 10^{-3}$ *(cm^{-1})*	f	$\nu \times 10^{-3}$ *(cm^{-1})*	f
9a	151·4	—	—	31·7	0·020
				35·5	0·003
				36·8	0·086
9b	67·7	25·2	0·002	29·6	0·010
		27·5	0·001	31·2	0·034
		37·3	0·033	37·0	0·035
14	105·4	24·9	0·002	25·4	0·169
		26·4	0·262	31·2	0·026
		31·5	0·004	40·8	0·185
2g	145·3	23·8	0·215	25·1	0·220
		24·7	0·029	34·7	0·015
		31·4	0·004	35·2	0·299
15a	53·3	27·3	0·014	28·0	0·497
		28·5	0·070	31·9	0·002
		30·9	0·462	35·7	0·026
15b	10·6	27·6	0·016	27·8	0·390
		28·5	0·093	31·3	0·014
		30·6	0·358	35·8	0·026
15c	48·8	—	—	31·2	0·248
				32·5	0·007
				35·6	0·012
15d	136·9	—	—	29·2	0·764
				32·6	0·005
				36·8	0·415
15e	93·7	—	—	29·5	0·604
				34·0	0·007
				36·9	0·347
15f	131·5	—	—	31·3	0·214
				34·2	0·018
				36·9	0·288
(*E*)-16a	93·1	26·6	0·023	28·0	0·471
		27·9	0·404	31·7	0·169
		32·6	0·072	32·4	0·009
(*Z*)-16a	93·8	26·8	0·032	29·4	0·491
		29·7	0·487	32·8	0·012
		32·5	0·006	33·3	0·121
(*E*)-16b	50·5	—	—	27·7	0·417
				31·0	0·044
				31·6	0·110
(*Z*)-16b	51·4	—	—	29·9	0·305
				32·2	0·005
				34·5	0·115
(*E*)-16c	88·1	—	—	29·8	0·257
				32·8	0·008
				33·1	0·125
(*Z*)-16c	87·4	—	—	29·8	0·288
				32·9	0·010
				34·7	0·116
(*E*)-16d	134·0	—	—	29·7	0·366
				34·0	0·013
				34·4	0·144

TABLE 1—*contd.*

Compound	*AM1*	*CNDO/S*		*AM1*	
	ΔH_f *(kcal mol^{-1})*	$\nu \times 10^{-3}$ *(cm^{-1})*	*f*	$\nu \times 10^{-3}$ *(cm^{-1})*	*f*
(*Z*)-16d	133·9	—	—	29·9	0·429
				33·9	0·013
				35·5	0·096
(*E*)-16e	90·5	—	—	27·3	0·414
				31·2	0·057
				32·2	0·140
(*Z*)-16e	91·2	—	—	29·9	0·469
				32·8	0·005
				35·1	0·075
(*E*)-16f	128·0	—	—	29·5	0·357
				33·2	0·009
				34·0	0·111
(*Z*)-16f	127·4	—	—	29·9	0·434
				33·4	0·010
				35·5	0·085
(*E*)-17a	98·9	26·0	0·153	27·4	0·498
		28·9	0·356	32·2	0·004
		32·5	0·027	32·4	0·159
(*Z*)-17a	98·8	26·8	0·060	28·4	0·633
		29·0	0·624	32·2	0·008
		32·5	0·007	32·6	0·027
(*E*)-17b	56·2	26·3	0·161	27·2	0·474
		29·1	0·341	30·9	0·015
		32·6	0·033	32·2	0·109
(*Z*)-17b	55·8	26·9	0·073	28·1	0·600
		29·0	0·563	31·2	0·013
		32·4	0·013	32·5	0·017
(*E*)-17c	93·9	26·5	0·105	29·5	0·347
		29·4	0·338	32·2	0·025
		32·3	0·046	32·4	0·081
(*Z*)-17c	93·3	27·1	0·051	30·1	0·374
		30·3	0·319	32·6	0·009
		32·1	0·074	33·3	0·128
(*E*)-17d	138·9	—	—	27·8	0·538
				32·9	0·006
				33·0	0·206
(*Z*)-17d	138·5	—	—	28·5	0·697
				33·0	0·011
				33·6	0·086
(*E*)-17e	96·1	—	—	27·9	0·536
				31·7	0·022
				33·1	0·140
(*Z*)-17e	96·1	—	—	28·5	0·691
				32·2	0·005
				33·6	0·053
(*E*)-17f	134·0	—	—	29·8	0·430
				33·1	0·007
				33·6	0·119
(*Z*)-17f	133·5	—	—	30·3	0·520
				33·3	0·010
				35·0	0·070

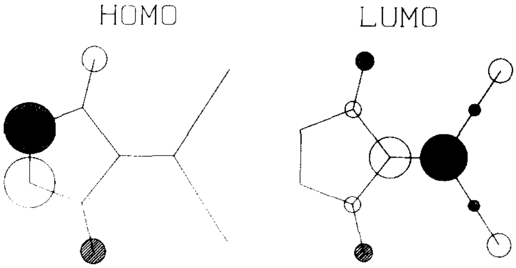


Fig. 1. Plot of HOMO and LUMO of compound **14**.

CNDO/S, replacement of NH by *N*-phenyl should have a rather profound effect on the UV/Vis spectra, e.g. compare compounds **14** and **2g**.[4] A similar, albeit much less pronounced effect is also predicted by AM1. In marked contrast, however, for **9a** and **9b** AM1 predicts a small hypsochromic effect in case of the two *N*-phenyl groups (**9a**). A possible explanation for these contrasting effects might be given by the different conformations of **9a** and **2g**. In **2g** the phenyl ring is nearly coplanar with the pyrazolinone ring ($\tau = 22°$), whereas in **9a** steric hindrance leads to an almost orthogonal arrangement of the two phenyl groups relative to the five-membered ring ($\tau = 75°$). As can be further seen from the data presented in Table 1 the CNDO/S method generally yields somewhat lower excitation energies than AM1. Even more important, in a number of cases a different ordering of states is obtained by the two methods. As is well known[14] CNDO/S tends to underestimate excitation energies of n–π^* transitions. In this respect, therefore, AM1 seems to give somewhat more reliable results.

In the case of the dyes derived from the parent compounds **9a**, **9b**, **14** and **2g** by exchange of one nitrile group with an anilino ring (**15a-f**, **16a-f**, **17a-f**) the AM1 geometry optimizations lead to a rather strong twisting of the phenyl ring, especially in the *ortho*-substituted derivatives. As an example, in Figs 2 and 3 the calculated rotational potential energy curves for **15a** and **15c**, respectively, are shown. Because of this twisting, the electronically excited states are generally calculated to be mixtures of several configurations. Therefore, a clearcut interpretation of the UV/Vis spectroscopic properties of these dyes in terms of qualitative concepts, e.g. the polymethine concept, is precluded. Nevertheless, in most cases the most intense transition is governed by the HOMO–LUMO single excitation. Furthermore, the compounds of series **16a-f** and **17a-f** might exist as *E*- and *Z*-isomers. The calculated energy differences are quite small and a dependence on which of these two conformations is more stable on the respective system is found. In general, the *Z*-isomers are predicted to absorb at somewhat shorter wavelengths. In addition, the effect depends on the *ortho*-substituent of the anilino group. The experimentally observed relationship

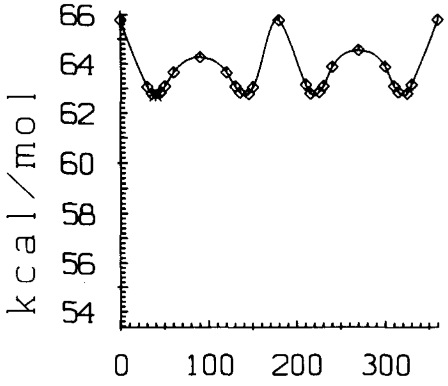


Fig. 2. Calculated rotational potential energy for compound **15a**.

between the absorption maxima and the nature of the substituent might, therefore, be obscured by the effect of *E*/*Z*-isomerism in these dyes. However, it should be noted that in series **15a-f**, where no such isomerism is possible, the AM1 calculations predict a hypsochormic shift for both the hydroxy and methyl groups (compare **15d** versus **15e** versus **15f**) in contrast to experimental evidence. As compared with dyes of series **16a-f** and **17a-f**, the excitation energies for those of series **15a-f** appear to be somewhat overestimated by the calculations. This discrepancy is probably due to the well known tendency of the AM1 method to overestimate pyramidalization and especially barriers to planarity in cyclic hydrazides.[15–18] Although a CSD search[19,20] of X-ray structures of related compounds revealed a certain amount of pyramidalization, the deviation from planarity appears to be exaggerated by AM1. The results for excitation energies appear to depend quite crucially on the conformation of these amidic nitrogens: so, for example, a calculation on **9b** in C_{2v} symmetry led to a bathochromic shift of 4700 cm^{-1} as compared with the fully optimized structure.

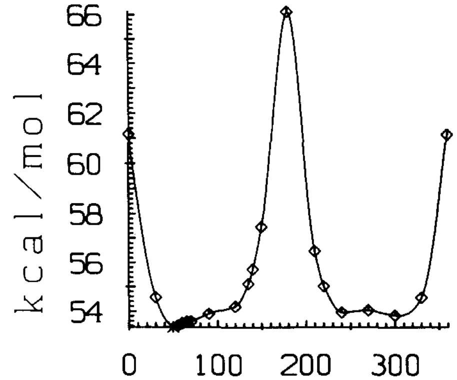


Fig. 3. Calculated rotational potential energy for compound **15c**.

3 CONCLUSIONS

Straightforward strategies for the synthesis of colorformers **4a-j**, **7**, **10** and **12** were found. Their transformation into dyes **5a-j**, **8**, **11** and **13** by light or by heat could be performed with sufficient speed. The resulting dyes were deeply colored blue to violet compounds, and generally of good lightfastness. At first sight, the structure–color relationships seemed to be a little surprising, but they could be explained by AM1 and CNDO/S calculations by taking steric and conformational properties into account.

4 EXPERIMENTAL

4.1 General

All melting points are uncorrected. A mercury lamp was used for photolysis (Hanau TNN 15/23). Spectral data were recorded with the following instruments: IR spectra, Perkin-Elmer Spectrophotometer 298 (KBr pellets); ^{1}H and ^{13}C NMR spectra, Varian EM 360A and Varian Gemini XL 200 (spectra are referenced to tetramethylsilane); UV/Vis spectra, Hitachi U-3501 spectrophotometer (quartz cuvettes); elemental analyses, C,H,N-analyser Carlo Erba 1106.

The anilines (**3a-g**) and the quinoline (**6**) were vacuum-distilled before use. The other starting materials were obtained from commercial suppliers and used without further purification. Ciba-Geigy AG, Switzerland, are thanked for providing the pyrazolones **1a-g**.

4.2 General procedure for the preparation of dicyanomethylene compounds 2a-g and 9a

The synthesis of **2g** from **1g** has been published previously.[4] Tetracyanoethylene (TCNE, 39 mmol) was heated to 50°C in acetonitrile (50 ml). The corresponding pyrazolone **1a-f** (35 mmol) was added with stirring. The mixture was stirred at 50°C for an additional 30 min, filtered under gravity and the filtrate cooled to room temperature. The products were collected by suction, washed with light petroleum and dried over calcium chloride *in vacuo*. Products **2a-g** were obtained in analytical purity.

*4.2.1 4-(Dicyanomethylene)-5-methyl-2-(*p*-tolyl)-pyrazole-3-one (**2a**)*
Yield 78%, m.p. 141°C. IR: 2930, 2230 (CN), 1710 (CO), 1600 cm^{-1}. ^{1}H NMR (60 MHz, d_6-DMSO): 2·3 (3H, s, CH_3), 2·4 (3H, s, CH_3), 7·1–7·6

(4H, arom. protons) ppm. UV/Vis (methanol) λ_{max} (log ε): 560 (2·80) nm. $C_{14}H_{10}N_4O$ (250·3): calculated C 67·2, H 4·0, N 22·4; found C 67·0, H 4·2, N 22·7.

*4.2.2 2-(*p*-Chlorophenyl)-4-(dicyanomethylene)-5-methylpyrazole-3-one (**2b**)*

Yield 72%, m.p. 172°C. IR: 1710 (CO), 1590, 1490 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): 2·6 (3H, s, CH_3), 7·4 and 7·8 (4H, 2d, arom. protons) ppm. UV/Vis (methanol) λ_{max} (log ε): 538 (2·74) nm. $C_{13}H_7ClN_4O$ (270·7): calculated C 57·7, H 2·6, N 20·7, Cl 13·1; found C 57·9, H 2·55, N 20·8, Cl 12·9.

*4.2.3 2-(*m*-Chlorophenyl)-4-(dicyanomethylene)-5-methylpyrazole-3-one (**2c**)*

Yield 52%, m.p. 181°C. IR: 1710 (CO), 1590, 1570, 1480 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): 2·6 (3H, s, CH_3), 7·3–7·9 (4H, 2d, arom. protons) ppm. UV/Vis (methanol) λ_{max} (log ε): 530 (2·79) nm. $C_{13}H_7ClN_4O$ (270·7): calculated C 57·7, H 2·6, N 20·7, Cl 13·1; found C 57·65, H 2·5, N 20·7, Cl 12·9.

*4.2.4 4-(Dicyanomethylene)-5-ethyl-2-phenylpyrazole-3-one (**2d**)*

Yield 53%, m.p. 130°C. IR: 2940, 1710 (CO), 1590, 1490 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): 1·4 (3H, t, CH_3), 2·6 (2H, q, CH_2), 7·3–7·9 (5H, m, arom. protons) ppm. UV/Vis (methanol) λ_{max} (log ε): 544 (2·77) nm. $C_{14}H_{10}N_4O$ (250·3): calculated C 67·2, H 4·0, N 22·4; found C 67·2, H 4·1, N 22·4.

*4.2.5 4-(Dicyanomethylene)-2-phenyl-5-propylpyrazole-3-one (**2e**)*

Yield 83%, m.p. 110°C. IR: 2960, 1710, 1590 cm^{-1}. ^1H NMR (60 MHz, d_6-DMSO): 1·1 (3H, t, CH_3), 1·8 (2H, m, CH_2), 2·4 (2H, t, CH_2), 7·5–8·5 (5H, m, arom. protons) ppm. UV/Vis (methanol) λ_{max} (log ε): 545 (2·77) nm. $C_{15}H_{12}N_4O$ (264·3): calculated C 68·2, H 4·6, N 21·2; found C 68·1, H 4·7, N 21·2.

*4.2.6 5-[2-(Cyclohexyl)ethyl]-4-(dicyanomethylene)-2-phenylpyrazole-3-one (**2f**)*

Yield 69%, m.p. 95°C. IR: 2920, 2850, 1710 (CO), 1700, 1595, 1490 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): 0·9–1·9 (13H, m, CH and 6 CH_2), 2·9 (2H, t, CH_2), 7·2–8·0 (5H, m, arom. protons) ppm. UV/Vis (methanol) λ_{max} (log ε): 548 (2·77) nm. $C_{20}H_{20}N_4O$ (332·4): calculated C 72·3, H 6·1, N 16·9; found C 72·5, H 6·1, N 16·7.

*4.2.7 4-(Dicyanomethylene)-1,2-diphenylpyrazol-3,5-dione (**9a**)*

Yield 85%, m.p. 140°C (decomp.). IR: 3470, 3070, 3040, 1760, 1725, 1650, 1605, 1495 cm^{-1}. ^{1}H NMR (60 MHz, $CDCl_3$): 7·2–7·5 (m, aromatic protons) ppm. UV/Vis (methanol) λ_{max} (log ε): 340 (3·13) 530 (2·42) nm. $C_{18}H_{10}N_4O_2$ (314·3): calculated C 68·8, H 3·2, N 17·8; found C 68·9, H 3·3, N 17·6.

4.3 General procedure for the preparation of malononitriles 4a-j, 7, 10 and 12

The aniline (**3a-g**, 20 mmol) or quinoline (**6**, 20 mmol) was added to a solution of the dicyanomethylene compound (**2a-g**, **9a**, 10 mmol) in acetic acid (40 ml) at 40–50°C and the mixture stirred until the color of the dicyanomethylene compound had faded. The colorless products precipitated or were precipitated by addition of water. They were collected by suction and washed thoroughly with water. For purification the raw products were dissolved in DMF and reprecipitated by addition of water. All products were off-white powders. They were dried *in vacuo* in the dark.

*4.3.1 2-(5-Hydroxy-3-methyl-1-*p*-tolyl-4-pyrazolyl)-2-(4-dimethylamino-1-phenyl)malononitrile (**4a**)*

Yield 78%, m.p. 182°C (decomp.). IR: 2900, 2810, 1615, 1560, 1520 cm^{-1}. ^{1}H NMR (60 MHz, d_6-DMSO): 1·8 (3H, s, CH_3), 2·3 (3H, s, CH_3), 3·0 (6H, s, 2 CH_3), 6·8 (2H, d, arom. protons), 7·3 (2H, d, arom. protons), 7·4 (2H, d, arom. protons), 7·6 (2H, d, arom. protons) ppm. $C_{22}H_{21}N_5O$ (371·4): calculated C 71·2, H 5·7, N 18·9; found C 71·1, H 5·7, N 18·9.

*4.3.2 2-[1-(4'-Chlorophenyl)-5-hydroxy-3-methyl-4-pyrazolyl)-2-(4-dimethylamino-1-phenyl)malononitrile (**4b**)*

Yield 84%, m.p. 192°C (decomp.). IR: 2900, 2810, 1615, 1580, 1525, 1490 cm^{-1}. ^{1}H NMR (60 MHz, d_6-DMSO): 1·8 (3H, s, CH_3), 2·9 (6H, s, 2 CH_3), 6·8 (2H, d, arom. protons), 7·3 (2H, d, arom. protons), 7·4 (2H, d, arom. protons), 7·6 (2H, d, arom. protons) ppm. $C_{21}H_{18}ClN_5O$ (391·9): calculated C 64·4, H 4·6, N 17·9, Cl 9·1; found C 64·4, H 4·6, N 17·9, Cl 9·4.

*4.3.3 2-(4-Dimethylamino-1-phenyl)-2-(3-ethyl-5-hydroxy-1-phenyl-4-pyrazolyl)malononitrile (**4c**)*

Yield 92%, m.p. 160°C (decomp.). IR: 3100–2800, 1625, 1565, 1520, 1495 cm^{-1}. ^{1}H NMR (60 MHz, d_6-DMSO): 0·9 (3H, t, CH_3), 2·1 (2H, q, CH_2), 2·9 (6H, s, 2 CH_3), 6·8 (2H, d, arom. protons), 7·2–7·7 (7H, m, arom. protons) ppm. $C_{22}H_{21}N_5O$ (371·4): calculated C 71·2, H 5·7, N 18·9; found C 71·0, H 5·7, N 18·7.

*4.3.4 2-(4-Dimethylamino-1-phenyl)-2-(5-hydroxy-1-phenyl-3-propyl-4-pyrazolyl)malononitrile (**4d**)*

Yield 84%, m.p. 154°C (decomp.). IR: 2970, 1615, 1560, 1525, 1500 cm^{-1}. ^{1}H NMR (60 MHz, d_6-DMSO): 0·7 (3H, t, CH_3), 1·4 (2H, m, CH_2), 2·1 (2H, t, CH_2), 3·0 (6H, s, 2 CH_3), 6·8 (2H, d, arom. protons), 7·2–7·6 (7H, m, arom. protons) ppm. $C_{23}H_{23}N_5O$ (385·5): calculated C 71·7, H 6·0, N 18·2; found C 71·6, H 6·1, N 18·3.

*4.3.5 2-[1-(2′-Cyclohexylethyl)-5-hydroxy-1-phenyl-4-pyrazolyl]-2-(4-dimethylamino-1-phenyl]malononitrile (**4e**)*

Yield 88%, m.p. 166°C (decomp.). IR: 2920, 2850, 1610, 1560, 1520, 1500 cm^{-1}. ^{1}H NMR (60 MHz, d_6-DMSO): 0·7–1·7 (13H, m, 6 CH_2 and CH), 2·1 (2H, t, CH_2), 3·0 (6H, s, 2 CH_3), 6·8 (2H, d, arom. protons), 7·3–7·6 (5H, m, arom. protons), 7·7 (2H, d, arom. protons) ppm. $C_{28}H_{31}N_5O$ (453·6): calculated C 74·1, H 6·9, N 15·4; found C 74·6, H 6·6, N 15·4.

*4.3.6 2-(4-Amino-3,5-diethyl-1-phenyl)-2-(4,5-dihydro-5-hydroxy-3-methyl-1-phenyl-4-pyrazolyl)malononitrile (**4f**)*

Yield 47%, m.p. 114°C (decomp.). IR: 3380, 2960, 1630, 1580, 1500 cm^{-1}. ^{1}H NMR (60 MHz, d_6-DMSO): 1·1 (6H, t, 2 CH_3), 1·7 (3H, s, CH_3), 2·5 (4H, q, 2 CH_2), 7·0–7·3 (7H, m, arom. protons) ppm. $C_{23}H_{23}N_5O$ (385·5): calculated C 71·7, H 6·0, N 18·2; found C 71·4, H 6·0, N 18·0.

*4.3.7 2-(4-Amino-3,5-diisopropyl-1-phenyl)-2-(4,5-dihydro-5-hydroxy-3-methyl-1-phenyl-4-pyrazolyl)malononitrile (**4g**)*

Yield 77%, m.p. 168°C (decomp.). IR: 3400, 2960, 1625, 1560, 1500 cm^{-1}. ^{1}H NMR (60 MHz, d_6-DMSO): 1·1 (12H, d, 4 CH_3), 1·6 (3H, s, CH_3), 3·0 (2H, m, 2 CH), 7·0 (2H, s, arom. protons of the aniline), 7·1–7·6 (5H, m, arom. protons) ppm. $C_{25}H_{27}N_5O$ (413·5): calculated C 72·6, H 6·6, N 16·9; found C 72·3, H 6·3, N 16·8.

*4.3.8 2-(4-Amino-3,5-dimethyl-1-phenyl)-2-[4,5-dihydro-5-hydroxy-3-methyl-1-(3′-chlorophenyl)-4-pyrazolyl]malononitrile (**4h**)*

Yield 89%, m.p. 106°C (decomp.). IR: 3470, 3380, 1680, 1620, 1585, 1480 cm^{-1}. ^{1}H NMR (60 MHz, d_6-DMSO): 1·8 (3H, s, CH_3), 2·2 (6H, s, 2 CH_3), 7·1 (2H, s, arom. protons of the aniline), 7·3 (1H, d, arom. proton), 7·5 (1H, t, arom. proton), 7·7 (1H, arom. proton), 7·9 (1H, s, arom. proton) ppm. $C_{21}H_{18}ClN_5O$ (391·9): calculated C 64·4, H 4·6, N 17·9, Cl 9·1; found C 64·1, H 4·7, N 17·7 Cl 9·1.

*4.3.9 2-(4-*N,N*-Diethylamino-2-methyl-1-phenyl)-2-[4,5-dihydro-5-hydroxy-3-methyl-1-phenyl-4-pyrazolyl]malononitrile (**4i**)*

Yield 73%, m.p. 176°C (decomp.). IR: 3060, 2970, 2930, 1605, 1550, 1500 cm^{-1}. ^{1}H NMR (60 MHz, d_6-DMSO): 1·2 (6H, t, 2 CH_3), 1·7 (3H, s, CH_3), 2·4 (3H, s, CH_3), 3·4 (4H, m, 2 CH_2), 6·7–7·7 (8H, m, arom. protons) ppm. $C_{24}H_{25}N_5O$ (399·5): calculated C 72·2, H 6·3, N 17·5; found C 72·3, H 6·2, N 17·7.

*4.3.10 2-(4-N,N-Diethylamino-2-ethoxy-1-phenyl)-2-[4,5-dihydro-5-hydroxy-3-methyl-1-phenyl-4-pyrazolyl]malononitrile (**4j**)*

Yield 67%, m.p. 170°C (decomp.). IR: 3080–3040, 2970, 2930, 2890, 2800–2600, 2230, 1610, 1560, 1520, 1500 cm^{-1}. ^{1}H NMR (60 MHz, d_6-DMSO): 1·1 (6H, t, 2 CH_3), 1·4 (3H, t, CH_3), 1·8 (3H, s, CH_3), 3·4 (4H, m, 2 CH_2), 4·2 (2H, q, CH_2), 6·6 (2H, m, arom. protons), 7·2–7·7 (6H, m, arom. protons) ppm. $C_{25}H_{27}N_5O_2$ (429·5): calculated C 69·9, H 6·3, N 16·3; found C 70·2, H 6·3, N 16·3.

*4.3.11 2-(1,2-Dihydro-2,2,4,7-tetramethyl-6-chinolyl)-2-(5-hydroxy-3-methyl-1-phenyl-4-pyrazolyl)malononitrile (**7**)*

Yield 53%, m.p. 140°C (decomp.). IR: 3380, 2960, 1610, 1570–1560, 1500 cm^{-1}. ^{1}H NMR: because of the instability of the compound a proton NMR spectrum could not be obtained. Sufficient purification of **7** was not possible as the compound was unstable when exposed to light or heat. Thus an accurate elemental analysis could not be obtained. However, as the product (**8**) obtained from **7** by photolysis showed the expected properties and had correct analytical and spectral data, the structure of **7** must be the implied one.

*4.3.12 2-(4-Diethylamino-1-phenyl)-2-(3-hydroxy-5-oxo-1,2-diphenyl-4-pyrazolinyl)malononitrile (**10**)*

Yield 65%, m.p. 148°C (decomp.). IR: 3380–3440, 3060–2900, 2660–2600, 1680, 1615, 1600, 1490 cm^{-1}. ^{1}H NMR: as the compound decomposed during the measurement a proton NMR spectrum could not be obtained. $C_{28}H_{25}N_5O_2$ (463·5): calculated C 72·6, H 5·4, N 15·1; found C 72·3, H 5·3, N 14·8.

*4.3.13 2-(1,2-Dihydro-2,2,4,7-tetramethyl-6-chinolyl)-2-(3-hydroxy-5-oxo-1,2-diphenyl-4-pyrazolinyl)malononitrile (**12**)*

Yield 56%, m.p. 154°C (decomp.). IR: 3605, 3410, 3320–3290, 3230–3150, 2990, 2210, 1670, 1610, 1585, 1485 cm^{-1}. ^{1}H NMR: because of the instability of the compound a proton NMR spectrum could not be obtained. Sufficient purification of **12** was not possible as the compound was unstable when exposed to light or heat. Thus an accurate elemental analysis could not be obtained. Since the product (**13**) obtained from **12** by photolysis showed the expected properties and had correct analytical and spectral data, the structure of **12** is assumed to be correct.

4.4 General procedure for the preparation of dyes 5a-j, 8, 11 and 13

Photolysis (method a): suspensions or solutions of the colorless adducts (2·00 g in 100 ml of solvent) were exposed to the light of a mercury lamp. When the starting material was no longer visible on TLC (silica, eluent: toluene/acetone 3/1) the reactions were stopped (photolyses took between 2 and 24 h). The solvent was evaporated *in vacuo* to obtain the crude products.

Thermolysis performed in DMF (method b): solutions of the addition products (5 mmol in 15 ml DMF) were kept at 140°C until all starting material had disappeared (3–4 h). After cooling the reaction mixtures to room temperature, the dyes were precipitated by addition of water, collected by suction, washed with water, recrystallized, and dried *in vacuo* at 40°C.

*4.4.1 2-(5-Oxo-3-methyl-1-*p*-tolyl-4-pyrazolinylidene)-2-(4-dimethylamino-1-phenyl)acetonitrile (5a)*

From **4a**, method a, yield 96%, m.p. 211°C (from methanol/water). IR: 1705, 1650, 1575, 1535 cm^{-1}. ^{1}H NMR (60 MHz, $CDCl_3$): 2·2 (3H, s, CH_3), 2·5 (3H, s, CH_3), 3·0 (6H, s, 2 CH_3), 6·7 (2H, d, arom. protons), 7·1 (2H, d, arom. protons), 7·7–8·1 (4H, m, arom. protons) ppm. UV/Vis (methanol) λ_{max} (log ε): 536 (4·33) nm. $C_{21}H_{20}N_4O$ (344·4): calculated C 73·2, H 5·9, N 16·3; found C 72·9, H 5·7, N 16·2. Method b gave the identical product in 70% yield.

4.4.2 2-[1-(4'-Chlorophenyl)-5-oxo-3-methyl-4-pyrazolinylidene]-2-(4-dimethylamino-1-phenyl)acetonitrile (5b)

From **4b**, method a, yield 96%, m.p. 198°C. IR: 1670, 1615, 1515, 1490 cm^{-1}. ^{1}H NMR (60 MHz, $CDCl_3$): 2·5 (3H, s, CH_3), 3·0 (6H, s, 2 CH_3), 6·7 (2H, d, arom. protons), 7·2 (2H, d, arom. protons), 7·7–8·1 (4H, m, arom. protons) ppm. UV/Vis (methanol) λ_{max} (log ε): 546 (4·34) nm. $C_{20}H_{17}ClN_4O$ (364·8): calculated C 65·9, H 4·7, N 15·4, Cl 9·7; found C 65·6, H 4·7, N 15·4, Cl 9·5. Method b gave the identical product in 57% yield.

4.4.3 2-(3-Ethyl-5-oxo-1-phenyl-4-pyrazolinylidene)-2-(4-dimethylamino-1-phenyl)acetonitrile (5c)

From **4c**, method a, yield 92%, m.p. 181°C (from methanol/water). IR: 1680, 1620, 1600, 1550, 1500 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): 1·3 (3H, t, CH_3), 3·0 (8H, m, 2 CH_3 and CH_2), 6·7 (2H, d, arom. protons), 7·1 (2H, d, arom. protons), 7·7–8·1 (4H, m, arom. protons) ppm. UV/Vis (methanol) λ_{max} (log ε): 538 (4·40) nm. $C_{21}H_{20}N_4O$ (344·4): calculated C 73·2, H 5·9, N 16·3; found C 73·3, H 5·9, N 16·3. Method b gave the identical product in 67% yield.

*4.4.4 2-(5-Oxo-1-phenyl-3-propyl-4-pyrazolinylidene)-2-(4-dimethylamino-1-phenyl)acetonitrile (**5d**)*

From **4d**, method a, yield 92%, m.p. 159°C. IR: 1680, 1610, 1560, 1525, 1495 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): 1·3 (3H, s, CH_3), 1·8 (2H, m, CH_2), 3·0 (5H, m, CH_2 and CH_3), 6·7 (2H, d, arom. protons), 7·2–8·0 (7H, m, arom. protons) ppm. UV/Vis (methanol) λ_{max} (log ε): 541 (4·32) nm. $C_{22}H_{22}N_4O$ (358·4): calculated C 73·7, H 6·2, N 15·6; found C 74·0, H 6·0, N 15·8.

*4.4.5 2-[1-(2'-Cyclohexylethyl)-5-oxo-1-phenyl-4-pyrazolinylidene]-2-(4-dimethylamino-1-phenyl)acetonitrile (**5e**)*

From **4e**, method a, yield 89%, m.p. 153°C (from methanol/water). IR: 2920, 2850, 1680, 1610, 1540, 1500 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): 1·0–1·9 (13H, m, CH and 6 CH_2), 3·0 (2H, t, CH_2), 6·7 (2H, d, arom. protons), 7·1–8·1 (7H, m, arom. protons) ppm. UV/Vis (methanol) λ_{max} (log ε): 543 (4·41) nm. $C_{27}H_{30}N_4O$ (426·6): calculated C 76·0, H 7·1, N 13·1; found C 76·0, H 7·0, N 13·0.

*4.4.6 2-(4-Amino-3,5-diethyl-1-phenyl)-2-(5-oxo-1-phenyl-3-propyl-4-pyrazolinylidene)acetonitrile (**5f**)*

From **4f**, method a, yield 90%, m.p. 186°C. IR: 3480, 3350, 2960, 1670, 1635, 1595, 1525, 1500 cm^{-1}. ^1H NMR (200 MHz, d_6-DMSO): two isomers could be observed (one is as shown for **5a-j** in Scheme 2; in the other, the positions of the anilino group and the nitrile group are changed), 1·2 (6H, t, 2 CH_3), 2·1 (s, CH_3 on the pyrazole ring, second isomer), 2·5 (m, CH_3 on the pyrazole ring, first isomer and —$\underline{CH_2}$—CH_3), 6·5 and 7·9 (2H, br. s, amino groups of both isomers), 7·1–8·0 (7H, m arom. protons; the signals for the protons of the aniline ring are situated at 7·3 and 7·8) ppm. UV/Vis (methanol) λ_{max} (log ε): 527 (4·11) nm. $C_{22}H_{22}N_4O$ (358·4): calculated C 73·7, H 6·2, N 15·6; found C 74·0, H 6·4, N 15·6.

*4.4.7 2-(4-Amino-3,5-diisopropyl-1-phenyl)-2-(-5-oxo-1-phenyl-3-propyl-4-pyrazolinylidene)acetonitrile (**5g**)*

From **4g**, method a, yield 93%, m.p. 183°C. IR: 3490, 3370, 2960, 1670, 1630, 1600, 1535, 1500 cm^{-1}. ^1H NMR (200 MHz, d_6-DMSO): two isomers could be observed (see above). 1·2 (12H, d, 4 CH_3), 2·15 (s, CH_3 on the pyrazole ring, second isomer), 2·5 (m, CH_3 on the pyrazole ring, first isomer and both —$\underline{CH}(CH_3)_2$), 6·6–7·9 (2H, br. s, amino groups of both isomers), 7·1–8·3 (7H, m arom. protons; the signals for the protons of the aniline ring are situated at 7·4 and 7·75) ppm. UV/Vis (methanol) λ_{max} (log ε): 531 (4·31) nm. $C_{24}H_{26}N_4O$ (386·5): calculated C 74·6, H 6·8, N 14·5; found C 74·7, H 6·8, N 14·5.

*4.4.8 2-(4-Amino-3,5-dimethyl-1-phenyl)-2-(1-[3-chlorophenyl]-5-oxo-3-propyl-4-pyrazolinylidene)acetonitrile (**5h**)*

From **4h**, method a, yield 96%, m.p. 188°C (from methanol). IR: 3460, 3340, 3230, 1640, 1605, 1595, 1510 cm^{-1}. ^{1}H NMR (200 MHz, d_6DMSO): two isomers could be observed (see above). 2·0 (s, CH_3 on the pyrazole ring, second isomer), 2·1 and 2·2 (6H, 2s, CH_3 of the aniline, both isomers), 2·5 (s, CH_3 on the pyrazole ring, first isomer), 6·5 and 6·9 (2H, br. s, amino groups of both isomers), 7·2–8·2 (6H, m arom. protons; the signals for the protons of the aniline ring are situated at 7·3 and 7·8 ppm. UV/Vis (methanol) λ_{max} (log ε): 537 (4·29) nm. $C_{20}H_{17}ClN_4O$ (364·8): calculated C 65·8, H 4·7, N 15·4, Cl 9·7; found C 65·9, H 4·7, N 15·3, Cl 9·5.

*4.4.9 2-(4-*N,N*-Diethylamino-2-methyl-1-phenyl)-2-(1-phenyl-5-oxo-3-methyl-4-pyrazolinylidene)acetonitrile (**5i**)*

From **4i**, method a, yield 90%, m.p. 166°C (from methanol). IR: 3600–3200, 2970, 2920, 2840, 1685, 1606, 1555, 1530, 1500 cm^{-1}. ^{1}H NMR (200 MHz, d_6-DMSO): 1·1 (6H, t, 2 CH_3), 1·8 (3H, s, CH_3), 2·3 (3H, s, CH_3), 3·4 (4H, m, 2 CH_2), 6·6 (2H, m, arom. protons), 7·2–7·7 (6H, m, arom. protons) ppm. UV/Vis (methanol) λ_{max} (log ε): 565 (4·35) nm. $C_{23}H_{24}N_4O$ (372·5): calculated C 74·2, H 6·5, N 15·0; found C 73·9, H 6·3, N 15·3.

*4.4.10 2-(4-*N,N*-Diethylamino-2-ethoxy-1-phenyl)-2-(1-phenyl-5-oxo-3-methyl-4-pyrazolinylidene)acetonitrile (**5j**)*

From **4j**, method a, yield 94%, m.p. 160°C (acetone/water). IR: 3080–3040, 2990, 1680, 1610, 1560–1550, 1500 cm^{-1}. ^{1}H NMR (200 MHz, d_6-DMSO: 1·2 (6H, t, 2 CH_3), 1·4 (3H, t, CH_3), 1·8 (3H, s, CH_3), 3·6 (4H, m, 2 CH_2), 4·2 (2H, q, CH_2), 6·2 (1H, s, arom. protons), 6·6 (1H, 1, arom. proton), 7·1–7·6 (6H, m, arom. protons) ppm. UV/Vis (methanol) λ_{max} (log ε): 548 (4·25) nm. $C_{25}H_{27}N_5O_2$ (429·5): calculated C 71·6, H 6·5, N 13·9; found C 71·3, H 6·3, N 14·2.

*4.4.11 2-(1,2-Dihydro-2,2,4,7-tetramethyl-6-chinolyl)-2-(4,5-dihydro-5-oxo-3-methyl-1-phenyl-4-pyrazolinylidene)acetonitrile (**8**)*

From **7**, method a, yield 54%, m.p. 153°C (from ethyl acetate/light petroleum). IR: 3380–3320, 2960, 2920, 2200, 1690, 1655, 1610, 1595, 1490 cm^{-1}. ^{1}H NMR (200 MHz, d_6-DMSO): 1·2 (6H, t, 2 CH_3), 1·9 (3H, s, CH_3), 2·5 (3H, s, CH_3), 2·6 (3H, s, CH_3), 5·4 (1H, s, arom. proton), 6·5 (1H, s, arom. proton), 7·0–7·3 (6H, m, arom. protons) ppm. UV/Vis (methanol) λ_{max} (log ε): 613 (4·03) nm. $C_{25}H_{24}N_4O$ (396·5): calculated C 75·8, H 6·1, N 14·1; found C 75·5, H 6·1, N 14·3.

4.4.12 2-(3,5-Dioxo-1,2-diphenyl-4-pyrazolidinylidene)-2-(diethylamino-1-phenyl)acetonitrile (11)

From **10**, method a, yield 63%, m.p. 174°C (from ethyl acetate/light petroleum). IR: 1710, 1685, 1615, 1505, 1480 cm^{-1}. ^{1}H NMR (60 MHz, d_6-DMSO): 1·2 (6H, t, 2 CH_3), 3·6 (4H, q, 2 CH_2), 7·0 (2H, d, arom. protons), 7·1–7·3 (2H, m, arom. protons), 7·3–7·5 (8H, m, arom. protons), 8·2 (2H, d, arom. protons) ppm. UV/Vis (methanol) λ_{max} (log ε): 570 (4·73) nm. $C_{27}H_{24}N_4O_2$ (436·5): calculated C 74·3, H 5·5, N 12·8; found C 74·2, H 5·7, N 12·8.

4.4.13 2-(1,2-Dihydro-2,2,4,7-tetramethyl-6-chinolyl)-2-(3-hydroxy-5-oxo-1,2-diphenyl-4-pyrazolidinylidene)acetonitrile (13)

From **12**, method a, yield 81%, m.p. 160°C (from ethyl acetate/light petroleum). IR: 3400–3300, 2980, 2910, 2200, 1685, 1615, 1590, 1485 cm^{-1}. ^{1}H NMR (360 MHz, d_6-DMSO): 1·3 (6H, t, H-9'), 1·9 (3H, s, H-10'), 2·5 (3H, s, H-11'), 5·45 (1H, s, H-3'), 6·4 (1H, s, H-8'), 7·1–7·5 (11H, m, H-7, H-8, H-9 and H-5'), 8·15 (1H, br. s, NH) ppm. ^{13}C NMR (360 MHz, d_6-DMSO): 17·7 (C-10'), 20·5 (C-11'), 31·5 (C-9'), 53·1 (C-2'), 114·6 (C-5' and C-8'), 115·8 (C-1), 117·2 (C-4a'), 119·9 (C-6'), 122·6 (C-7), 125·8 (C-4'), 126·1 (C-9), 128·0 (C-2), 128·6 (C-8 and C-3'), 129·9 (C-4), 136·9 (C-6), 143·6 (C-7'), 149·8 (C-8a'), 161·3 (C-3 and C-5) ppm. UV/Vis (methanol) λ_{max} (log ε): 628 (4·42) nm. $C_{30}H_{26}N_4O_2$ (474·6): calculated C 75·9, H 5·5, N 11·8; found C 75·6, H 5·6, N 11·9.

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