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Structure–Color Correlations of Penta- and Heptamethines. Syntheses with Nitriles XCIV*

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ABSTRACT

The synthesis of asymmetric cyanine dyes (penta- and heptamethines), prepared by coupling Fischer's base with indandione, benzo[b]*thiophene and pyrazole derivatives via a C-1 unit, is described. Three different synthetic strategies for substituted polymethines are presented. Dye characteristics are given and the correlation between the chemical structures and the dye properties are discussed by means of semiempirical PPP calculations.*

1 INTRODUCTION

In recent years the focus of research on dye chemistry has largely changed from traditional dyes and pigments to colorants for special applications. Organic dyes have become increasingly important in the high technology industries.[1] For some purposes, special properties of the colorants are utilized, and not their color ('functional dyes', as described by Griffith[2] e.g. dyes for optical data storage, non-linear optics, IR absorbers[3]). In other applications, the dyes are used in their traditional role, must have additional physical and chemical properties for special uses (e.g. dyes and pigments for colored toners in photocopiers and laser

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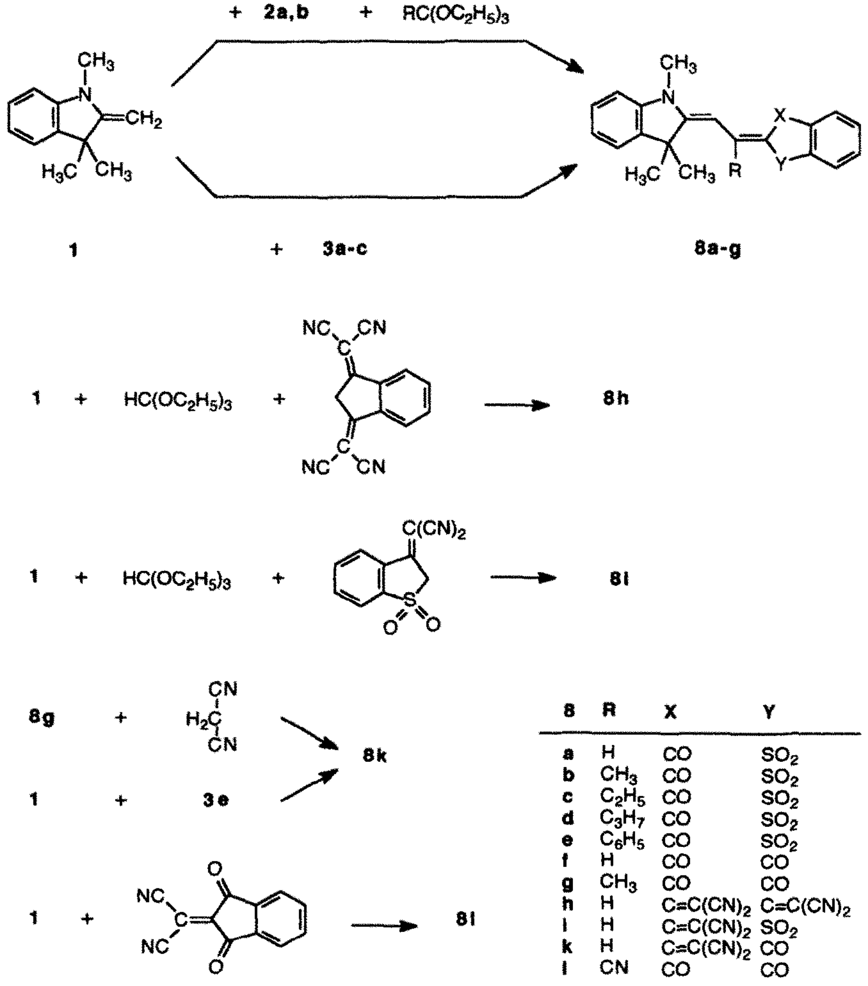
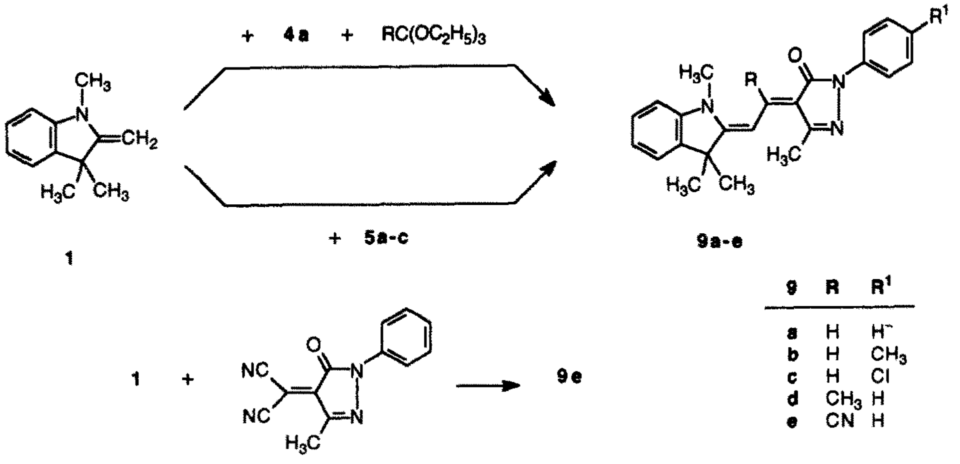
printers, colorformers,[4,5] dyes for thermal transfer printing[6] and for electrophotography). When designing such specialty dyes, one has to keep in mind two aspects. Firstly a suitable chromophoric system with particular physical and chemical properties has to be found and then convenient synthetic steps must be developed to obtain colorants of different maximum absorption wavelengths by substitutions of the basic chromophore.

Polymethines provide a route to tailor-made dyes by introducing donor and/or acceptor substituents into the methine system. In this paper we describe pentamethines and heptamethines, which formally consist of Fischer's base (**1**) as electron donor, a (benzofused) (hetero)cycle (**2**, **4**, **6**) as electron acceptor and a C-1 fragment connecting them.



8	R	X	Y
a	H	CO	SO_2
b	CH_3	CO	SO_2
c	C_2H_5	CO	SO_2
d	C_3H_7	CO	SO_2
e	C_6H_5	CO	SO_2
f	H	CO	CO
g	CH_3	CO	CO
h	H	$C{=}C(CN)_2$	$C{=}C(CN)_2$
i	H	$C{=}C(CN)_2$	SO_2
k	H	$C{=}C(CN)_2$	CO
l	CN	CO	CO

Scheme 1



9	R	R^1
a	H	H
b	H	CH_3
c	H	Cl
d	CH_3	H
e	CN	H

Scheme 2

To obtain the systems described above, containing different substitution patterns, the following strategies were applied:

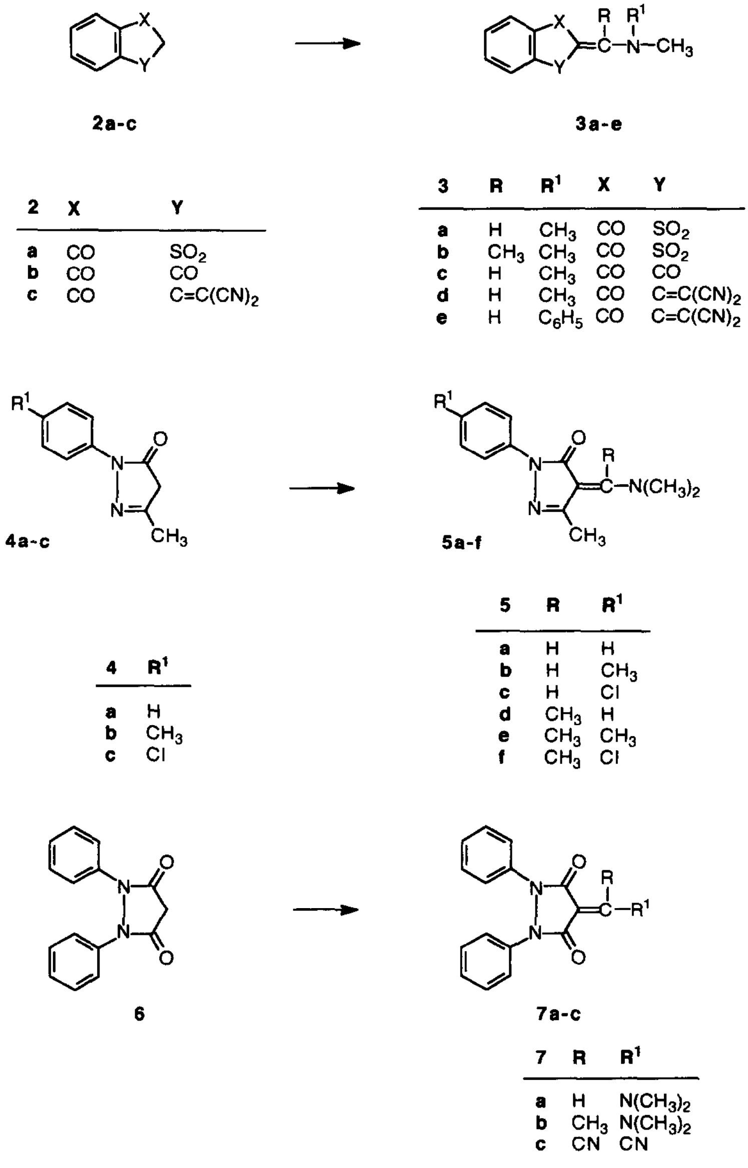
(A) **1** was reacted with triethyl orthoalkylate and trioxobenzo[*b*]thiophene (**2a**), indandione (**2b**), 1,3-bis(dicyanomethylene)indan, 2,3-dihydro-3-dicyanomethylene-1,1-dioxo-benzo[*b*]thiophene, methylphenylpyrazolone (**4a**) and diphenylpyrazoledione (**6**) to yield dyes **8a–e**, **8g–i**, **9a–d** and **10a,b**, respectively.

(B) Heterocycles **2a,b**, **4a–c** and **6** were reacted with dimethylformamide–dimethylacetal (DMF–DMA) or dimethylacetamide–dimethylacetal (DMA–DMA) to yield the corresponding (amino)-methylene compounds **3a–c**, **5a–c** and **7a**, which were subsequently reacted with **1**, yielding **8a,b,f,k**, **9a,c** and **10a**, respectively.

(C) Dyes with a nitrile group substituent in the polymethine chain (propionitriles **8l**, **9e** and **10c**) were obtained by combining **1** with 2-dicyanomethylene-indan-1,3-dione, 4-dicyanomethylenemethyl-phenyl-pyrazolone and **7c**, respectively. The reaction occurs with elimination of hydrocyanic acid. This method gave better results than reactions of thioketene acetals[7] or direct substitution by a cyano group.[8]

2 RESULTS AND DISCUSSION

Alkylidene compounds with a methyl group (ethylidene derivatives **3d**, **5d–e** and **7b**), as well as **3e** (containing a phenyl group) could not be reacted with **1**. Therefore, method A was the method used to obtain



2	X	Y
a	CO	SO_2
b	CO	CO
c	CO	$C{=}C(CN)_2$

3	R	R¹	X	Y
a	H	CH_3	CO	SO_2
b	CH_3	CH_3	CO	SO_2
c	H	CH_3	CO	CO
d	H	CH_3	CO	$C{=}C(CN)_2$
e	H	C_6H_5	CO	$C{=}C(CN)_2$

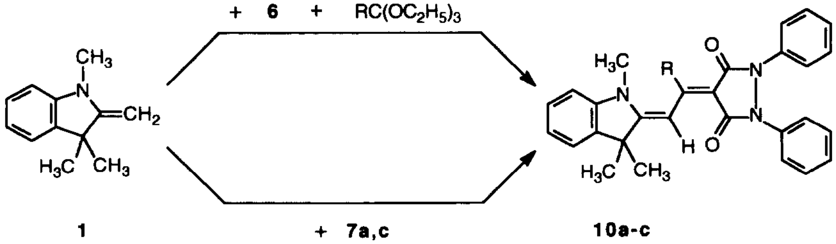
4	R¹
a	H
b	CH_3
c	Cl

5	R	R¹
a	H	H
b	H	CH_3
c	H	Cl
d	CH_3	H
e	CH_3	CH_3
f	CH_3	Cl

7	R	R¹
a	H	$N(CH_3)_2$
b	CH_3	$N(CH_3)_2$
c	CN	CN

Scheme 3

the alkyl substituted derivatives **8b–d**; compound **8f** had to be prepared via the methylene derivative **3c**, hence under the conditions for the three component reaction, dimerization of indandione (**2b**) took place. Compound **8a** has been previously synthesized by interaction of Fischer's aldehyde (obtained from **1** by Vilsmeier formylation) with **2a**.[9] (For details see experimental section.)



10	R
a	H
b	CH_3
c	CN

Scheme 4

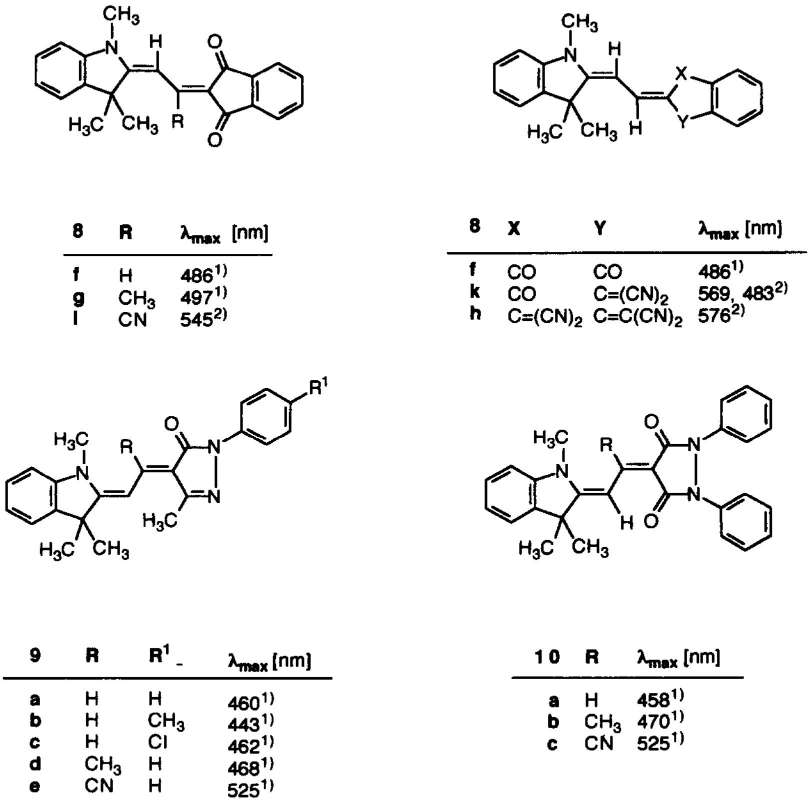
The experimental results with respect to the electronic spectra of the investigated compounds can be summarized as follows:

(i) Comparison of compounds **9** and **10** shows that the symmetry of the pyrazolone residue has not effect on the wavelength of maximum absorption.

(ii) Replacement of an oxygen atom in **8f** by dicyanomethylene groups leads to a significant bathochromic shift (compare **8f** vs. **8k** vs. **8h**). This result is in accord with the observations described in previous investigations[9,10] on anilinomethylene derivatives and aryl-cyanomethylene derivates, respectively, of **8f**.

(iii) Substitution in the conjugated polyene chain by both a nitrile and a methyl group results in a red shift in each series of dyes (**8f–8g–8l**; **9a–9d–9e**; **10a–10b–10c**) (see Scheme 5). The effect of methyl-substitution is surprising, since according to the polymethine concept, donor substitution at an even position of the polymethine chain should lead to a blue shift.[11-13]

To obtain some insight into this behavior, semi-empirical Pariser–Parr–Pople[14] calculations were performed. The parameters used (valence state ionization potentials, resonance and electron repulsion integrals) were those compiled by Griffith.[13] Methyl groups were taken into account as described in Ref. 15 except for scaling of β-values in order to conform to those proposed by Griffith.[13] The saturated dimethylmethine-bridge in the indoline moiety was neglected in the computations. Calculated results (wavenumbers $\tilde{\nu}$ (cm^{-1}) and oscillator strengths f of the color band) are compared to the corresponding experimental results in Table 1. As can be seen from the data presented there, the agreement between experimental and calculated excitation energies is generally excellent. Except for compounds **9a**, **9d** and **9e**, where the PPP method



8	R	λ_{max} [nm]
f	H	486[1)]
g	CH_3	497[1)]
l	CN	545[2)]

8	X	Y	λ_{max} [nm]
f	CO	CO	486[1)]
k	CO	$C{=}(CN)_2$	569, 483[2)]
h	$C{=}(CN)_2$	$C{=}C(CN)_2$	576[2)]

9	R	R^1	λ_{max} [nm]
a	H	H	460[1)]
b	H	CH_3	443[1)]
c	H	Cl	462[1)]
d	CH_3	H	468[1)]
e	CN	H	525[1)]

10	R	λ_{max} [nm]
a	H	458[1)]
b	CH_3	470[1)]
c	CN	525[1)]

Scheme 5. Maximum absorption wavelengths of selected dyes: [1)] spectra taken in dioxane; [2)] spectra taken in dimethylformamide.

TABLE 1

Comparison Between Calculated Values (Wavenumbers $\tilde{\nu}$ (cm^{-1} and Oscillator Strengths (f) and Corresponding Experimental Results for dyes **8f-h,k, l, 9a,d,e** and **10a–c**

Compound no.	*$\tilde{\nu}$ (cm^{-1}) (exp.)*	*$\tilde{\nu}$ (cm^{-1}) (calc.)*	*log ε (exp.)*	*F (calc.)*
8f	20 284	20 852	5·000	1·594 5
8g	20 121	20 674	4·661	1·284 4
8l	18 349	18 950	4·302	0·883 2
8k	17 575	19 555	4·387	1·217 0
8h	17 361	17 796	4·389	0·257 7
9a	21 739	20 475	4·601	1·304 2
9d	21 368	20 219	4·386	0·864 8
9e	19 048	17 012	4·474	0·792 4
10a	21 834	22 953	4·917	1·773 5
10b	21 276	22 475	4·775	1·494 9
10c	19 048	17 973	4·768	0·759 5

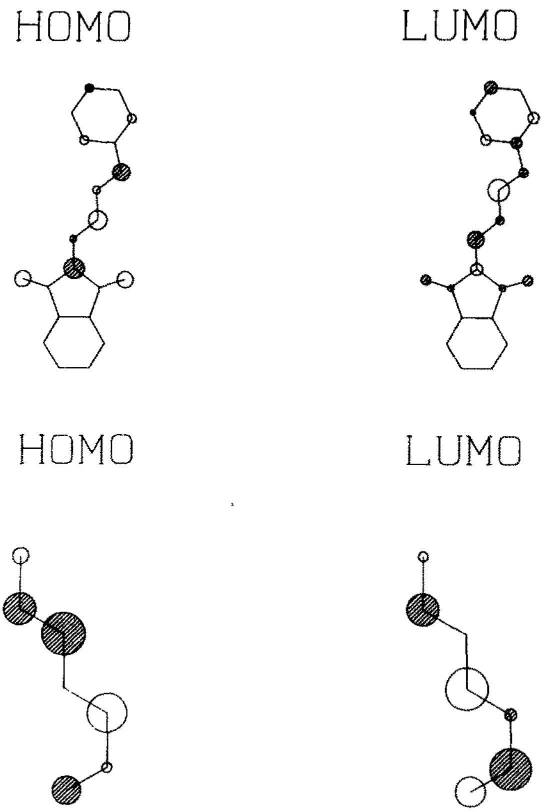


Fig. 1.

yields somewhat too long wavelength absorption maxima, the difference from the experimental values is less than 1000 cm^{-1}. In each series, the effect of both nitrile and methyl substitution on the absorption maxima is very adequately reproduced. Similarly, the bathochromic shift observed when replacing the carbonyl group in **8f** by dicyanomethylene moieties is also satisfactorily predicted by the calculations, although the effect of the second dicyanomethylene groups seems somewhat exaggerated. In all cases the longest wavelength transition is dominated by the HOMO → LUMO transition (>90%); therefore, as an example, these two orbitals for compounds **8f** are compared to those of the parent merocyanine in Fig. 1. Although both HOMO as well as LUMO of **8f** are very similar to those of the parent chromophore, the difference in the coefficients at position 4 (where substitution by nitrile or methyl groups is made) between HOMO and LUMO is considerably less pronounced in the case of **8f**. Since the effect of a substituent not only depends on the magnitude of the orbital coefficient at the site of substitution, but also on the energy difference between the orbitals of the parent chromophore and the substituent (which in the case of a donor clearly is lower for the HOMO than the LUMO, this finding might explain the unusual effect of methyl-substitution.

3 EXPERIMENTAL

3.1 General

All melting points are uncorrected. Spectral data were recorded with the following instruments: IR spectra: Perkin-Elmer 298 Spectrophotometer (KBr); ^1H NMR spectra: Varian Gemini 200 (spectra are referenced to tetramethylsilane); UV–Vis spectra: Hitachi U-3501 spectrophotometer (quartz cuvettes).

The synthesis of **3a** has previously been described.[16]

3.2 2-(1-Dimethylaminoethylidene)-3-oxo-2,3-dihydrobenzo[*b*]thiophene-1,1-dioxide (3b)

0·90 g (5 mmol) of **2a**[17,18] and 3·00 g (23 mmol) of DMA–DMA were stirred at room temperature for 30 min. The product was collected by suction and washed with methanol, giving orange crystals, 1·20 g (95%) mp 180–185°C (methanol). IR: 2940, 1630, 1580, 1550, 1340 cm^{-1}. ^1H NMR d$_6$-DMSO: δ 2·55 (s, 3H, CH_3), 3·25 (s, 3H, N—CH_3), 3·35 (s, 3H, N—CH_3), 7·70–7·92 (m, 4H, aromatic protons) ppm.

$C_{12}H_{13}NO_3S$	Calcd.:	C 57·38	H 5·18	N 5·58	S 12·76
(251·20)	Found:	C 57·52	H 5·01	N 5·59	S 12·85

3.3 2-(*N*,*N*-Dimethylaminomethylene)-1,3-indandione (3c)

1·46 g (10 mmol) of 1,3-indandione (**2b**) and 2·38 g (20 mmol) DMF–DMA were refluxed in 7 ml of methanol for 90 min. The mixture was cooled to room temperature, the product was filtered and washed with methanol, giving yellow platelets, 0·50 g (25%), m.p. 135–137°C (water). IR: 1700, 1620, 1590, 1490 cm^{-1}. ^1H NMR (d$_6$-DMSO): δ 3·40 (s, 3H, CH_3, 3·70 (s, 3H, CH_3), 7·55 (s, 1H, CH), 7·60–7·70 (m, 4H, aromatic protons) ppm.

$C_{12}H_{11}NO_2$	Calcd.:	C 71·66	H 5·47	N 6·96
(201·14)	Found:	C 71·89	H 5·31	N 6·88

3.4 1-Dicyanomethylene-2-dimethylaminomethylene-indan-3-one (3d)

0·97 g (5 mmol) of **2c**[10] and 1·19 g (10 mmol) of DMF–DMA were refluxed in 6 ml of methanol for one hour. After cooling to room temperature and filtering, the product was washed with methanol then with hot ethanol, giving dark brown crystals, 0·70 g (56%), m.p. 275°C (decomp.). IR: 2200, 1670, 1590, 1480 cm^{-1}. ^{1}H NMR d$_6$-DMSO: δ 3·12 (s, 6H, N—CH$_3$), 7·70 (s, 1H, CH), 7·72–8·38 (m, 4H, aromatic protons) ppm. UV–Vis (dimethylformamide) λ_{max} (log ε) 459 (3·77), 606 (4·22) nm.

$C_{15}H_{11}N_3O$	Calcd.:	C 72·31	H 4·41	N 16·86
(249·17)	Found:	C 72·17	H 4·46	N 16·98

3.5 1-Dicyanomethylene-2-(*N*-methyl-anilinomethylene)-indan-3-one (3e)

2·22 g (15 mmol) of triethyl orthoformate and 1·07 g (10 mmol) of *N*-methylaniline were heated to 50°C in 13 ml of acetic acid, and after addition of 1·78 g (10 mmol) of **2c**[10] the mixture was stirred for 4 h at 70°C, during which time the product crystallized. It was filtered and washed with methanol, giving yellow crystals, 2·30 g (74%), m.p. 115–117°C (decomp.) (acetic acid). IR: 2200, 1680, 1560, 1370 cm^{-1}. UV–Vis (dimethylformamide) λ_{max} (log ε) 372 (3·97), 447 (3·92) nm.

$C_{20}H_{13}N_3O$	Calcd.:	C 77·19	H 4·18	N 13·50
(311·22)	Found:	C 76·70	H 3·96	N 13·77

3.6 4-(Dimethylaminomethylene)-3-methyl-5-oxo-1-phenyl-4,5-dihydro-1*H*-pyrazole (5a)

A mixture of 1·74 g (10 mmol) of **4a**[19] and 2·38 g (20 mmol) of DMF–DMA was refluxed for 45 min. Compound **5a** precipitated on cooling to room temperature and was filtered and washed with methanol, giving yellow crystals, 1·07 g (47%), m.p. 134°C. IR: 2900, 1660, 1600, 1580 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 2·18 (s, 3H, CH$_3$), 3·28 (s, 3H, N—CH$_3$), 3·85 (s, 3H, N—CH$_3$), 6·98 (s, 1H, CH), 7·05–7·95 (m, 5H, aromatic protons) ppm.

$C_{13}H_{15}N_3O$	Calcd.:	C 68·14	H 6·55	N 18·34
(229·16)	Found:	C 68·45	H 6·69	N 18·08

3.7 4-(Dimethylaminomethylene)-3-methyl-1-(4-methylphenyl)-5-oxo-4,5-dihydro-1*H*-pyrazole (5b)

1·88 g (10 mmol) of **4b**[19] and 2·38g (20 mmol) of DMF–DMA were refluxed in 6 ml of methanol. The product started to precipitate immediately, and after one hour the mixture was cooled to room temperature and the product filtered and washed with methanol, giving yellow crystals, 1·80 g (74%), m.p. 200°C. IR: 2900, 1660, 1600 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ2·18 (s, 3H, CH_3), 2·32 (s, 3H, CH_3), 3·28 (s, 3H, N-CH_3), 3·88 (s, 3H, N—CH_3), 6·95 (s, 1H, CH), 7·16 (d, 2H, protons in positions 2 and 6 of the aromatic ring), 7·81 (d, 2H, protons in positions 3 and 5 of the aromatic ring) ppm.

$C_{14}H_{17}N_3O$	Calcd.:	C 69·15	H 6·99	N 17·28
(243·17)	Found:	C 69·13	H 7·08	N 17·17

3.8 1-(4-Chlorophenyl)-4-(dimethylaminomethylene)-3-methyl-5-oxo-4,5-dihydro-1*H*-pyrazole (5c)

A mixture of 2·08 g (10 mmol) of **4c** and 2·38 g (20 mmol) of DMF–DMA were refluxed for one hour; **5c** precipitated from the boiling solution and it was filtered and washed with methanol to give yellow crystals, 2·14 g (81%), m.p. 198°C. IR: 2900, 1675, 1600 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ2·18 (s, 3H, CH_3), 3·33 (s, 3H, N—CH_3), 3·86 (s, 3H, N—CH_3), 6·98 (s, 1H, CH), 7·30 (d, 2H, protons in positions 2 and 6 of the aromatic ring), 7·92–7·98 (d, 2H, protons in positions 3 and 5 of the aromatic ring) ppm.

$C_{13}H_{14}N_3OCl$	Calcd.:	C 59·23	H 5·31	N 15·94
(263·61)	Found:	C 59·25	H 5·41	N 15·78

3.9 4-(1-Dimethylaminoethylidene)-3-methyl-5-oxo-1-phenyl-4,5-dihydro-1*H*-pyrazole (5d)

3·48 g (20 mmol) of **4a**[19] and 1·33 g (10 mmol) of DMA–DMA were stirred at room temperature for 2 h. The precipitate was filtered and washed with methanol, giving orange crystals, 0·63 g (26%), m.p. 126°C. IR: 3120, 1850–1770, 1600 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2·15 (s, 6H, CH_3), 3·40 (s, 6H, N—CH_3), 7·18–7·38 (m, 5H, aromatic protons) ppm.

$C_{14}H_{17}H_3O$	Calcd.:	C 69·15	H 6·99	N 17·28
(243·17)	Found:	C 68·87	H 6·76	N 16·94

3.10 4-(1-Dimethylaminoethylidene)-3-methyl-1-(4-methylphenyl)-5-oxo-4,5-dihydro-1*H*-pyrazole (5e)

1·88 g (10 mmol) of 4b[19] and 1·33 g (10 mmol) of DMA–DMA were stirred in 2 ml of methanol at room temperature for one hour. The product was filtered and washed with methanol, giving yellow crystals, 1·60 g (62%), m.p. 190°C (decomp.). IR: 2920, 1630, 1610 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2·32 (s, 6H, CH_3), 2·45 (s, 3H, CH_3), 3·40 (s, 6H, N—CH_3), 7·17 (d, 2H, protons in positions 2 and 6 of the phenyl ring), 7·82–7·88 (d, 2H, protons in positions 3 and 5 of the phenyl ring) ppm.

$C_{15}H_{19}H_3O$	Calcd:	C 70·05	H 7·39	N 16·34
(257·19)	Found:	C 69·83	H 7·38	N 16·28

3.11 1-(4-Chlorophenyl)-4-(1-dimethylaminoethylidene)-3-methyl-5-oxo-4,5-dihydro-1*H*-pyrazole (5f)

2·08 g (10 mmol) of **4c** and 1·33 g (10 mmol) of DMA–DMA were stirred in 2 ml of methanol at room temperature for one hour. The precipitate was filtered and washed with methanol; yellow crystals, 1·70 g (61%), m.p. 196°C (acetonitrile). IR: 2920, 1900, 1630 cm^{-1} ^1H NMR ($CDCl_3$): δ 2·30 (s, 3H, CH_3), 2·42 (s, 3H, CH_3), 3·35 (s, 6H, N—CH_3), 7·30 (d, 2H, protos in positions 2 and 6 of the aromatic ring), 7·98–8·02 (d, 2H, protons in positions 3 and 5 of the aromatic ring) ppm.

$C_{14}H_{16}N_3OCl$	Calcd.:	C 60·57	H 5·76	N 15·14
(277·62)	Found:	C 60·27	H 5·79	N 14·95

3.12 4-Dimethylaminomethylene-3,5-dioxo-1,2-diphenyl-1*H*,2*H*-pyrazole (7a)

1·26 g (5 mmol) of **6**,[20,21] 1·19 g (10 mmol) of DMF–DMA and 3 ml of methanol were refluxed for 5 min; compound **7a** precipitated immediately and was filtered and washed with methanol; yellow crystals, 0·80 g (52%), mp 230°C. IR: 3020, 1700, 1650, 1630 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3·32 (s, 3H, N—CH_3), 3·80 (s, 3H, N—CH_3), 7·21–7·41 (m, 10H, aromatic protons), 7·58 (s, 1H, CH) ppm.

$C_{18}H_{17}N_3O_2$	Calcd.:	C 70·37	H 5·53	N 13·68
(307·22)	Found:	C 70·12	H 5·51	N 13·56

3.13 4-(1-Dimethylaminoethylidene)-3,5-dioxo-1,2-diphenyl-1*H*,2*H*-pyrazole (7b)

A mixture of 1·26 g (5 mmol) of **6**[20] and 0·67 g (5 mmol) of DMA–DMA in 4 ml of methanol was stirred for one hour at room temperature. The product was isolated by filtration and was washed with methanol to give yellow crystals, 0·40 g (25%), m.p. 222°C. IR: 1640, 1570 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2·70 (s, 3H, CH_3), 3·27 (s, 3H, N—CH_3), 3·50 (s, 3H, N—CH_3), 7·05–7·45 (m, 10H, aromatic protons) ppm.

$C_{19}H_{19}N_3O_2$	Calcd.:	C 71·04	H 5·91	N 13·08
(321·23)	Found:	C 71·01	H 5·98	N 12·91

3.14 4-(1-Dicyanomethylene)-3,5-dioxo-1,2-diphenyl-1*H*,2*H*-pyrazole (7c)

To a hot solution (*c*. 80°C) of 1·28 g (10 mmol) of tetracyanoethylene in 25 mol of acetonitrile, 2·52 g (10 mmol) of **6**[20] were added in small portions.

The mixture was then refluxed for 2 h, cooled to room temperature and the product was precipitated by addition of water, giving violet crystals, 1·95 g (62%), m.p. 199°C (acetonitrile/water). IR: 3400, 3280, 3140, 2200, 1790, 1675 cm^{-1}. ^{1}H NMR (d_6-DMSO): δ 7·20–7·60 (m, aromatic protons) ppm.

$C_{18}H_{10}N_4O_2$	Calcd.:	C 68·78	H 3·21	N 17·83
(314·30)	Found:	C 68·75	H 3·41	N 18·08

3.15 1-(2,3-Dihydro-1,3,3-trimethyl-1*H*-indol-2-ylidene)-2-(2,3-dihydro-1,1,3-trioxo-benzo[*b*]thiophene-2-ylidene)ethane (8a)

(*Method A*): 1·82 g (10 mmol) of **2a**, 1·48 g (10 mmol) of triethyl orthoformate and 1·73 g (10 mmol) of **1** were refluxed in 7 ml of ethanol for 3 h. After cooling the reaction mixture to room temperature, the product was filtered and washed with ethanol; 2·00 g (55%).

(*Method B*): 1·19 g (5 mmol) of **3a** and 2·30 g (13 mmol) of **1** were heated until a clear solution was formed. On cooling to room temperature, red crystals precipitated. These were filtered and washed with ethanol; 1·65 g (90%).

Red crystals, m.p. >300°C (acetic acid). IR: 1670, 1535, 1470, 1330 cm^{-1}. ^{1}H, NMR ($CDCl_3$): δ 1·75 (s, 6H, CH_3) 3·53 (s, 3H, N—CH_3), 6·34 (d, 1H, CH), 7·00–8·05 (m, 8H, aromatic protons), 8·20–8·28 (d, 1H, CH) ppm. UV-Vis (acetone) λ_{max} (log ε) 471 (4·75), 485 (4·78) nm.

$C_{21}H_{19}NO_3S$	Calcd.:	C 69·05	H 5·20	N 3·82	S 8·78
(365·27)	Found:	C 68·94	H 5·32	N 3·73	S 8·53

3.16 2-(2,3-Dihydro-1,3,3-trimethyl-1H-indol-2-ylidene)-1-(2,3-dihydro-1,1,3-trioxo-benzo[*b*]thiophene-2-ylidene)propane (8b)

(*Method A*): A mixture of 1·82 g (10 mmol) of **2a**, 3·24 g (20 mmol) of triethyl orthoacetate and 1·73 g (10 mmol) of **1** was refluxed for 10 min. After cooling to room temperature, 20 ml of ethanol was added and the product then filtered and washed with ethanol; 3·25 g (86%).

(*Method B*): A mixture of 0·60 g (2·4 mmol) of **3b** and 1·60 g (9·2 mmol) of **1** were refluxed for 3 h. After cooling to room temperature *c*. 10 ml of diethyl ether was added and the product filtered 0·40 g (43%).

Brown crystals, mp 214°C. IR: 1630, 1580, 1460, 1330 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1·53 (s, 6H, CH_3), 2·70 (s, 3H, CH_3), 3·15 (s, 3H, N—CH_3), 6·48 (s, 1H, CH), 7·03–7·91 (m, 8H, aromatic protons) ppm. UV–Vis (dimethylformamide) λ_{max} (log ε) 492 (4·56) nm.

$C_{22}H_{21}NO_3S$	Calcd.:	C 69·67	H 5·54	N 3·69	S 8·45
(379·28)	Found:	C 69·56	H 5·62	N 3·52	S 8·07

3.17 1-(2,3-Dihydro-1,3,3-trimethyl-1*H*-indol-2-ylidene)-2-(2,3-dihydro-1,1,3-trioxo-benzo[*b*]thiophene-2-ylidene)butane (8c)

(*Method A*): 1·82 (10 mmol) of **2a**, 3·53 g (10 mmol) of triethyl orthopropionate and 1·73 g (10 mmol) of **1** were refluxed for 20 min. Approximately 10 ml of petroleum ether was added and the mixture filtered, giving red crystals, 3·80 g (97%), m.p. (decomp.) 187°C (ethanol). IR: 1630, 1580, 1460, 1310 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1·42 (t, 3H, CH_2—CH_3), 1·55 (s, 6H, CH_3), 2·78 (s, 3H, N—CH_3), 3·06 (q, 2H, CH_2), 5·52 (s, 1H, CH), 6·95–7·94 (m, 8H, aromatic protons). UV–Vis (dimethyl formamide) λ_{max} (log ε) 487 (4·39) nm.

$C_{23}H_{23}NO_3S$	Calcd.:	C 70·24	H 5·85	N 3·56
(393·32)	Found:	C 69·98	H 5·78	N 3·41

3.18 1-(2,3-Dihydro-1,3,3-trimethyl-1*H*-indol-2-ylidene)-2-(2,3-dihydro-1,1,3-trioxo-benzo[*b*]thiophene-2-ylidene)pentane (8d)

(*Method A*): 0·91 g (5 mmol) of **2a**, 1·48 g (10 mmol) of triethyl orthobutyrate and 0·87 g (5 mmol) of **1** were refluxed for one h and 10 ml of cold ethanol then added and the product filtered; red needles, 1·55 g (76%), m.p. 129–131°C (ethanol) IR: 1630, 1580, 1460, 1330 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1·11 (t, 3H, —CH_2—CH_3), 1·55 (s, 6H, 2 CH_3), 1·86 (m, 2H, —CH_2—CH_2—CH_3), 2·78 (s, 3H, N—CH_3), 2·98 (t, 2H, —CH_2—CH_2—CH_3), 5·53 (s 1H, CH), 6·94–7·92 (m, 8H, aromatic protons) ppm. UV–Vis (dimethylformamide) λ_{max} (log ε) 488 (4·44) nm.

$C_{24}H_{25}NO_3S$	Calcd.:	C 70·76	H 6·14	N 3·44
(407·33)	Found:	C 70·23	H 6·18	N 3·22

3.19 1-Phenyl-2-(2,3-dihydro-1,3,3-trimethyl-1*H*-indol-2-ylidene)-1-(2,3-dihydro-1,1,3-trioxo-benzo[*b*]thiopene-2-ylidene)ethane (8e)

(*Method A*): 0·91 g (5 mmol) of **2a**, 2·24 g (10 mmol) of triethyl orthobenzoate and 0·87 g (5 mmol) of **1** were refluxed for 90 min. Approximately 10 ml of cyclohexane was added at room temperature and the mixture filtered, giving red crystals, 2·00 g (91%), m.p. 190°C (decomp.) (ethanol). IR: 1725, 1650, 1630, 1330 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1·58 (s, 6H, 2 CH_3), 2·62 (s, 3H, N—CH_3), 4·10 (s, 1H, CH), 7·13–8·09 (m, 13H, aromatic protons) ppm. UV–Vis (dimethylformamide) λ_{max} (log ε) 512 (4·72) nm.

$C_{27}H_{23}NO_3S$	Calcd.:	C 73·48	H 5·21	N 3·17
(441·36)	Found:	C 73·61	H 5·28	N 2·98

3.20 1-(2,3-Dihydro-1,3-dioxo-1*H*-indan-2-ylidene)-2-(2,3-dihydro-1,3,3-trimethyl-1*H*-indol-2-ylidene)ethane (8f)

(*Method B*): 0·40 g (2 mmol) of **3c** and 0·87 g (5 mmol) of **1** were refluxed for 2 h. After cooling the reaction mixture to room temperature, 10 ml of petroleum ether was added and the product filtered as dark red colored platelets, 0·65 g (98%), m.p. 208°C (methanol) (Lit.: 210°C[22]). IR: 1695, 1650, 1590, 1460 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1·65 (s, 6H, CH_3), 3·48 (s, 3H, N—CH_3), 6·90–7·75 (m, 8H, aromatic protons), 7·40 (d, 1H, CH), 8·10 (d, 1H, CH) ppm. UV–Vis (dioxane) λ_{max} (log ε) 486 (5·03) nm. UV–Vis (chloroform) λ_{max} (log ε) 493 (5·00) nm.

$C_{19}H_{19}NO_2$	Calcd.:	C 80·26	H 5·77	N 4·25
(329·23)	Found:	C 80·14	H 5·64	N 4·22

3.21 2-(2,3-Dihydro-1,3-dioxo-1*H*-indan-2-ylidene)1-(2,3-dihydro-1,3,3-trimethyl-1*H*-indol-2-ylidene)propane (8g)

(*Method A*): 1·46 (10 mmol) of 1,3-indandione (**2b**), 3·24 g (20 mmol) of triethyl orthoacetate and 1·73 g (10 mmol) of **1** were refluxed in 7 ml of acetic anhydride for 2 h. After evaporating the solvent *in vacuo*, 5 ml of acetonitrile was added and the product filtered, giving dark red crystals, 0·30 g (9%), m.p. 163–165°C. IR: 1680, 1630, 1590, 1460 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1·55 (s, 6H, CH_3), 2·65 (s, 3H, CH_3), 3·15 (s, 3H, N—CH_3), 6·50 (s, 1H, CH), 6·98–7·25 (m, 8H, aromatic protons) ppm. UV–Vis (dioxane) λ_{max} (log ε) 497 (4·66) nm.

$C_{23}H_{21}NO_2$	Calcd.:	C 80·48	H 6·12	N 4·08
(343·26)	Found:	C 80·05	H 6·19	N 3·82

3.22 1-(1,3-bis(Dicyanomethylene)indan-2-yliden)-2-(2,3-dihydro-1,3,3-trimethyl-1*H*-indol-2-ylidene)ethane (8h)

(*Method A*): 1·21 g (5 mmol) of 1,3-bis(dicyanomethylene) indane,[10] 0·74 g

(5 mmol) of triethyl orthoformate and 0·87 g (5 mmol) of **1** were refluxed in 7 ml of acetic acid for 2 h. After cooling to room temperature, the product was filtered and washed with a little acetic acid and then with hot methanol, giving brown–violet crystals, 1·50 g (71%), m.p. 195°C (decomp.). IR: 2200, 1580, 1470 cm^{-1}. ^{1}H NMR (d_6-DMSO): δ 1·75 (s, 6H, CH_3), 3·84 (s, 3H, N—CH_3), 6·27 (d, 1H, CH), 7·40–8·40 (m, 8H, aromatic protons), 8·75 (d, 1H, CH) ppm. UV–Vis (dimethylformamide) λ_{max} (log ε) 370 (4·22), 576 (4·39) nm.

$C_{28}H_{19}N_5$	Calcd.:	C 79·07	H 4·47	N 16·47
(425·34)	Found:	C 78·88	H 4·60	N 16·40

3.23 1-(3-Dicyanomethylene-2,3-dihydro-1,1-dioxo-benzo[*b*]thiophene-2-ylidene)-2-(2,3-dihydro-1,3,3-trimethyl-1*H*-indol-2-ylidene)ethane (8i)

(*Method A*): 1·15 g (5 mmol) of 2,3-dihydro-3-dicyanomethylene-1,1-dioxo-benzo[*b*]thiophene,[23] 0·74 g (5 mmol) of triethyl orthoformate and 0·87 g (5 mmol) of **1** were refluxed in 10 ml of acetic acid for 90 min. The product crystallized at room temperature and was filtered and washed with ethanol; green crystals, 1·86 g (90%), m.p. > 300°C. IR: 2200, 1580, 1470, 1330 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ1·80 (s, 6H, CH_3), 3·65 (s, 3H, N—CH_3), 6·66 (d, 1H, CH), 7·11–8·92 (m, 8H, aromatic protons), 9·17 (d, 1H, CH) ppm. UV–Vis (acetone) λ_{max} (log ε) 570 (4·74), 349 (4·42) nm. UV–Vis (dimethylformamide) λ_{max} (log ε) 571 (4·69), 352 (4·37) nm.

$C_{24}H_{19}N_3O_2S$	Calcd.:	C 69·74	H 4·60	N 10·17	S 7·76
(413·33)	Found:	C 69·65	H 4·80	N 9·90	S 7·08

3.24 1-(1-Dicyanomethylene-2,3-dihydro-3-oxo-1*H*-indan-2-ylidene)-2-(2,3-dihydro-1,3,3-trimethyl-1*H*-indol-2-ylidene)ethane (8k)

1·00 g (3 mmol) of **8f** and 0·40 g (6 mmol) of malononitrile were stirred in 11 ml of absolute ethanol at room temperature. After 15 min, 0·33 g (4 mmol) of sodium acetate was added and stirring continued for a further 60 min. Water (50 ml) was then added and the mixture acidified to pH 2 with conc. HCl. After stirring for 10 min, the product was filtered and washed with hot methanol; 0·95 g (84%),

(*Method B*): 0·60 g (2 mmol) of **3e** and 0·35 g (2 mmol) of were refluxed for 2 h in 3 ml of acetic acid; *c.* 10 ml of methanol was added, and the product filtered and washed with hot methanol; 0·43 g (57%). Green crystals, m.p. 245°C IR: 2200, 1730, 1670, 1450 cm^{-1}. ^{1}H NMR (d_6-DMSO): δ 1·75 (s, 6H, CH_3), 3·70 (s, 3H, N—CH_3), 7·30–8·95 (m, 10H, aromatic protons and CH) ppm. UV–Vis (dimethylformamide) λ_{max} (log ε) 483 (4·39), 569 (4·56) nm.

$C_{25}H_{19}N_3O$	Calcd.:	C 79·69	H 5·04	N 11·13
(377·28)	Found:	C 79·39	H 4·96	N 10·57

3.25 2-(2,3-Dihydro-1,3-dioxo-1*H*-indan-2-ylidene)-3-(2,3-dihydro-1,3,3-trimethyl-1*H*-indol-2-ylidene)propionitrile (81)

(*Method C*): To a boiling solution of 2·08 g (10 mmol) of 2-dicyanomethylene-1,3-indandione[24] in 25 ml of ethanol, 1·73 g (10 mmol) of **1** in 20 ml of ethanol was added dropwise. After refluxing the mixture for 90 min it was cooled to room temperature and the precipitate filtered and washed with cold ethanol; violet crystals, 1·45 g (41%), m.p. 210°C (decomp.) (dioxane/water) IR: 2200, 1695, 1645, 1590, 1460 cm^{-1}.^{1}H NMR ($CDCl_3$): δ 1·70 (s, 6H, CH_3), 3·65 (s, 3H, N—CH_3), 7·12–7·89 (m, 9H, aromatic protons and CH) ppm. UV–Vis (dimethylformamide) λ_{max} (log ε) 545 (4·30) nm.

$C_{23}H_{18}N_2O_2$	Calcd.:	C 77·98	H 5·08	N 7·91
(354·25)	Found:	C 77·65	H 5·04	N 7·85

3.26 1-(4,5-Dihydro-3-methyl-5-oxo-1-phenyl-1*H*-pyrazole-4-ylidene)-2-(2,3-dihydro-1,3,3-trimethyl-1*H*-indol-2-ylidene)ethane (9a)

(*Method A*): 1·74 (10 mmol) of **4a**, 1·48 g (10 mmol) of triethyl orthoformate and 1·73 g (10 mmol) of **1** were refluxed in 5 mol of acetonitrile for 30 min. The mixture was stored in the refrigerator overnight and the product was then filtered and washed with a little acetonitrile; 1·20 g (34%).

(*Method B*) 0·57 g (3 mmol) of **5a** and 1·04 g (6 mmol) of **1** were refluxed in 2 ml of acetic acid for 3 h; 5 ml of acetonitrile and 8 ml of water were added and the product filtered; 0·75 g (84%).

Orange crystals, m.p. 196°C (acetonitrile) IR: 2960, 1660, 1580 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1·70 (s, 6H, CH_3), 2·30 (s, 3H, CH_3), 3·50 (s, 3H, N—CH_3), 6·95–8·05 (m, 11H, aromatic protons and CH) ppm. UV–Vis (dioxane) λ_{max} (log ε) 460 (4·60) nm.

$C_{23}H_{23}N_3O$	Calcd.:	C 77·32	H 6·44	N 11·76
(357·27)	Found:	C 77·60	H 6·48	N 11·61

3.27 1-[4,5-Dihydro-3-methyl-1-(4-methylphenyl)-5-oxo-1*H*-pyrazole-4-ylidene]-2-(2,3-dihydro-1,3,3-trimethyl-1*H*-indol-2-ylidene)ethane (9b)

(*Method B*): 1·22 g (5 mmol) of **5b** and 2·07 g (12 mmol) of **1** were refluxed for 2·5 h. Methanol (10 ml) was added and the product then filtered and washed with hot methanol; red crystals, 1·50 g (81%), m.p. 192°C. IR: 2980–2950, 1660, 1620 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1·70 (s, 6H, CH_3), 2·30 (s, 3H, CH_3), 2·35 (s, 3H, CH_3), 3·45 (s, 3H, N—CH_3), 6·92–7·92 (m, 10H, aromatic protons and CH) ppm. UV–Vis (dioxane) λ_{max} (log ε) 443 (4·64) nm.

$C_{24}H_{25}N_3O$	Calcd.:	C 77·64	H 6·73	N 11·32
(371·28)	Found:	C 77·54	H 6·82	N 11·10

3.28 1-[1-(4-Chlorophenyl)-4,5-dihydro-3-methyl-5-oxo-1*H*-pyrazole-4-ylidene]-2-(2,3-dihydro-1,3,3-trimethyl-1*H*-indol-2-ylidene)ethane (9c)

(*Method B*): 1·85 g (7 mmol) of **5c** and 2·60 g (15 mmol) of **1** were refluxed for 3 h; *c.* methanol 10 ml was added at room temperature, the product then filtered, giving red, shining crystals, 2·34 g (85%), m.p. 224°C (acetonitrile). IR: 2960, 1660, 1570 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1·70 (s, 6H, CH_3), 2·30 (s, 3H, CH_3), 3·48 (s, 3H, N—CH_3), 6·95–8·02 (m, 10H, aromatic protons and CH) ppm. UV–Vis (dioxane) λ_{max} (log ε) 462 (4·75) nm.

$C_{23}H_{22}H_3OCl$	Calcd.:	C 70·52	H 5·62	N 10·72
(391·72)	Found:	C 70·51	H 5·51	N 10·62

3.29 2-(4,5-Dihydro-3-methyl-5-oxo-1-phenyl-1*H*-pyrazole-4-ylidene)-1-(2,3-dihydro-1,3,3-trimethyl-1-*H*-indole-2-ylidene)propane (9d)

(*Method A*): 1·74 g (10 mmol) of **4a**, 1·62 g (10 mmol) of triethyl orthoacetate and 1·73 g (10 mmol) of **1** were refluxed in 5 ml of acetic acid for one hour. After cooling the mixture in the refrigerator, the product was precipitated by scratching with a glass rod and then collected by suction and washed with acetonitrile and methanol; dark red crystals, 1·20 g (32%), m.p. 182°C, IR: 2960, 1640, 1590 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1·50 (s, 6H, CH_3), 2·43 (s, 3H, CH_3), 2·45 (s, 3H, CH_3), 3·21 (s, 3H, N—CH_3), 6·82–8·00 (m, 10H, aromatic protons and CH) ppm. UV–Vis (dioxane) λ_{max} (log ε) 468 (4·39) nm.

$C_{24}H_{25}N_3O$	Calcd.:	C 77·64	H 6·73	N 11·31
(371·28)	Found:	C 77·40	H 6·61	N 11·14

3.30 2-(4,5-Dihydro-3-methyl-5-oxo-1-phenyl-1*H*-pyrazole-4-ylidene)-3-(2,3-dihydro-1,3,3-trimethyl-1*H*-indole-2-ylidene)propionitrile (9e)

(*Method C*): To a hot solution of 2·36 g (10 mmol) of 4,5-dihydro-2-(dicyanomethylene)-3-methyl-5-oco-1-phenyl-1*H*-pyrazole[19] in 5 ml of chloroform, a solution of 1·73 g (10 mmol) of **1** in 2 ml of ethanol was added.

The mixture was refluxed for 2 h and then chilled in a refrigerator, ethanol (10 ml) was added and the mixture was filtered, giving dark brown crystals, 1·35 g (35%), m.p. 210°C (decomp.). IR: 3300, 3100, 2200, 1710, 1660, 1600 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1·75 (s, 6H, CH_3), 2·58 (s, 3H, CH_3), 3·60 (s, 3H, N—CH_3), 7·06–7·40 (m, 7H, aromatic protons), 7·78 (s, 1H, CH), 7·91–7·97 (d, 2H, aromatic protons) ppm. UV–Vis (dioxane) λ_{max} (log ε) 525 (4·47) nm.

$C_{24}H_{22}H_4O$	Calcd.:	C 75·40	H 5·75	N 14·66
(382·29)	Found:	C 75·17	H 5·75	N 14·67

3.31 1-(3,5-Dioxo-1,2-diphenyl-1*H*,2*H*-pyrazole-4-ylidene)2-(2,3-dihydro-1,3,3-trimethyl-1*H*-indol-2-ylidene)ethane (10a)

(*Method A*): 2·52 g (10 mmol) of **6**[20] 1·48 g (10 mmol) of triethyl orthoformate and 1·73 g (10 mmol) of **1** were refluxed in 9 ml of acetic acid (or acetonitrile). After cooling the reaction mixture to room temperature the product was filtered and washed with methanol; 3·65 g (84%).

(*Method B*): A mixture of 0·60 g (2 mmol) of **7a** and 1·54 g (9 mmol) of **1** was gently heated until a clear solution was formed. On cooling to room temperature, the product precipitated and was filtered and washed with methanol. 0·70 g (80%)

Orange crystals, m.p. 260°C (acetonitrile) IR: 1670, 1570 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1·70 (s, 6H, CH_3), 3·50 (s, 3H, N—CH_3), 7·00–7·48 (m, 15H, aromatic protons and CH), 8·23–8·30 (d, 1H, CH) ppm. UV–Vis (dioxane) λ_{max} (log ε) = 458 (4·92) nm.

$C_{28}H_{25}N_3O_2$	Calcd.:	C 77·25	H 5·74	N 9·65
(435·33)	Found:	C 77·46	H 5·66	N 9·69

3.32 2-(3,5-Dioxo-1,2-diphenyl-1*H*,2*H*-pyrazole-4-ylidene)-1-(2,3-dihydro-1,3,3-trimethyl-1*H*-indol-2-ylidene)propane (10b)

(*Method A*): 2·52 g (10 mmol) of **6** 1·62 g (10 mmol) of triethyl orthoacetate and 1·73 g (10 mmol) of **1** were refluxed in 10 ml of acetic acid for 2 h. The reaction mixture was cooled to room temperature and the product collected by suction and washed with methanol; orange crystals, 3·59 g (80%), m.p. 206°C. IR: 1650, 1600 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1·50 (s, 6H, CH_3), 2·67 (s, 3H, CH_3). 3·40 (s, 3H, N—CH_3), 7·05–7·48 (m, 15H, aromatic protons and CH) ppm. UV–Vis (dioxane) λ_{max} (log ε) 470 (4·76) nm.

$C_{29}H_{27}N_3O_2$	Calcd.:	C 77·52	H 6·01	N 9·35
(449·34)	Found:	C 77·59	H 5·90	N 9·31

3.33 2-(3,5-Dioxo-1,2-diphenyl-1*H*,2*H*-pyrazole-4-ylidene)-3-(2,3-dihydro-1,3,3-trimethyl-1*H*-indol-2-ylidene)propionitrile (10c)

(*Method C*) To a boiling solution of 0·53 g (2 mmol) of **7c** in 5 ml of ethanol, a solution of 0·30 g (2 mmol) of **1** in 2 ml of ethanol was added and the mixture was refluxed for 2·5 h. Ethanol (10 ml) was added at room temperature and the product filtered to give dark green crystals, 0·30 g (38%), m.p. 278°C (acetonitrile) IR: 2960, 1670, 1600 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1·70 (s, 6H, CH_3), 3·75 (s, 3H N—CH_3), 7·08–7·50 (m, 14H, aromatic protons), 7·72 (s, 1H, CH) ppm. UV–Vis (dioxane) λ_{max} (log ε) = 525 (4·77) nm.

$C_{29}H_{24}N_4O_2$	Calcd.:	C 75·66	H 5·21	N 12·17
(460·35)	Found:	C 75·81	H 5·38	N 11·90

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