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Hydroxyphenyl-pyrazolyl-malononitriles, a New Class of Polymethine-Type Colorformers. Syntheses with Nitriles XCII[1]

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ABSTRACT

Addition of phenols ***2a–h*** *to 4-(dicyanomethylene)-pyrazolones* ***1a–c*** *yielded disubstituted malononitriles* ***3a–g*** *or benzofuran-3-carbonitriles* ***5a–c*** *depending on the substitution of the phenol.* ***3a–g*** *were converted into dyes* ***4a–g*** *by heating or UV irradiation. The phenolic OH groups in* ***4a–g*** *are easily deprotonated, forming anionic polymethine dyes (oxonoles). The color formation in poly(vinylchloride) films containing* ***3g*** *was studied.*

INTRODUCTION

In modern dye development functional dyes for new applications are of practical interest.[2] Colorless thermosensitive compounds are used for carbonless copying paper and different thermographic recording processes. They may also have potential in ultra-high-density information storage media, since reaction occurs at molecular level.

Most of the known colorformers[3–5] need a co-reactive substance for the development of the color and are based on triarylmethane type compounds (fluorans). Inoue *et al.*[6] recently reported on neutral allyl–aryl ethers of fluorans, which form colored phenols by heat induced Claisen

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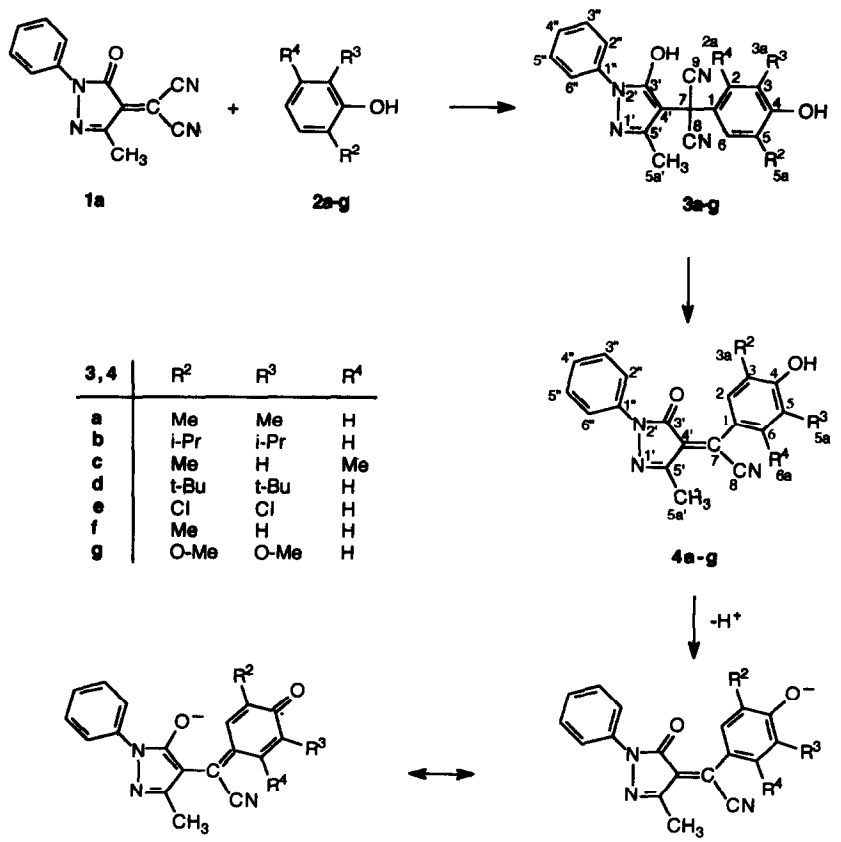
rearrangement and subsequent intramolecular acid–base reaction. Junek & Klade[7] have reacted dicyanomethylene-pyrazolones with N-alkylanilines to obtain colorless adducts, which are suitable one-component-colorformers.[8] These compounds yielded deeply colored heptamethines with good light fastness when they were heated or irradiated.

For the synthesis of colorformers reported in this paper the known reactivity of phenols towards tetracyanoethylene (TCNE) or activated dicyanomethylene compounds was used. Smith & Persmark[9] have reported that TCNE can be used to characterize certain phenols by the formation of *p*-tetracyanoethylphenols and *p*-tricyanovinylphenols. They did not mention, however, that these compounds are pH indicators. Junek and coworkers[10,11] have shown that 2-(dicyanomethylene)-1,3-indandione reacts with phenols at relatively high temperatures to yield hydroxyphenyl-1,3-dioxo-2-indanylidene-acetonitriles (oxonole type polymethines in the deprotonated form), which can be used as pH-indicators.



3,4	R^2	R^3	R^4
a	Me	Me	H
b	i-Pr	i-Pr	H
c	Me	H	Me
d	t-Bu	t-Bu	H
e	Cl	Cl	H
f	Me	H	H
g	O-Me	O-Me	H

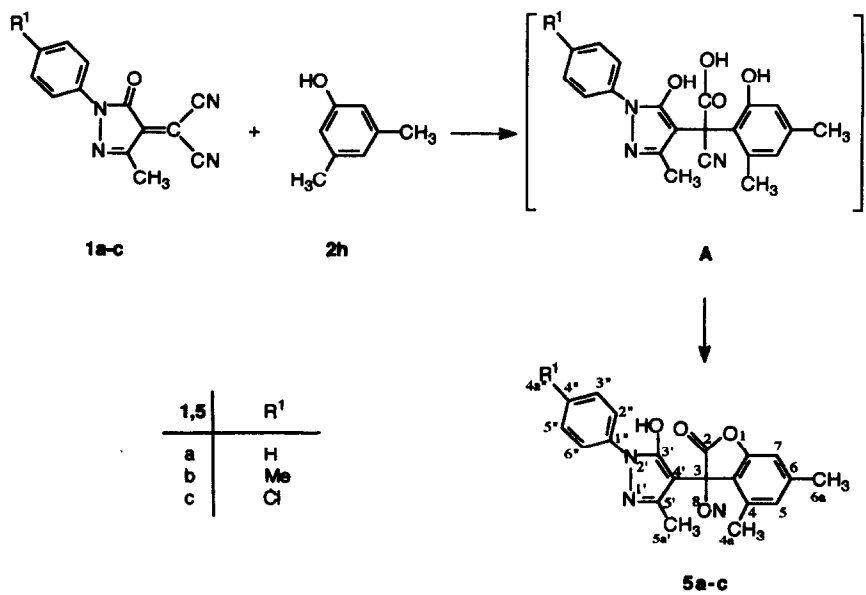
Scheme 1

RESULTS AND DISCUSSION

Dicyanomethylene-pyrazolones **1a–c**[12] form colorless products with substituted phenols **2a–h** in acetic acid at 50–65°C. Two different types of products are obtained depending on the substitution of the phenol. 2,5-, 2,6-disubstituted and 2-monosubstituted phenols (**2a–g**) react in their *p*-positions as expected to yield disubstituted malononitriles **3a–g**. If both *m*-positions of the phenol are substituted (**2h**), position 2 is the reactive site. Hydrolysis of one cyano group (intermediate **A**) gives rise to the formation of benzofuranones **5a–c**.

Structures **3** and **5** can be easily distinguished by ^{13}C-NMR spectroscopy (see also experimental section). Benzofuranones **5** show a signal of the carbonyl C atom at about 168 ppm which is of course not observed for compounds **3**. There is also a significant difference between the quaternary C atoms C-7 (**3**) and C-3 (**5**) the signals of which appear at 37 and 42 ppm, respectively. The signals of C-4' are observed at about 95 ppm for both structures. These values are comparable with the ones we have reported earlier.[13]

By exposing compounds **3a–g** to light or heat, hydrocyanic acid was eliminated and hydroxyphenyl-pyrazolylidene-acetonitriles **4a–g** were formed. It has to be mentioned that Metwally and coworkers[14] recently reported on a reaction of **1a** with *o*-cresol and resorcinol, leading to products of structure **4** by refluxing the starting materials in ethanol. We



Scheme 2

TABLE 1
pK_A Values and VIS Data of Compounds **4a–g**

No.	pK_A[a]	*pH < 3*[b]		*pH > 9*[c]	
		λ_{max}	*Log ε*	λ_{max}	*Log ε*
4a	6·0	421	4·04	577	4·24
4b	6·2	432	4·42	566	4·65
4c	[d]	432	3·74	590	[d]
4d	[d]	422	3·98	535	[d]
4e	[d]	425	3·80	575	[d]
4f	6·6	429	3·97	574	4·32
4g	5·5	449	3·99	584	4·17

[a] pK_A values determined by standard procedures.
[b] VIS spectra taken in methanol/HCl.
[c] VIS spectra taken in methanol/NaOH.
[d] Insufficient stability.

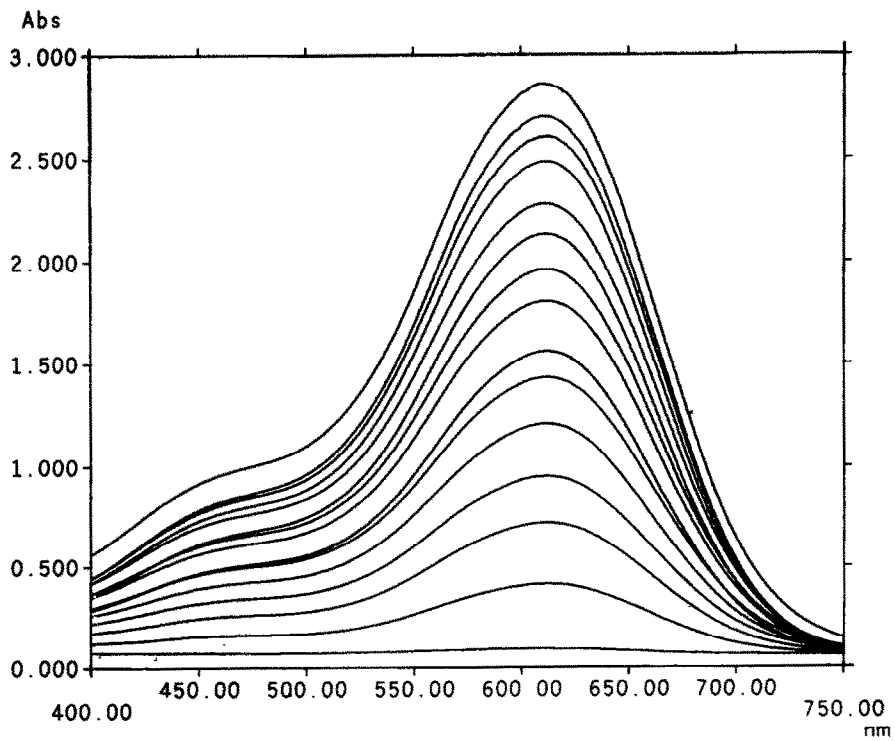


Fig. 1. **3g**, 6 wt% in PVC, thermal dye formation, total 14 h.

could not reproduce these experiments. The authors did not mention any dye properties of the compounds.

Hydroxyphenyl-pyrazolylidene-acetonitriles **4a–g** give yellow to slightly red solutions in ethanol. Deprotonation by alkalihydroxide yields anionic polymethines with a long wave absorption at approx. 570–580 nm, the products are pH indicators, the pK_A values are between 5·5 (**4g**) and 6·2 (**4b**, see Table 1). An additional bathochromic shift of about 25 nm occurs, if triethylamine is used for the deprotonation.

Hence, we have investigated the colorformer properties of **3g** in films of PVC containing triethylamine. The almost colorless films were exposed to 60°C or UV light for 14 h and VIS spectra were recorded every 60 min.

Figure 1 shows the thermal dye formation in PVC films containing 6% weight of **3g**. Nearly identical spectra were obtained for photochemical transformation. In Fig. 2 the thermal dye formation in a PVC film containing 2 wt% **3g** over 320 min is shown (VIS spectra were recorded every 40 min). At a very early stage of the colorforming process an additional absorption band at about 460 nm appeared. The λ_{max} of the

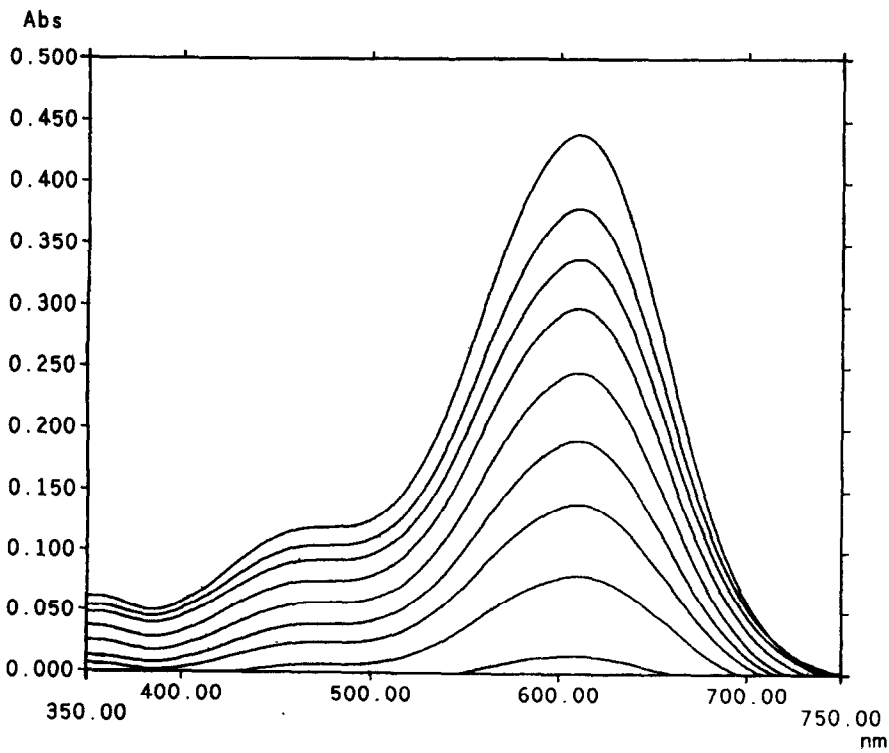


Fig. 2. **3g**, 2 wt% in PVC, thermal dye formation, total 320 min.

exposed films was found at 610 nm, the colored films appeared dark blue to black and were stable for months.

CONCLUSION

Since the velocity of the dye formation can be increased easily by using temperatures higher than 60°C, the products fulfil important requirements of colorformers like fast color development, irreversibility of dye formation, intense dark blue to black coloring and stability.

EXPERIMENTAL

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-NMR spectra: Varian Gemini 200; ^{13}C-NMR spectra: Gemini 200 and Bruker 369 AM (internal standard tetramethylsilane). UV-VIS spectra: Hitachi U-3501 spectrophotometer (quartz cuvettes). Elemental analyses: C,H,N-analyzer Carlo Erba 1106. Satisfactory microanalyses were obtained for all compounds.

Preparation of compounds 1b,c. General procedure

Pyrazolone (35 mmol) was added to a solution of tetracyanoethylene (TCNE, 40 mmol) in 50 ml of acetonitrile over a period of 10 min at 50°C. After stirring for an additional 10 min the warm solution was filtered and the filtrate cooled in a refrigerator. Products **1b,c** were collected by suction, washed with hexane and dried at 40°C. Further purification was not necessary.

*4-(Dicyanomethylene)-5-methyl-2-*p*-tolyl-pyrazolone-3 (**1b**)*
$C_{14}H_{10}N_4O$ (250·26); yield 78%, m.p. 141°C. IR: ν = 2930, 2230, 1710, 1600 cm^{-1}. ^{1}H-NMR ([D$_6$]DMSO): δ = 2·33 (s, 3H, CH_3), 2·46 (s, 3H, CH_3), 7·12 (d, 2H, arom. protons), 7·60 (d, 2H arom. protons) ppm. UV-VIS (methanol), λ_{max} (log ε): 560 (2·80) nm.

*4-(Dicyanomethylene)-5-methyl-2-(4-chlorphenyl)-pyrazolone-3 (**1c**)*
$C_{13}H_7N_4OCl$ (270·68); yield 72%, m.p. 172°C. IR: ν = 1710, 1590, 1490 cm^{-1}.

^{1}H-NMR ($CDCl_3$): δ = 2·66 (s, 3H, CH_3), 7·48 (d, 2H, arom. protons), 7·81 (d, 2H, arom. protons) ppm. UV-VIS (methanol), λ_{max} (log ε): 538 (2·74) nm.

Preparation of adducts 3a–g and compounds 5a–c. General procedure

The phenol (**2a–h**, 20 mmol) was added to a solution of (dicyanomethylene)-pyrazolone (**1a–c**, 10 mmol) in 35 ml of acetic acid at 50–65°C. After 3·5–70 h the colorless products precipitated (reaction times and temperatures are given below). They were collected by suction and washed with water. For purification **3a–g** were dissolved in methanol and reprecipitated by addition of water. **5a–c** were recrystallized. All products are off-white powders. They were dried *in vacuo* and in the dark.

*2-(4-Hydroxy-3,5-dimethyl-phenyl)-2-(3-hydroxy-5-methyl-2-phenyl-4,5-2H-pyrazol-4-yl)-malononitrile (**3a**)*
$C_{21}H_{18}N_4O_2$ (358·40); 3·5 h at 55°C, yield 81%, m.p. 203°C (dec.). IR: ν = 3450, 2910, 1620, 1555, 1495 cm^{-1}. ^{1}H-NMR ([D$_6$]DMSO): δ = 1·89 (s, 3H, 5a'-H), 2·22 (s, 6H, 3a- and 5a-H), 7·19 (s, 2H, 2- and 6-H), 7·32 (t, 1H, 4"-H), 7·52 (t, 2H, 3"- and 5"-H), 7·72 (d, 2H, 2"- and 6"-H) ppm.

*2-(4-Hydroxy-3,5-diisopropyl-phenyl)-2-(3-hydroxy-5-methyl-2-phenyl-2H-pyrazol-4-yl)-malononitrile (**3b**)*
$C_{25}H_{26}N_4O_2$ (414·51); 24 h at 50°C, yield 93%, m.p. 184°C (dec.). IR: ν = 3380, 2860–2340, 1610, 1560, 1500 cm^{-1}. ^{1}H-NMR ([D$_6$]DMSO): δ = 1·22 (d, 12H, methyl groups on 3a and 5a), 1·70 (s, 3H, 5a'-H), 7·10–7·90 (m, 7H, 2-, 6-, and 2"- to 6"-H) ppm.

*2-(4-Hydroxy-2,5-dimethyl-phenyl)-2-(3-hydroxy-5-methyl-2-phenyl-2H-pyrazol-4-yl)-malononitrile (**3c**)*
$C_{21}H_{18}N_4O_2$ (358·40); 24 h at 50°C, yield 82%, m.p. 210°C (dec.). IR: ν = 3430, 2500–3100, 2260, 1625, 1525, 1500 cm^{-1}. ^{1}H-NMR ([D$_6$]DMSO): δ = 1·73 (s, 3H, 5a'-H), 2·16, 2·25 (2s, 6H, 2a-, and 5a-H), 6·80 (s, 1H, 3-H), 7·34 (m, 2H, 6- and 4"-H), 7·51 (t, 2H, 3"-, and 5"-H), 7·72 (d, 2H, 2"- and 6"-H) ppm.

*2-(3,5-Di-tert.-butyl-4-hydroxy-phenyl)-2-(3-hydroxy-5-methyl-2-phenyl-2H-pyrazol-4-yl)-malononitrile (**3d**)*
$C_{27}H_{30}N_4O_2$ (442·56); 50 h at 55°C, yield 67%, m.p. 184°C (dec.). IR: ν = 3630, 2940, 1700, 1620, 1560, 1500 cm^{-1}. ^{1}H-NMR ([D$_6$]DMSO): δ = 1·41

(s, 18H, methyl groups on carbon atoms 3a and 5a), 1·74 (s, 3H, 5a'-H), 7·34 (m, 1H, 4"-H), 7·39 (s, 2H, 2- and 6-H), 7·53 (t, 2H, 3"- and 5"-H), 7·68 (d, 2H, 2"- and 6"-H) ppm.

*2-(3,5-Dichlor-4-hydroxy-phenyl)-2-(3-hydroxy-5-methyl-2-phenyl-2H-pyrazol-4-yl)-malononitrile (**3e**)*

$C_{19}H_{12}Cl_2N_4O_2$ (399·24); 70 h at 60°C, yield 91%, m.p. 212°C (dec.). IR: ν = 3640–2690, 1620, 1555, 1490 cm^{-1}. ^{1}H-NMR ([D$_6$]DMSO): δ = 1·80 (s, 3H, 5a'-H), 6·80 (s, 2H, 2- and 6-H), 7·33 (m, 1H, 4"-H), 7·52 (t, 2H, 3"- and 5"-H), 7·70 (d, 2H, 2"- and 6"-H) ppm. ^{13}C-NMR ([D$_6$]DMSO): δ = 12·1 (C-5a'), 36·8 (C-7), 94·1 (C-4'), 113·6 (C-8, C-9), 120·1 (C-2", C-6"), 123·1 (C-3, C-5), 124·6 (C-1), 125·8 (C-4"), 126·5 and 129·1 (C-2, C-6, C-3", C-5"), 136·1 (C-1"), 145·5 (C-5'), 150·8 (C-4), 158·7 (C-3') ppm.

*2-(4-Hydroxy-3-methyl-phenyl)-2-(3-hydroxy-5-methyl-2-phenyl-2H-pyrazol-4-yl)-malononitrile (**3f**)*

$C_{20}H_{16}N_4O_2$ (344·37); 12 h at 55°C, yield 73%, m.p. 136°C (dec.). IR: ν = 3600–3500, 3200–2900, 1620, 1570, 1500 cm^{-1}. ^{1}H-NMR ([D$_6$]DMSO): δ = 1·36 (s, 3H, 5a'-H), 2·19 (s, 3H, 5a-H), 6·95 (d, 1H, 3-H), 7·30 (m, 3H, 2-, 6- and 4"-H), 7·51 (t, 2H, 3"- and 5"-H), 7·72 (d, 2H, 2"- and 6"-H), 10·00 (br. s, 1H, OH) ppm.

*2-(4-Hydroxy-3,5-dimethoxy-phenyl)-2-(3-hydroxy-5-methyl-2-phenyl-2H-pyrazol-4-yl)-malononitrile (**3g**)*

$C_{21}H_{18}N_4O_4$ (390·40); 8 h at 60°C, yield 84%, m.p. 177°C (dec.). IR: ν = 3420, 3200–3160, 1620, 1560, 1520, 1500 cm^{-1}. ^{1}H-NMR ([D$_6$]DMSO): δ = 1·84 (s, 3H, 5a'-H), 3·83 (s, 6H, 3a- and 5a-H), 6·87 (s, 2H, 2-, and 6-H), 7·32 (t, 1H, 4"-H), 7·52 (t, 2H, 3"- and 5"-H), 7·73 (d, 2H, 2"- and 6"-H), 9·09 (br. s, 1H, OH) ppm.

*2,3-Dihydro-4,6-dimethyl-2-oxo-3-(3-hydroxy-5-methyl-2-phenyl-pyrazol-4-yl)-benzofuran-3-carbonitrile (**5a**)*

$C_{21}H_{17}N_3O_3$ (359·38); 24 h at 65°C, yield (methanol) 61%, m.p. 210°C (dec.). IR: ν = 3160–3060, 2240, 1815, 1620, 1570, 1490 cm^{-1}. ^{1}H-NMR ([D$_6$]DMSO): δ = 2·24, 2·34 (2s, 6H, 4a- and 6a-H), 2·51 (s, 3H, 5a'-H), 6·94 (s, 1H, 7-H), 7·07 (s, 1H, 5-H), 7·24 (t, 1H, 4"-H), 7·44 (t, 2H, 3"-H), 7·63 (d, 2H, 2"-H), 12·25 (br. s, 1H, 3'-OH) ppm. ^{13}C-NMR ([D$_6$]DMSO): δ = 10·5, 15·9, 20·2 (C-4a, C-6a, C-5a'), 41·8 (C-3), 94·5 (C-4'), 113·3 (C-7 and C-2"), 118·2 (C-3a, C-3", and C-6"), 124·7 (C-5), 124·8 (C-4"), 126·8 (C-5"), 133·9 (C-6), 138·2 (C-1"), 140·7 (C-4), 145·4 (C-5'), 152·2 (C-7a), 158·5 (C-3'), 168·4 (C-2) ppm.

*2,3-Dihydro-4,6-dimethyl-2-oxo-3-(3-hydroxy-5-methyl-2-p-tolyl-pyrazol-4-yl)-benzofuran-3-carbonitrile (**5b**)*

$C_{22}H_{19}N_3O_3$ (373·41); 8 h at 50°C, yield (methanol) 46%, m.p. 190°C (dec.). IR: ν = 3250–2800, 1825, 1800, 1615, 1580, 1515 cm^{-1}. ^{1}H-NMR ([D$_6$]DMSO): δ = 2·23, 2·32, 2·36 (3s, 9H, 4a-, 6a- and 4a"-H), 2·53 (s, 3H, 5a'-H), 6·97 (s, 1H, 7-H), 7·08 (s, 1H, 5-H), 7·27 (d, 2H, 3"-H), 7·52 (d, 2H, 2"-H) ppm. ^{13}C-NMR ([D$_6$]DMSO): δ = 11·3, 16·6, 20·4, 21·1 (C-6a, C-4a, C-5a', C-4a"), 42·3 (C-3), 96·7 (C-4'), 109·3 (C-7), 114·0 (C-8), 119·0 (C-2", C-6"), 119·2 (C-3a), 123·9 (C-5), 127·9 (C-3", C-5"), 133·6 (C-4"), 134·7 (C-6), 137·4 (C-1"), 141·4 (C-4), 145·6 (C-5'), 152·9 (C-7a), 158·0 (C-3'), 169·1 (C-2) ppm.

*2,3-Dihydro-4,6-dimethyl-2-oxo-3-(3-hydroxy-5-methyl-2-(p-chlorophenyl)-pyrazol-4-yl)-benzofuran-3-carbonitrile (**5c**)*

$C_{21}H_{16}N_3O_3Cl$ (393·83); 8 h at 50°C, yield (methanol) 40%, m.p. 200°C (dec.). IR: ν = 3420, 3250–2800, 2210, 1825, 1800, 1660, 1640, 1590, 1570, 1490 cm^{-1}. ^{1}H-NMR ([D$_6$]DMSO): δ = 2·25, 2·36 (2s, 6H, 4a- and 6a-H), 2·52 (s, 3H, 5a'-H), 6·97 (s, 1H, 7-H), 7·09 (s, 1H, 5-H), 7·53 (d, 2H, 2"-H), 7·67 (d, 2H, 3"-H) ppm.

Preparation of 4a–g. General procedure

Photolysis (method a): Suspensions or solutions of the colorless adducts **3a–g** (2·00 g in 100 ml of ethanol or acetone) were exposed to the light of a mercury lamp (reaction times 8–48 h). After evaporation of the solvent *in vacuo*, the crude products were purified by recrystallization.

Thermolysis can be performed either in DMF (method b) or in *n*-butanol (method c): Solutions of the addition products **3a–g** (approx. 1·50 g in 10 ml DMF or in 20 ml *n*-butanol) were kept at 140°C for 3–4 h (DMF) or refluxed for 9–12 h (*n*-Butanol). After cooling the reaction mixtures to room temperature, the dyes were precipitated by addition of water, collected by suction, washed with water, and recrystallized.

*2-(4-Hydroxy-3,5-dimethyl-phenyl)-2-(3-oxo-5-methyl-2-phenyl-4,5-dihydro-2H-pyrazol-4-ylidene)-acetonitrile (**4a**)*

$C_{20}H_{17}N_3O_2$ (331·37); 8 h, method a, yield (methanol) 94%, m.p. 119°C. IR: ν = 3500–3200, 2940, 1700, 1605, 1500 cm^{-1}. ^{1}H-NMR ([D$_6$]DMSO): δ = 2·11 (s, 6H, 3a- and 5a-H), 2·26 (s, 3H, 5a'-H), 7·24 (t, 1H, 4"-H), 7·43 (s, 2H, 2- and 6-H), 7·48 (t, 2H, 3"- and 5"-H), 7·86 (d, 2H, 2"- and 6"-H), 9·64 (br. s, 1H, phenolic H) ppm. UV-VIS: see Table 1.

*2-(4-Hydroxy-3,5-diisopropyl-phenyl)-2-(3-oxo-5-methyl-2-phenyl-4,5-dihydro-2H-pyrazol-4-ylidene)-acetonitrile (**4b**)*
$C_{24}H_{25}N_3O_2$ (387·48); 3 h, method b, yield (methanol) 88%, m.p. 161°C. IR: ν = 3380, 2960, 2320, 1670, 1500 cm^{-1}. ^{1}H-NMR ([D$_6$]DMSO): δ = 2·45 (s, 3H, 5a'-H), 7·25 (t, 1H, 4"-H), 7·30 (s, 2H, 2- and 6-H), 7·47 (t, 2H, 3"- and 5"-H), 7·85 (d, 2H, 2"- and 6"-H) ppm. ^{13}C-NMR ($CDCl_3$): δ = 16·7 (C-5a'), 22·6 (C-3b, C-5b), 27·3 (C-3a, C-5a), 116·5 (C-8), 118·8 (C-2"), 122·1 and 124·0 (C-7, C-4'), 125·4 (C-4"), 127·7 (C-2, C-6), 129·0 (C-3", C-5"), 134·4 (C-3, C-5), 137·6 (C-1"), 147·4 (C-1, C-5'), 155·3 (C-4), 160·4 (C-3') ppm. UV-VIS: see Table 1.

*2-(4-Hydroxy-2,5-dimethyl-phenyl)-2-(3-oxo-5-methyl-2-phenyl-4,5-dihydro-2H-pyrazol-4-ylidene)-acetonitrile (**4c**)*
$C_{20}H_{17}N_3O_2$ (331·37); 10 h, method c, yield (ethanol/water) 73%, m.p. 148°C. IR: ν = 3300, 2200, 1700, 1590, 1490 cm^{-1}. ^{1}H-NMR ([D$_6$]DMSO): δ = 1·68 (s, 3H, 6a-H), 2·15 and 2·55 (2s, 3H, 5a'-H of E- and Z-isomer), 2·31 (s, 3H, 3a-H), 6·81 (s, 1H, 5-H), 7·18 (s, 1H, 2-H), 7·26 (t, 1H, 4"-H), 7·50 (m, 2H, 3"- and 5"-H), 7·81 (d, 2H, 2"- and 6"-H) ppm. UV-VIS: see Table 1.

*2-(3,5-Di-tert.-butyl-4-hydroxy-phenyl)-2-(3-oxo-5-methyl-2-phenyl-4,5-dihydro-2H-pyrazol-4-ylidene)-acetonitrile (**4d**)*
$C_{26}H_{29}N_3O_2$ (415·53); 3·5 h, method b, yield (ethanol/water) 64%, m.p. 140°C. IR: ν = 3620, 2950, 2200, 1610, 1645, 1615, 1595, 1560, 1500 cm^{-1}. ^{1}H-NMR ([D$_6$]DMSO): δ = 1·36 (m, 18H, methyl groups on 3a and 5a), 2·53 (s, 3H, 5a'-H), 7·15–7·93 (m, 7H, 2-, 6- and 2"- to 6"-H) ppm. UV-VIS: see Table 1.

*2-(3,5-Dichlor-4-hydroxy-phenyl)-2-(3-oxo-5-methyl-2-phenyl-4,5-dihydro-2H-pyrazol-4-ylidene)-acetonitrile (**4e**)*
$C_{18}H_{11}Cl_2N_3O_2$ (372·21); 2·5 h, method b, yield (ethanol/water) 86%, m.p. 198°C. IR: ν = 3600–3000, 1675, 1625, 1590, 1570, 1555 cm^{-1}. ^{1}H-NMR ([D$_6$]DMSO): δ = 2·53 (s, 3H, 5a'-H), 7·26 (t, 1H, 4"-H), 7·15 (s, 2H, 2- and 6-H), 7·48 (t, 2H, 3"- and 5"-H), 7·85 (d, 2H, 2"- and 6"-H) ppm. UV-VIS: see Table 1.

*2-(4-Hydroxy-3-methyl-phenyl)-2-(3-oxo-5-methyl-2-phenyl-4,5-dihydro-2H-pyrazol-4-ylidene)-acetonitrile (**4f**)*
$C_{19}H_{15}N_3O_2$ (317·35); 24 h, method a, yield (methanol/water) 95%, m.p. 115°C. IR: ν = 3200, 1655, 1610, 1560, 1545, 1500 cm^{-1}. ^{1}H-NMR ([D$_6$]DMSO): δ = 2·21 (s, 3H, 5a-H), 2·53 (s, 3H, 5a'-H), 6·99 (d, 1H, 3-

H), 7·26 (t, 1H, 4"-H), 7·48 (m, 4H, 2-, 6-, 3"-, and 5"-H), 7·86 (d, 2H, 2"- and 6"-H), 10·67 (br. s, 1H, OH) ppm. UV-VIS: see Table 1.

*2-(4-Hydroxy-3,5-dimethoxy-phenyl)-2-(3-oxo-5-methyl-2-phenyl-4,5-dihydro-2H-pyrazol-4-ylidene)-acetonitrile (**4g**)*
$C_{20}H_{17}N_3O$ (363·37); 24 h, method a, yield (methanol) 87%, m.p. 131°C. IR: $\nu = 1680, 1600, 1550, 1500\ cm^{-1}$. ^1H-NMR ([D_6]DMSO): $\delta = 2{\cdot}53$ (s, 3H, 5a'-H), 3·86 (s, 6H, 3a- and 5a-H), 7·13 (s, 2H, 2- and 6-H), 7·26 (t, 1H, 4"-H), 7·49 (t, 2H, 3"- and 5"-H), 7·87 (2"- and 6"-H) ppm. UV-VIS: see Table 1.

Preparation of PVC films for thermal and photochemical dye formation

(A) Films for 14 h test: A solution of PVC (8 wt%) and **3g** (0·5 wt%) in a mixture of 2-butanone (99 vol.%) and triethylamine (1 vol.%) was applied to slides (25 × 75 mm, 1·0 g solution per slide) and distributed evenly. The slides were dried at room temperature and in the dark for 24 h. The resulting films contain approx. 6 wt% of **3g**. Films without colorformer were prepared in the same way and used as reference samples. Three slides were kept at 60°C, three others were exposed to the light of a Hg lamp. Three VIS measurements of each slide were taken every hour.

(B) Films for 320 min test: A solution of PVC (8 wt%) and **3g** (approx. 0·16 wt%) in a mixture of 2-butanone (99 vol.%) and triethylamine (1 vol.%) was applied to slides and the slides were dried as above. The resulting films contained approx. 2 wt% of **3g**. Films without colorformer were prepared in the same way and used as reference samples. Three slides were kept at 60°C. Three VIS measurements of each slide were taken every 40 min.

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