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The Relationship between Photographic Activity and Structure of Masked Pyrazolone Colour Couplers

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ABSTRACT

Nine masked pyrazolone colour couplers were synthesised and their photographic activities (A) determined by the Elvegard γ–t equation:

$$\gamma = A \log t + B$$

where A is the slope of the line.

The superdelocalisabilities S_{re} and electron densities Q_r at the coupling position of the colour couplers were calculated using Hückel molecular orbital theory. From a plot of ln *A against S_{re}, a linear relationship was observed, viz.*

$$\ln A = 31{\cdot}84 S_{re} - 33{\cdot}16$$

($n = 9$ and $r = 0{\cdot}95$).

1 INTRODUCTION

Masked colour couplers, discovered by Hanson (Kodak Company, USA), eliminate the unwanted absorption of coloured images formed after the colour couplers are chromogenically developed.[1] The technique is now frequently used in colour photography and the chemistry of masked colour couplers has been the subject of many investigations.

In this present paper, calculations have been made of superdelocalisabilities and electron densities at the coupling position of cyan- and magenta-forming colour couplers by using HMO or PPP–CI MO theory.

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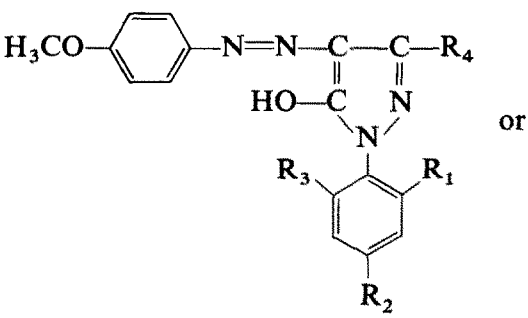
The photographic activities (A) of these colour couplers, defined in the Elvegard equation are determined by using the γ–log t relationship. Linear relationships have been observed between S_{re} and ln A in the case of phenolic colour couplers,[2] and between Q_r and ln A in pyrazolone colour couplers.[3] These relationships indicate that the photographic activities of colour couplers may be predicted by quantum-mechanical methods and that the development of a colour coupler is a reaction either electrostatically controlled or orbital-controlled.

In this paper we investigate whether the photographic activities of masked pyrazolone colour couplers could be determined by the γ–log t relationship and whether the S_{re} or Q_r at the coupling site of these coloured couplers could be correlated to photographic activity.

2 EXPERIMENTAL

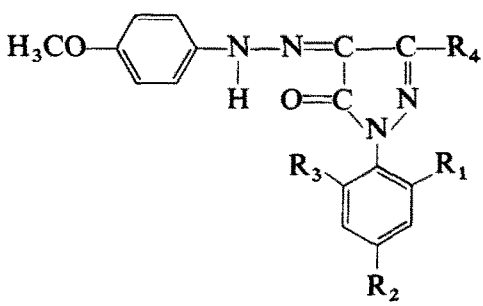
2.1 Preparation of masked pyrazolone colour couplers

The general structure of the coloured pyrazolone couplers used was:



or

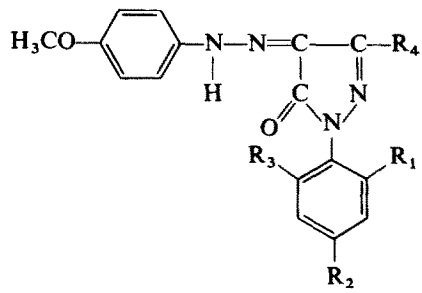
Azo form



Hydrazone form

Nine couplers were prepared according to known methods. Analytical data, melting points and other physical properties are given in Tables 1 and 2.

TABLE 1
Analytical Data of Masked Pyrazolone Colour Couplers



					C(%)		*H*(%)		*N*(%)	
No.	R_1	R_2	R_3	R_4	*Calc.*	*Found*	*Calc.*	*Found*	*Calc.*	*Found*
M1	H	H	H	CH_3	66·22	66·50	5·23	5·21	18·17	18·27
M2	Cl	Cl	Cl	NHCONHPh	51·95	52·14	3·22	2·81	15·80	15·29
M3	Cl	CH_3	CH_3	NHCONHPh	61·16	60·40	4·72	4·87	17·12	16·84
M4	Cl	Cl	Cl	NH_2	46·57	47·00	2·93	3·10	16·97	16·43
M5	H	H	H	NH_2	62·13	61·85	4·89	4·87	22·64	22·46
M6	H	H	H	NHPh(*p*-OCH_3)	66·49	65·91	5·09	5·10	16·86	16·62
M7	H	H	H	NHPh(*p*,*m*-CH_3)	69·72	69·50	5·61	5·77	16·94	16·56
M8	H	H	H	NHPh(*p*-CH_3)	69·16	68·96	5·30	5·68	17·53	17·67
M9	H	H	H	NHPh(*p*-Cl)	62·94	62·22	4·32	4·61	16·68	16·63

2.2 Determination of photographic activity

The film used was reversal black–white film (8 DIN), exposed in a sensitometer CG-125 (made in China). The time of exposure was 1 s, with light source 2859 K, using TSS as colour developer (reagent grade, Shanghai Reagent Chemicals Works, Shanghai). The coloured pyrazolone colour coupler was added to the developing solution and the film developed in the darkroom, bleached, fixed and washed.[4] The colour densities D were measured in a densitometer CMT (Shanghai Optical Instrument Works, Shanghai). The conditions for developing are summarised in the Appendix. The colour contrasts γ obtained at different times (minutes) are summarised in Table 3.

From a plot of γ versus $\log t$, a series of straight lines were obtained. From Fig. 1, it can be seen that the experimental results are in good agreement with the Elvegard equation:

$$\gamma = A \log t + B$$

(where A is the slope of the line).

TABLE 2
Some Physical Properties of the Masked Pyrazolone Colour Couplers

No.	*M.wt*	*M.p*(°C)	λ_{max}(*nm*)	$\varepsilon \times 10^{-4}$	*m/e*	*Crystal form*
M1	308·34	155–156·5	413	2·509	308	Orange crystals
M2	531·79	201–203	417	2·650	530	Orange crystals
M3	490·95	194–195	416	2·875	490	Orange crystals
M4	412·67	213–214	402	2·539	411	Orange crystals
M5	309·33	172–174	407	2·794	309	Brownish crystals
M6	415·46	172·5–174·5	418	2·579	415	Brown powder
M7	413·48	183–185	419	2·576	413	Brown powder
M8	399·46	185–187	417	2·624	399	Brownish crystals
M9	419·87	209·5–211·5	419	2·613	419	Brown powder

A, thus determined, is the photographic activity, and B the induction constant. The values of A and B of the various pyrazolone couplers are summarised in Table 3.

From the results, it can be seen that the Elvegard equation may be used not only in the case of the usual colour couplers, but also in the case of the coloured pyrazolone couplers.

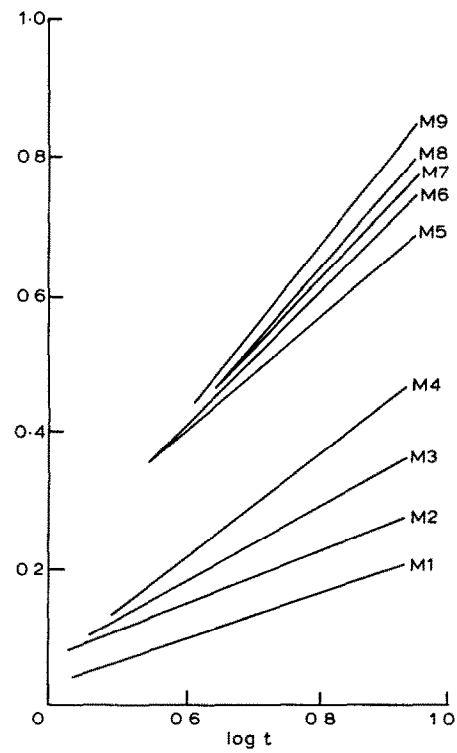


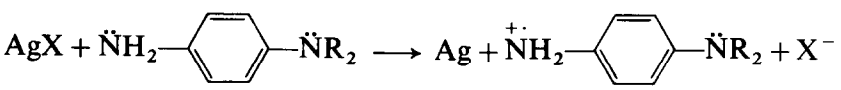
Fig. 1. Plot of contrasts γ versus log t for various coloured magenta couplers.

TABLE 3
Colour Contrast at Different Times and *A* and *B* values

	γ						*A*	*B*
No.	*3 min*	*4 min*	*5 min*	*6 min*	*8 min*	*10 min*		
M1	0·04	0·11	0·13	0·17	0·21	0·24	0·373	−0·127
M2	0·12	0·16	0·20	0·24	0·29	0·38	0·480	−0·125
M3	0·11	0·15	0·21	0·28	0·35	0·40	0·586	−0·186
M4	0·14	0·22	0·28	0·33	0·44	0·52	0·726	−0·218
M5	0·30	0·40	0·51	0·59	0·67	0·74	0·865	−0·107
M6	0·29	0·39	0·49	0·63	0·74	0·80	1·034	−0·212
M7	0·33	0·41	0·52	0·60	0·78	0·84	1·039	−0·192
M8	0·28	0·41	0·52	0·60	0·72	0·86	1·087	−0·243
M9	0·28	0·46	0·57	0·67	0·80	0·92	1·202	−0·277

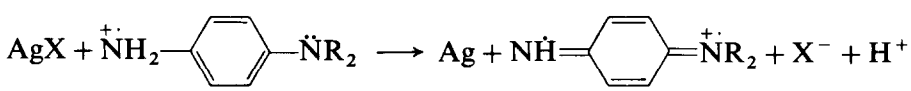
3 RESULTS AND DISCUSSION

It has been shown that the colour coupling is a second-order reaction. Initially, the molecule of the developer PPD loses an electron, forming a positively charged semiquinone.



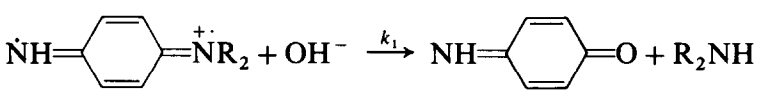
PPD SH$^+$

This may be followed by a heterogeneous reaction or by the homogeneous formation of a quinone-diimine by disproportionation following desorption of the semiquinone:



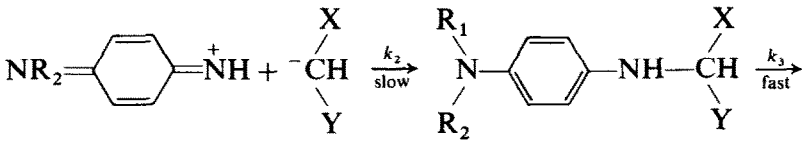
SH$^+$ QDI

Once the quinone-diimine has been formed, it reacts further in two ways. The first reaction is deamination with the formation of the quinone-monoimine. The specific rate constant of the deamination is denoted by k_1:

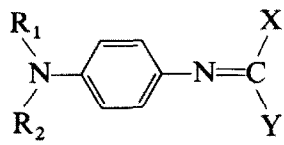


QDI QMI

The second reaction is the coupling reaction, i.e. the electrophilic attack on the coupler ion by QDI. The specific rate constant of this reaction is denoted by k_2.



QDI Coupler ion Leuco dye



Dye

We used equal times of exposure, the same developing temperature and the same pH of developing solution. Under these conditions, the rate constant of deamination of quinone-diimine may be assumed to be the same. The diffusion of different masked pyrazolone colour couplers in the developing solution and in the swollen emulsion layer may also be assumed to be constant. Therefore the photographic activities of the different masked pyrazolone colour couplers may be considered to be dependent only on the rate of the colour coupling.

Brand has previously shown that in plots of A versus k_2/k_1 an exponential curve is obtained.[8,9] When the values of A are in the range 0–3·0, A is linearly correlated with k_2/k_1. The values of A of the pyrazolone colour couplers studied in this present paper lie between 0 and 3·0. Since, as has been previously noted, the specific rate constant of deamination is constant under the same developer and developing conditions, the photographic activity A will be directly proportional to k_2, the specific rate constant of colour coupling.

$$A \propto k_2 \quad \text{or} \quad \log A \propto \log k_2$$

3.1 Quantum-mechanical calculations of various reactive indexes at the coupling site of the masked pyrazolone couplers

By Hückel molecular orbital theory, the reactive indexes, Q_r and S_{re}, and the localisation energy at the reaction site of the masked pyrazolone coupler may be computed using a microcomputer program. According to Fukui's theory of frontier molecular orbitals, superdelocalisability is a measure of

TABLE 4
Some Empirical Parameters Used in HMO Calculation

Atom	*h*	*h**	*k*
OCH_3	1·9	0·19	0·8
CH_3	2·0	0·2	1
Cl	2	0·2	0·4
$C(H_3)$	−0·1		0·8
$H_3(C)$	−0·5		3·0
OH	2	0·2	0·8
O=C	1	0·1	1
—N=	0·5	0·05	1
—N—N=	0·5		0·8
—N<	1·5	0·15	0·8

perturbational energy between the vacant orbital of the attacking agent and the occupied orbital of the coupler ion.

The empirical parameters used in HMO calculation of masked pyrazolone couplers are listed in Table 4. In HMO theory, the electron density and superdelocalisability at the reaction site *r* are defined by:

$$Q_r = \sum_{i=1}^{occ} 2C_{ir}^2 \qquad S_{re} = \sum_{i=1}^{occ} \frac{2C_{ir}^2}{\lambda_i}$$

where C_{ir} is the coefficient of the atomic orbital r in the *i*th molecular orbital, λ_i is the energy parameter of the *i*th molecular orbital,[10-13] and Q_r is the electronic charge density at r. The results of the calculations are given in

TABLE 5
The Q_r and S_{re} Values Calculated for Various Masked Pyrazolone Couplers Together with ln *A*

No.	Q_r	S_{re}	ln*A*
M1	1·097	1·007	−0·99
M2	1·099	1·021	−0·73
M3	1·100	1·030	−0·53
M4	1·104	1·035	−0·32
M5	1·105	1·039	−0·15
M6	1·103	1·042	0·03
M7	1·103	1·043	0·04
M8	1·103	1·043	0·08
M9	1·103	1·040	0·18

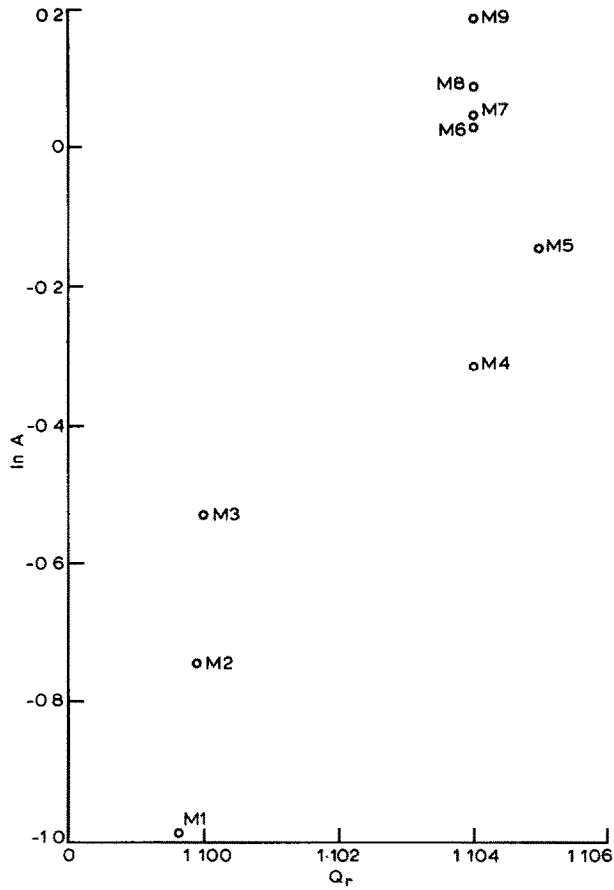


Fig. 2. Plot of electron densities Q_r against ln A.

Table 5. By plotting Q_r and S_{re} against ln A, Figs 2 and 3 respectively are obtained.

From Fig. 2 and Fig. 3, it is apparent that only S_{re} correlates well with ln A, the correlation equation being

$$\ln A = 31{\cdot}84 S_{re} - 33{\cdot}16 \quad (n = 9,\ r = 0{\cdot}95)$$

Thus, the photographic activity of a masked pyrazolone colour coupler may be predicted by HMO calculation of S_{re} at the coupling site r. This relationship may be used to simplify the tedious laboratory synthesis of pyrazolones in order to obtain structures of higher photographic activity.

Since superdelocalisability measures the energy between two reacting molecules, the logarithm of the rate constant of the coupling may be assumed to correlate with S_{re} in a series of similar reactions such as the

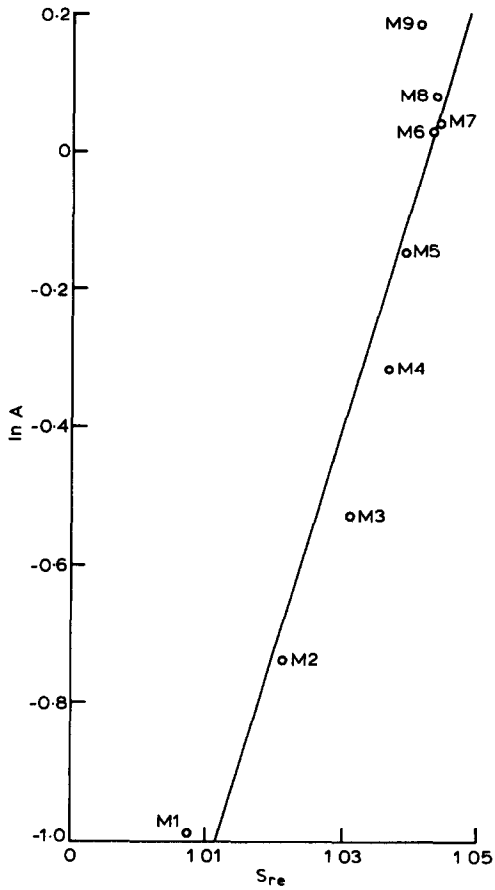


Fig. 3. Plot of superdelocalisabilities S_{re} against ln A.

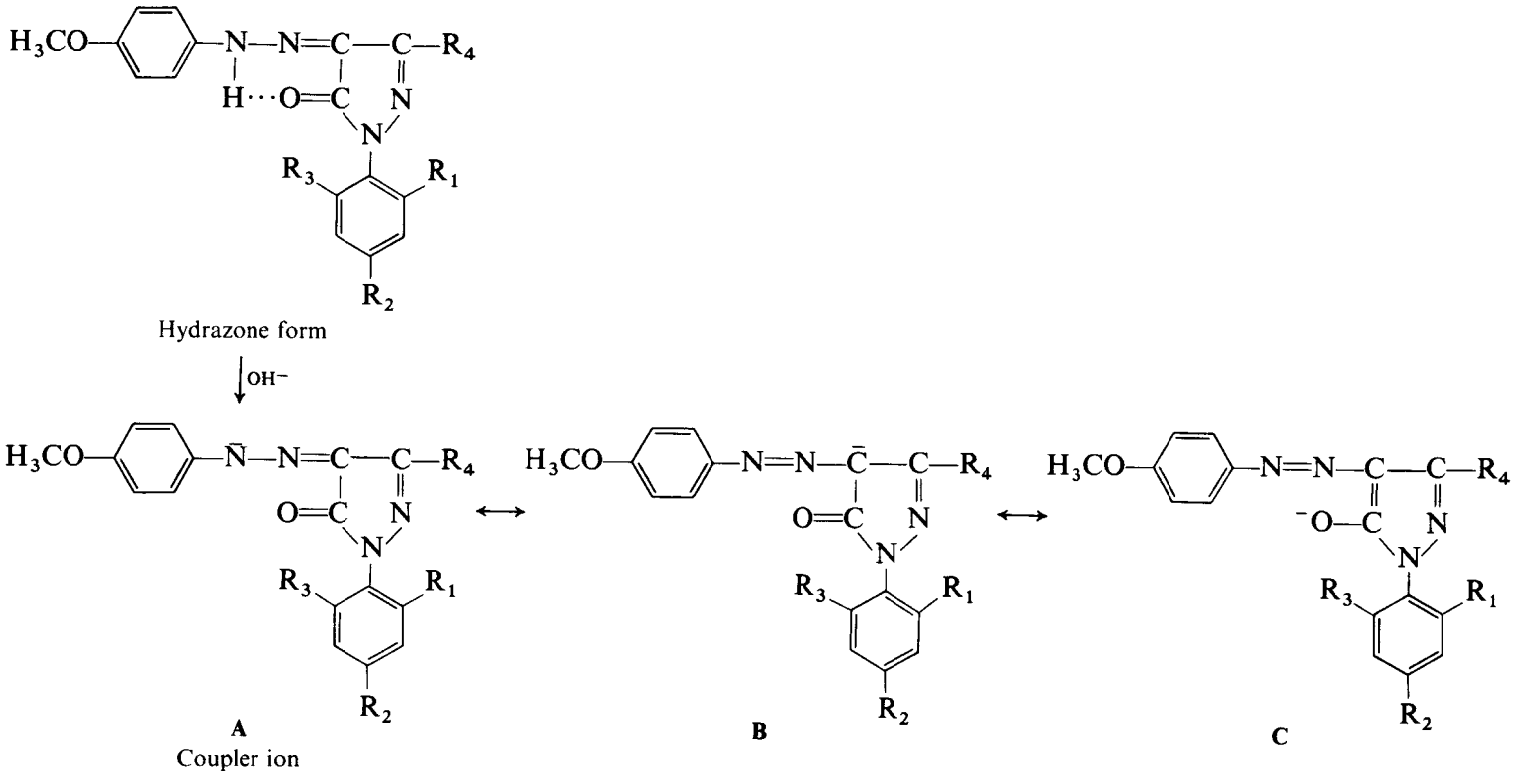
colour development of the masked pyrazolone colour couplers using the same developer. Therefore:

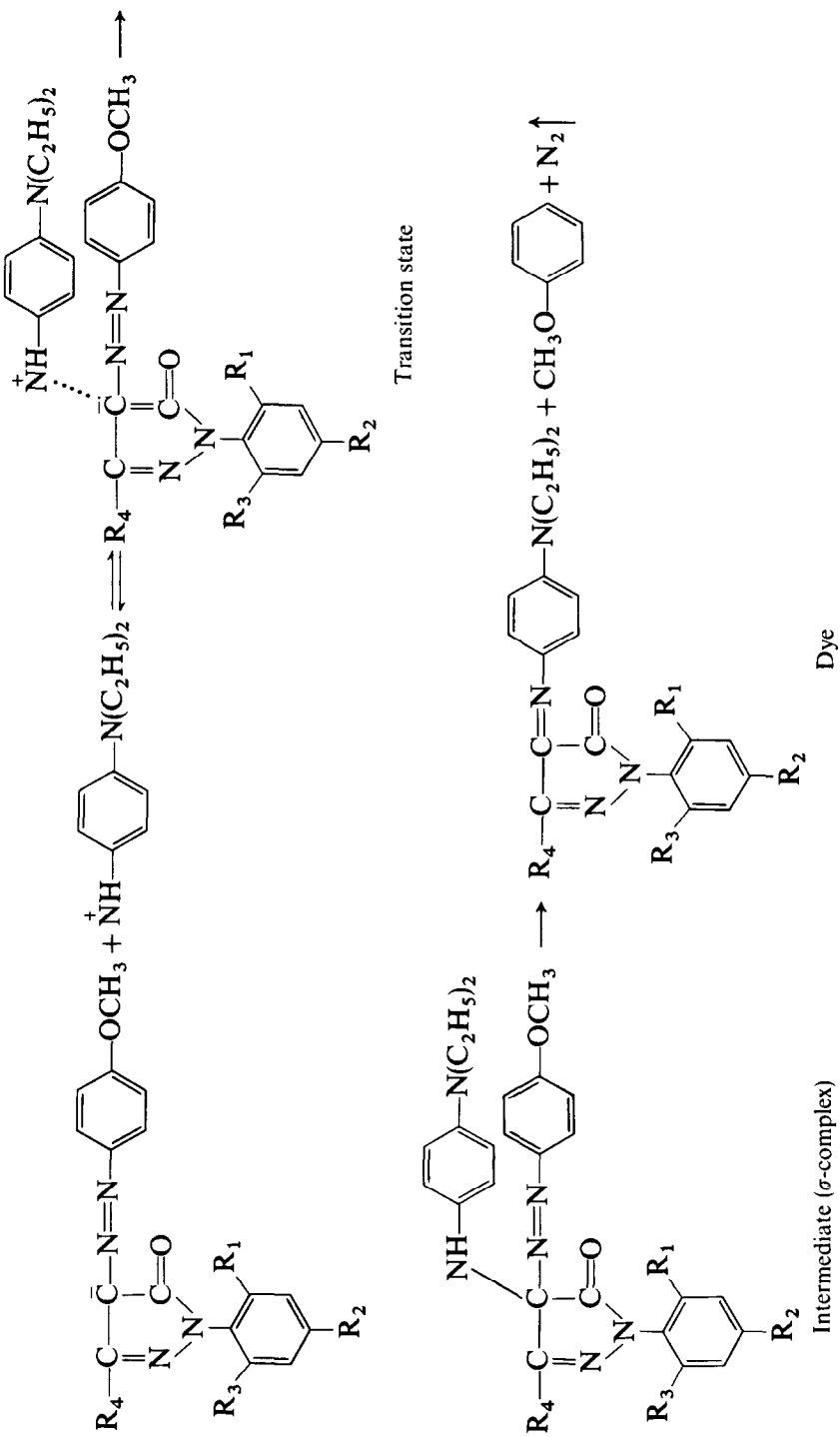
$$\log k_2 \propto S_{re}$$

When the values of A are in the range 0–3, A is linearly related to k_2/k_1 and thus a correlation between photographic activities A and superdelocalisabilities S_{re} results.

The reaction stages in the colour development of the masked pyrazolone couplers may thus be as depicted on page 128.

The coupler ion is a resonance hybrid of the electronic structures **A**, **B** and **C**. By resonance, a partial electronic charge is located at reaction site r, and the C_r–N bond has some double-bond character. In the course of the colour development the reaction sequences are as shown on page 129.


Hydrazone form
OH⁻
A
Coupler ion
B
C


Transition state
Intermediate (σ-complex)
Dye

4 CONCLUSIONS

Nine masked pyrazolone couplers were synthesised, and their photographic activities determined using the Elvegard equation.

The superdelocalisabilities, S_{re}, at the coupling site r, were calculated and a good correlation between ln A and S_{re} was obtained, viz.

$$\ln A = 31{\cdot}84 S_{re} - 33{\cdot}16 \quad (n = 9, r = 0{\cdot}95)$$

The equation may be used as a first guide to the structure design of masked pyrazolone couplers having higher photographic activity.

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APPENDIX

Composition of developing solution

TSS	0·6 g
Mask pyrazolone colour coupler	0·7 g
Sodium hydroxide	1·0 g
Potassium bromide	0·5 g
Sodium bisulphite, anhydrous	1·5 g
Hydroxylamine sulphate	1·0 g
Sodium phosphate tribasic	2·0 g
Dioxane	100 ml

Dilute with water to 600 ml; pH = 11·9.

Composition of bleaching solution

Potassium ferricyanide	50 g
Potassium bromide	25 g
Sodium acetate	60 g
Boric acid	5 g
Potassium aluminium sulphate	50 g

Dilute with water to 1000 ml; pH = 5·1–5·6.

Composition of fixing solution

Sodium thiosulphate	200 g

Dilute with water to 1000 ml; pH = 7–8.

Conditions of colour developing

	Time (min)	*Temperature (°C)*
Colour developing	3, 4, 5, 6, 8, 10	24 ± 1
Washing—1	2	12 ± 1
Washing—2	1	12 ± 1
Bleaching	3	12 ± 1
Washing	2	12 + 1
Fixing	5	12 + 1
Washing	5	12 + 1