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Development-Accelerator-Releasing (DAR) Couplers Part 2: Effect of the DAR Couplers with a Different Divalent Linking Group on the Photographic Characteristics of Color Negative Material

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ABSTRACT

In order to clarify the affect of the DAR couplers' divalent linking group's absorption to the photographic characteristics, two development-accelerator-releasing couplers were synthesized with a different linking group. The structure of the compounds was confirmed by elemental analysis: MS, NMR and IR spectroscopy. The effect of the DAR couplers on the photographic characteristics of color negative material has been studied. © 1997 Elsevier Science Ltd

Keywords: DAR coupler, effect, synthesis, divalent linking group, photographic characteristics, color negative material.

INTRODUCTION

The development-accelerator-releasing (DAR) coupler can be represented by the general formula Cp-L-A, in which Cp represents a coupler residue, A represents a development accelerating function group such as aryl hydrazine, and L represents a divalent linking group. We have previously studied the effect of the coupler residue on photographic characteristics, and in this paper, the effect of the linking group is studied. In order to clarify the affect of the L group's interaction with silver halide on the photographic

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characteristics of color negative material, 4-hydroxybenzene carbonic acid, which adsorbed on silver halide weakly [1] was used as divalent linking group and compared with the divalent 1.3.4-thiadiazole linking group system. It was found that the 1.3.4-thiadiazole system chemically interacts with the surface of silver halides [2].

SYNTHESIS OF THE DAR COUPLERS

Results and discussion

The DAR couplers can be synthesized by various routes, typically as shown in Scheme 1.

Relevant data on yields, melting points, elemental analysis and spectra of the compounds are given in Table 1.

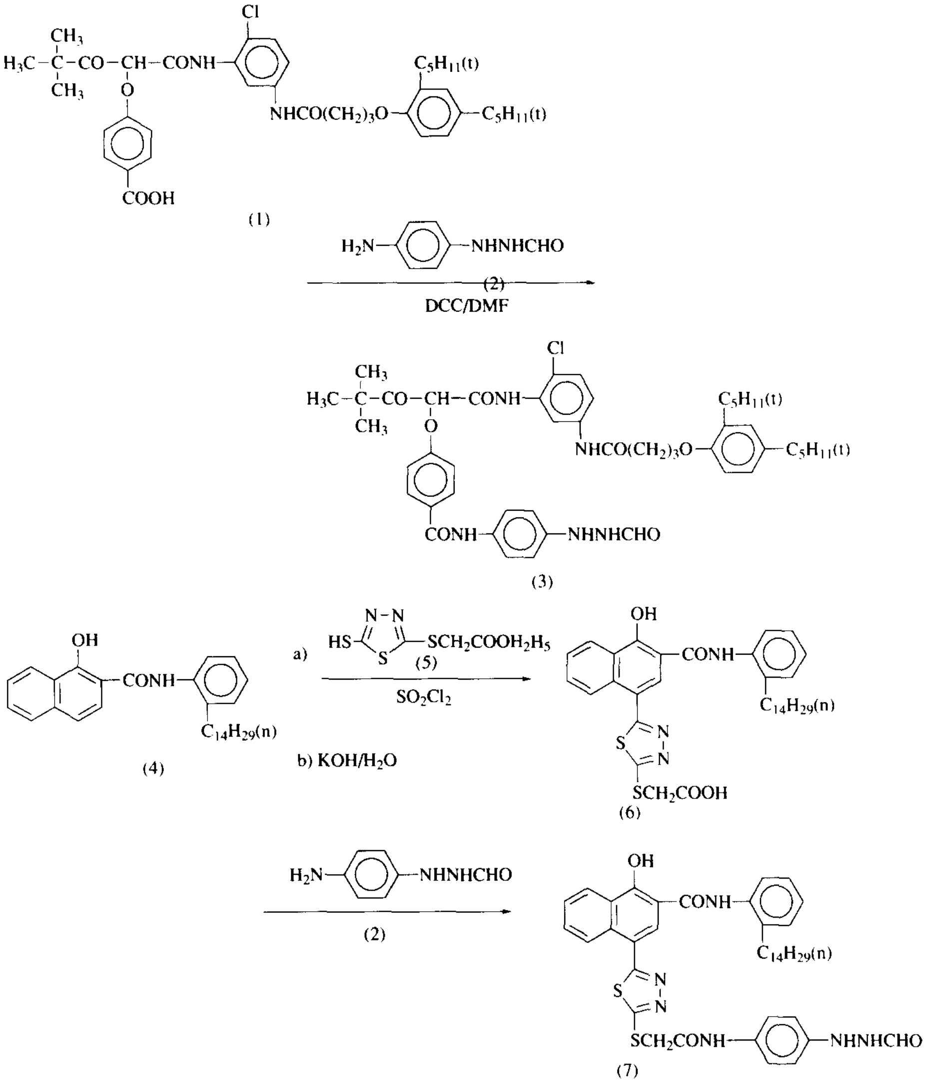
Experimental

General

Melting points are uncorrected. Elemental analyses were obtained using a Carlo Erba 1160R element analyser. Mass spectra were recorded on a Hitachi M-80 spectrometer with either FD or EI ionization. IR spectra were recorded on a 7650 spectrometer and ^{1}H-NMR spectra on a Bruker WP-100SY spectrometer. 1-Hydroxyl-N-(2-n-tetradecyloxyphenyl)-2-naphthamide (**1**) [3,4], 2.5-mercapto-1.3.4-thiodiazole [5,6], 1-formyl-2-(4-aminophenyl)-hydrazide (**5**) [7,8] and 2-ethoxycarbonylmethythio-5-mercapto-1,3,4-thiaadiazole (**4**) [9] were prepared by the literature procedure. 2-Pivaloyl-2-(4-carboxyphenoxy)-2-chloro-5-γ (2,4-ditert-pentylphenoxy)-butylformamido] acetanilide (**1**) was purchased from a related factory.

2-Pivaloyl-2-{4′-[4″-(2-formylhydrazino)anilinocarbonyl]phenoxy}-2-chloro-5-[γ-(2,4-ditert-pentylphenoxy)-butylformamido] acetanilide(3)

2-Pivaloyl-2-(4-carboxyphenoxy)-2-chloro-5-γ (2,4-ditert-pentylphenoxy)-butylformamido] acetanilide (**1**) (0.05 mol) and 1-formyl-2-(4-aminophenyl) hydrazine (**2**) (0.05 mol) were dissolved in DMF (100 ml). A solution of DCC (dicyclodihexylcarbodiimide) (0.05 mol) in DMF (20 ml) was added dropwise over 30 min at 0°C and stirring was continued at room temperature for 2 h, the solution was then filtered and the filtrate poured into cold water (100 ml); the products precipitated readily and were filtered, washed several times with water and recrystallized to give (**3**) as colorless solids. The yields melting points and analytical data are present in Tables 1 and 2.



Scheme 1

*1-Hydroxy-4-(2-carboxymethylthio-1.3.4-thiadiazole-5-thio)-N-(2-n-tetradecyloxy-phenyl)-2-naphthamide (**6**)*

To a solution of 2-ethoxycarbonylmethylthio-5-mercapto-1.3.4-thiadiazole (**2**) (0.1 mol) in CCl_4, a solution of sulfurylchloride (0.1 mol) in CCl_4 was added dropwise over 1 hr with ice cooling. Stirring was continued for 1 hr and then at room temperature for a further 0.5 hr. The solution of the Cyan coupler (0.1 mol) in CCl_4 was then added, and the mixture refluxed with

TABLE 1
Yields, Melting Points and Elemental Analysis

Compound	*Yield (%)*	*M.P. solvent (°C)*	*Molecular formula*	*Analysis found/calculated (%)* C	H	N
2	87	124–126[7,8]	$C_7H_9N_3O$	55.73 55.68	5.89 6.01	27.39 27.79
3	52	138–141	$C_{47}H_{58}N_5O_7Cl$	67.17 67.31	6.96 7.03	8.33 8.18
4	86	50–52[3,4]				
5	95	68–70	$C_6H_8N_2O_2S_3$	30.47 30.51	3.39 3.39	11.78 11.86
6	66	92–95				
7	49	165–169	$C_{42}H_{50}N_6O_5S_3$	62.10 61.91	6.27 6.18	10.08 10.31

stirring for 4 hr. After removal of CCl_4 by distillation, the residue was dissolved in EtOH. A solution of KOH (0.1 mol) in water was added, and stirring was continued at 60°C for 0.7 hr. After cooling, the solution was poured into a mixture of cold concentrated hydrochloric acid (20 ml) and water (100 ml). The products precipitated and were filtered, washed several times with water and recrystallized. Yields, melting points and analytical data are shown in Table 1.

TABLE 2
Spectral Data for Compounds **3** and **7**

Product	*IR KBr ν (cm^{-1})*	*H'-NMR(CD$_3$SOCD$_3$TMS) (ppm)*	*MS(FD)*m/z
3	3250(m,NH) 2959(s,CH_3C-H) 2867(m,CH_2,C-H) 1665(s,C = 6; O) 1600(s,C = C) 1510(s,N-H) 1230(m,Ph-O)	0.4–1.0(m,6H,2CH_3) 1.2(s,12H,4CH_3) 1.3(s,9H,3CH_3) 1.4–2.4(m,.,6H,CH_2,2CH_2Me) 2.4–2.7(t,2H,CH_2CON) 3.9–4.2(t,2H,-CH_2OPh) 5.6–5.7(d,1H,NHNHCHO) 5.8–6.0(d,1H,PhNHN) 6.6–7.7(m,13H,Ph) 8.1(s,1H,CHO) 7.8,8.2,8.8(s,3H,CONH)	815(M^+)
7	3323(m,NH) 2924(s,CH_3,C-H) 2850(m,CH_2,C-H) 1623(s,C = O) 1527(s,C = N) 1536(s,NH) 1450(m,$(CH_2)_4$ 1387(m,C-N) 1243(M,Ph-O) 761,745(m,Ph-1.2)	0.6–1.5(m,27H,$C_{13}H_{27}$) 3.9–4.3(m,4H,OCH_2,SCH_2) 6.6–8.6(m,13H,Ph) 8.1(s,1H,CHO) 8.8(s,1H,OH) 9.3–9.5(d,1H,NHNHCHO) 9.7(s,1H,CONHPh) 10.0–10.1(d,1H,PhNHN) 10.5(s,1H,CONHPh)	815(M^+)

Preparation of DAR coupler (7)
1-Hydroxy-4-(2-carboxymethylthio-1.3.4-thiadiazole-5-thio)-N-(2-n-tetradecyloxy-phenyl)-2-naphthamide (**6**) (0.05 mol) and 1-formyl-2-(4-aminophenyl)-hydrazide (0.05 mol) were dissolved in DMF. A solution of DCC (0.05 mol) in DMF was added dropwise at 0°C over 0.5 hr, and stirring was continued at room temperature for 2 hr. The solution was filtered, and the filtrate poured into cold water. When the product precipitated, it was filtered, washed several times with water and recrystallized to give compounds **7**. Yields, melting points and analytical data are shown in Tables 1 and 2.

EFFECT OF THE DAR COUPLERS ON THE PHOTOGRAPHIC CHARACTERISTIC OF THE COLOR NEGATIVE MATERIALS

Experimental

To examine the effect of DAR couplers on the photographic characteristics, a single-layer color negative coating structure was employed. For most of the experimentation, one coating contained an experimental 400-speed bromo-iodide T-grain emulsion sensitized to blue light together with the yellow dye-forming image coupler; another coating contained an experimental 400-speed bromo-iodide T-grain emulsion sensitized to red light, together with a cyan dye-forming image coupler.

To obtain dye sensitometric response curves, the coating was exposed stepwise to white light, followed by C-41 processing. The densities of the processed blue-sensitive and red-sensitive coating was measured using blue and red light.

Results and discussion

It is apparent from Table 3 that the photographic speed was not increased for the coatings incorporating the DAR yellow coupler **3** compared with the

TABLE 3
Effect of DAR Couplers on the Photographic Characteristics of Middle-speed Blue-sensitive Coatings

DAR coupler	*Laydown mol%**	*Relative sensitivity*	*Contrast*	*Fog*
	0	95	1.79	0.12
3	0.1	76	1.78	0.11
	0.5	100	1.72	0.13
	1.0	105	2.04	0.16

*The relative mol percent to the image coupler.

TABLE 4

Effect of DAR Couplers on the Photographic Characteristics of Middle-speed Red-sensitive Coatings

DAR coupler	*Laydown mol%**	*Relative sensitivity*	*Contrast*	*Fog*
	0	76	1.03	0.2
7	0.03	174	1.09	0.1
	0.17	191	0.98	0.11
	0.33	166	0.8	0.16

coating without DAR coupler. However, from Table 4, it can be seen that the increase in sensitivity was excellent for the coatings incorporating compound **7** when compared with the coatings without this compound for the middle-speed red-sensitive coatings; no increase in fogging was observed.

CONCLUSIONS

Two DAR couplers have been synthesized with different divalent linking groups. Photographic speed showed no increase when the DAR couplers adsorbed weakly on the silver halides. However, the more strongly the divalent linking group of the DAR coupler adsorbed on the silver halides, the more the photographic speed was increased.

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