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Synthesis and Electronic Absorption Spectra of 3-Cyano-4,6-Dinitro- and 3-N,N-Dialkylcarbamoyl-4,6-Dinitro-Phenylazo Dyes

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ABSTRACT

The synthesis of a series of the title compounds is described. The electronic absorption spectra are discussed on the basis of σ-frame-polarisation PPP–CI calculations.

1 INTRODUCTION

A large number of azo dyes exhibiting long wavelength absorption, and which contain a 2,4,6-acceptor-group substitution pattern in the diazocomponent of the dye (e.g. **1**[1], Fig. 1) have been described in the literature. These dyes have been developed because of the relative simplicity of their synthesis. However, an example (**2**[2], Fig. 1) showing the unusual 3,4,6-substitution pattern indicates that this arrangement may also provide a similar longwave absorption range.

Attempts to replace the 3-thiocyano group by other nucleophiles such as cyano, nitro or azido functions in an analogous manner, as was successful for **2** (i.e. nucleophilic substitution of the 3-chloro derivative of **2** by sodium or potassium cyanide, nitrite or azide respectively in dimethylformamide), failed in all cases. The current paper therefore presents a different synthetic pathway to a series of the title compounds and discusses their electronic-absorption-spectral properties, comparing the effect of transferring one acceptor group from the 2- to the 3-position.

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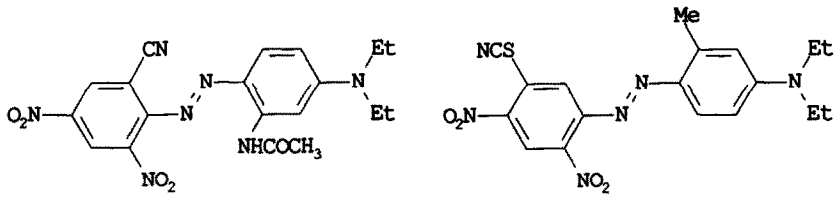


Fig. 1.

2 SYNTHESIS

The synthesis of the 3-substituted 4,6-dinitroanilines **3a–3c**, the precursors of the title compounds, was initiated by nitration of the commercially available 3-chlorobenzoic acid, yielding 3-chloro-4,6-dinitrobenzoic acid **4**[3], followed by transformation of the acid group to the corresponding amides **5** (Fig. 2). In order to obtain the cyano derivative **6**[3], the carboxamide **5a** was dehydrated with $SOCl_2$.[3]

Nucleophilic replacement of the chloro atom in **5b**, **5c** and **6** by means of ethanolic ammonia, to yield the anilines **3**, only occurred under drastic conditions. However, it is worth mentioning that the cyano derivative **6** was distinctly more reactive towards ammonia than the amides **5**, which not only can be explained by the larger acceptor effect of the cyano

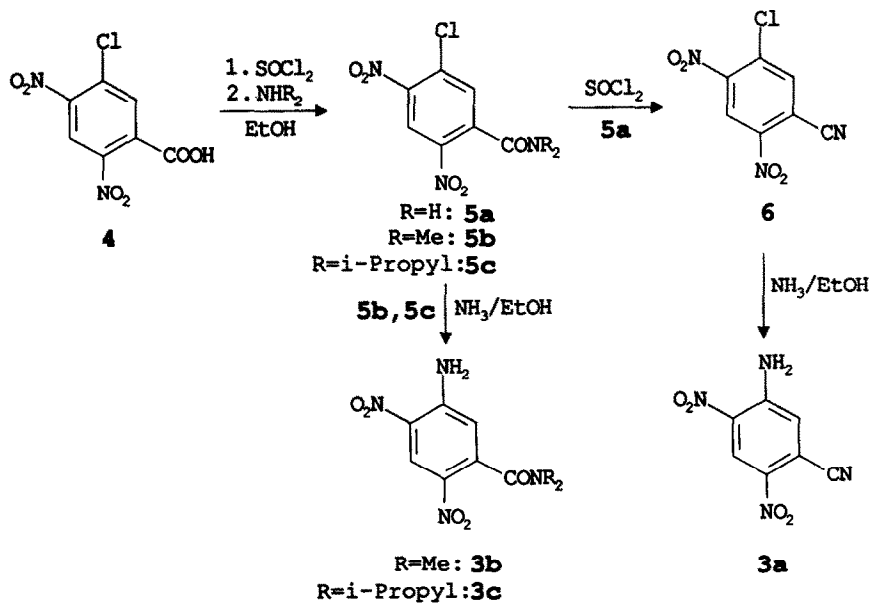
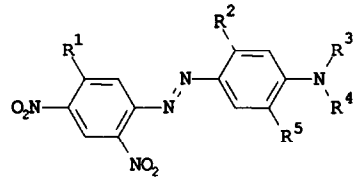


Fig. 2.

TABLE 1



7

7	R^1	R^2	R^3	R^4	R^5
a	CN	Me	Et	Et	H
b	CN	NHCOMe	Et	Et	H
c	CN	Me	Me	$C(Me)_2CH_2CH(Me)$	
d	$CONMe_2$	H	Et	Et	H
e	$CONMe_2$	H	C_2H_4OCOMe	C_2H_4OCOMe	H
f	$CONMe_2$	NHCOMe	Et	Et	H
g	$CONMe_2$	NHCOMe	*n*-Propyl	*n*-Propyl	H
h	$CON(CH(Me_2)_2$	H	Et	Et	H
i	$CON(CH(Me_2)_2$	NHCOMe	Et	Et	H

group in **6** compared with the carbonamide function in **5**, but also by the fact that the latter function, due to its spatial geometry in a position ortho to a nitro group, is no longer in planarity with the phenyl ring (cf. next section) hence further reducing its acceptor effect. Therefore, while **6** reacted at 70° under normal pressure within 1 h, **5** only underwent ammonolysis at 120° under *c.* 2·7 MPa pressure and several hours' reaction time.

Diazotisation was achieved in a 1:1 mixture of acetic and propionic acids at low temperature with nitrosyl sulphuric acid; coupling with the corresponding anilines was successful in an acetic acid/ethanol mixture (2:1) yielding the azo dyes **7a–7i** (Table 1).

3 ELECTRONIC ABSORPTION SPECTRA AND DISCUSSION

The electronic absorption spectra of the azo dyes **7** were measured quantitatively in dimethylsulphoxide and are compared in Table 2 with the first electronic transition from quantum-theoretical calculations based on a PISYSTEM-FOR-WINDOWS software package (R. Naef, unpublished). The same installed parameter set has been applied throughout. (The methyl group in **7a** was included as a pseudo heteroatom; the bis[2-(acetyloxy)ethyl]amino group in **7e** was simulated by slightly increasing the electronegativity of the nitrogen atom compared with that

TABLE 2
Experimental and Calculated Visible Absorption Maxima of Azo Dyes **1**[1c] and **7**

Dye	*Experimental*[a]		*Calculated*	
	λ_{max} *(nm)*	*log ε*	λ_{max} *(nm)*	f_{osc}
1	621[b]	4·72	590	1·17
7a	595	4·66	583	0·89
7b	593	4·71	594	0·91
7c	599	4·65		
7d	559	4·61	557	1·02
7e	531	4·53	529	0·99
7f	571	4·69	567	1·06
7g	572	4·72	567	1·06
7h	556	4·60	557	1·02
7i	569	4·62	567	1·06

[a] Solvent: dimethylsulphoxide.
[b] Solvent: chloroform.

of the diethylamino nitrogen atoms of the remaining dyes.) Force-field calculations suggest values of 23° and 53° respectively for the dihedral angles at the bonds between the 4-nitro group and the phenyl ring and between the 3-carboxamide function and the phenyl ring in the dyes **7d–7i**, which have been incorporated into the quantum-theoretical calculations.

Reviewing the experimental data in Table 2, three observations seem worth mentioning: first, transferring the cyano group from the 2- (in **1**) to the 3-position (in **7b**) moderately shifts the longwave absorption band to shorter wavelengths. Second, comparing the couple **7b/7f**, **7b/7i**, **7a/7d** or **7a/7h**, replacement of the cyano group by dialkylcarboxamide functions displaces the visible absorption band a further 20–30 nm to shorter wavelengths. This reflects the lower electron-acceptor nature of the carboxamides, further reduced in this case by distortion of the bond between this group and the phenyl ring mentioned above. Third, the dye pairs **7d/7h** and **7f/7i** show that increasing the steric bulk in the dialkylcarboxamide function by replacing the methyl by the isopropyl group has only a slight effect on the absorption spectra, which is consistent with the experience that force-field calculations revealed no significant difference in the dihedral angles between the phenyl ring and these two dialkylcarboxamide substituents.

The calculated results in Table 2 correlated fairly well with the experimental data, except for **1**, which was measured in a different solvent. Tentative variations of the electronegativity of the nitrogen atom in the

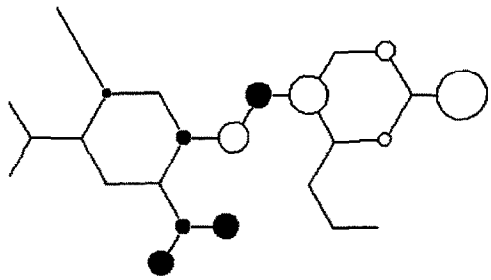


Fig. 3. π-Electron-density alterations for the electronic S^0–S^1 transition in **7b**. (Shaded circles: increase; empty circles: decrease; radius proportional to value).

acetylamino group indicate that different specific solvation effects at this function may account for this deviation.

The electron-density shift upon S^0–S^1 excitation in dyes **1** and **7** greatly resemble each other, essentially revealing a displacement of the π electrons from the dialkylamino group towards the 2-nitro group, as shown in example **7b** (Fig. 3).

4 EXPERIMENTAL

4.1. General

Melting points were measured using Dr Tottoli equipment (W. Büchi Glasapparatefabrik, Flawil, Switzerland). Microelemental analyses were carried out by the microanalytical department of Ciba-Geigy Ltd. ^{1}H-NMR spectra were recorded on a Bruker AM-360 spectrometer and electronic absorption spectra on a Perkin-Elmer Lambda 9 spectrophotometer at the Physics Department of Ciba-Geigy Ltd.

Theoretical calculations were executed on a Highscreen 486/33 computer. A PISYSTEM-FOR-WINDOWS software package (Naef, R., unpublished) was used for quantum-theoretical calculations, which is based on a PPP-CI method including a σ-frame polarisation procedure and consideration of all nonbonding interactions. Force-field computations were carried out by means of an ALCHEMY-Molecular-Modeling software package from Tripos Associates.

4.2 Synthesis of Intermediates

*4.2.1 3-Chloro-N,N-dimethyl-4,6-dinitrobenzamide (**5b**)*

3-Chloro-4,6-dinitrobenzoic acid **4** (10 g) (41 mmol) and 10 g (48 mmol) phosphorus pentachloride were blended homogeneously, allowing the

mixture to heat exothermally to a clear yellow liquid, which was maintained at 125° for 1 h. After distilling off the volatile phosphorus by-products under reduced pressure, the benzoyl chloride derivative, an oily residue, was dissolved in 100 ml diethylether, after which 10·2 g (226 mmol) gaseous dimethylamine were introduced within 1 h at −30°. The suspension was allowed to warm, filtered, the organic phase washed with water and evaporated. The residue was recrystallised from toluene/hexane to yield 5·2 g (47·5%) yellowish crystals, m.p. 172–74°C.

$C_9H_8N_3O_5Cl$ (273·6)

Calc.	C 39·51	H 2·95	N 15·36	O 29·24	Cl 12·96%
Found	C 40·0	H 3·1	N 15·2	O 28·3	Cl 13·3%

4.2.2 N,N-Bis(1-methylethyl)-3-chloro-4,6-dinitrobenzamide (5c)
After treating 10 g (41 mmol) 3-chloro-4,6-dinitrobenzoic acid **4** and 10 g (48 mmol) phosphorous pentachloride analogously to the previous example, the isolated benzoyl chloride was dissolved in 100 ml toluene, after which 20 g (200 mmol) diisopropylamine were introduced within 1 h with ice-cooling. After a further 90 min stirring at room temperature, the suspension was filtered, the organic phase washed with water, dried with sodium sulphate and evaporated. The crude product was recrystallised from chloroform/hexane, yielding 3 g (22%) yellow crystals, m.p. 178–79°C (decomposition).

$C_{13}H_{16}N_3O_5Cl$ (329·7)

Calc.	C 47·31	H 4·89	N 12·74	O 24·26	Cl 10·75%
Found	C 47·53	H 4·78	N 12·81	O 24·02	Cl 11·09%

*4.2.3 3-Amino-4,6-dinitrobenzonitrile (**3a**)*
To a suspension of 4·55 g (20 mmol) 3-chloro-4,6-dinitrobenzonitrile in 50 ml ethanol, 20 ml 30% aqueous ammonia were added and the mixture heated to 70–75°C for 1 h, resulting in a clear orange solution. After cooling to room temperature, 30 ml water were added and the brownish precipitate filtered. Recrystallisation from isopropanol gave 2·7 g (64·9%) yellowish crystals, m.p. 196–98°C.

$C_7H_4N_4O_4$ (208·1)

Calc.	C 40·40	H 1·94	N 26·92	O 30·75%
Found	C 40·3	H 2·0	N 26·6	O 30·4%

*4.2.4 3-Amino-N,N-dimethyl-4,6-dinitrobenzamide (**3b**)*
In a solution of 30 ml ethanol and 11 g gaseous ammonia, 2·94 g (10·7 mol), 3-chloro-N,N-dimethyl-4,6-dinitrobenzamide (**5b**) were heated

to 120°C under 28 MPa pressure for 6 h. After cooling to room temperature the resulting suspension was filtered and the precipitate washed with ethanol to yield 2·4 g (88%) yellow crystals, m.p. 250–52°C (decomposition).

$C_9H_{10}N_4O_5$ (254·2)

Calc.	C 42·52	H 3·97	N 22·04	O 31·47%
Found	C 42·57	H 4·01	N 22·24	O 31·57%

4.2.5 3-Amino-N,N-bis(1-methylethyl)-4,6-dinitrobenzamide (3c)
Treating 3 g (9 mmol) 3-chloro-N,N-bis(1-methylethyl)-4,6-dinitrobenzamide (**5c**) analogously to the previous example (**5b**) yielded 2·37 g (85%) yellow crystals, m.p. 286–89°C (decomposition).

$C_{13}H_{18}N_4O_5$ (310·3)

Calc.	C 50·32	H 5·85	N 18·06	O 25·78%
Found	C 50·33	H 5·97	N 18·22	O 25·76%

4.3 Synthesis of Azo Dyes (7)

4.3.1 General procedure
In a mixture of 3 ml acetic acid and 3 ml propionic acid, 1 mmol of the corresponding amine **3** was suspended. After admixing a solution of 0·5 ml acetic acid, 0·5 ml propionic acid and 0·5 ml sulphuric acid with cooling, 0·2 ml 40% nitrosyl-sulphuric acid was added slowly at 0–5°C over 30 min and the mixture stirred for a further hour. The clear yellow diazonium solution was then gradually transferred at 0–5°C to a solution of 1 mmol of the corresponding coupling component in a mixture of 1·5 ml ethanol and 2·5 ml acetic acid, buffered with sodium acetate. After stirring the deeply coloured solution for 20 min, the product was precipitated with water, filtered and dried.

3-[[4-(Diethylamino)-2-methylphenyl]azo]-4,6-dinitrobenzonitrile (7a). From 208 mg **3a** and 150 mg N,N-diethyl-3-methylbenzenamine. Purification by recrystallisation from isopropanol. Yield 94 mg (24·6%); m.p. 216°C (decomposition).

$C_{18}H_{18}N_6O_4$ (382·4)

Calc.	C 56·64	H 4·74	N 21·98	O 16·74%
Found	C 56·8	H 4·8	N 21·2	O 16·8%

N-[2-[(3-Cyano-4,6-dinitrophenyl)azo]-5-(diethylamino)phenyl]acetamide (7b). From 208 mg **3a** and 206 mg N-[3-(diethylamino)phenyl]acetamide.

Purification on a silica-gel column with toluene/ethylacetate (20:1). Yield 190 mg (44·7%); m.p. 243–44°C.

$C_{19}H_{19}N_7O_5$ (425·4)

Calc.	C 53·65	H 4·50	N 23·05	O 18·80%
Found	C 53·7	H 4·6	N 22·9	O 18·6%

*4,6-dinitro-3-[[1,2,3,4-tetrahydro-1,2,2,4,7-pentamethylquinolyl-6]azo]-benzonitrile (**7c**).* From 208 mg **3a** and 190 mg 1,2,3,4-tetrahydro-1,2,2,4,7-pentamethylquinoline. Purification by recrystallisation from toluene/isopropanol. Yield 137 mg (33·5%); m.p. 231–32°C.

$C_{20}H_{20}N_6O_4$ (408·4)

Calc.	C 58·82	H 4·94	N 20·58	O 15·67%
Found	C 58·9	H 5·1	N 20·5	O 15·7%

*3-[[4-(Diethylamino)phenyl]azo]-N,N-dimethyl-4,6-dinitrobenzamide (**7d**).* From 250 mg **3b** and 150 mg N,N-diethylbenzenamine. Purification on a silica-gel column with toluene/acetone (8 : 2). Yield 360 mg (87%); m.p. 212°C.

$C_{19}H_{22}N_6O_5$ (414·4)

Calc.	C 55·07	H 5·35	N 20·28	O 19·30%
Found	C 54·96	H 5·38	N 20·46	O 19·30%

*3-[[4-[bis{2-(acetoxy)ethyl}amino]phenyl]azo]-N,N-dimethyl-4,6-dinitrobenzamide (**7e**).* From 250 mg **3b** and 265 mg 2,2'-(phenylimino)-bisethanol, diacetate. Purification on a silical-gel column with toluene/acetone (9 : 1). Yield 310 mg (58%); m.p. 102°C.

$C_{23}H_{26}N_6O_9$ (530·5)

Calc.	C 52·07	H 4·94	N 15·84	O 27·14%
Found	C 58·04	H 5·10	N 15·81	O 27·14%

*3-[[2-(Acetylamino)-4-(diethylamino)phenyl]azo]-N,N-dimethyl-4,6-dinitrobenzamide (**7f**).* From 250 mg **3b** and 206 mg N-[3-(diethylamino)phenyl]-acetamide. Purification on a silical-gel column with toluene/acetone/acetic acid (8 : 1 : 1). Yield 260 mg (76%); m.p. 266–68°C.

$C_{21}H_{25}N_7O_6$ (471·5)

Calc.	C 53·50	H 5·34	N 20·80	O 20·36%
Found	C 53·30	H 5·47	N 20·25	O 20·78%

3-[[2-(Acetylamino)-4-(dipropylamino)phenyl]azo]-N,N-dimethyl-4,6-dinitrobenzamide (7g). From 250 mg **3b** and 250 mg N-[3-(dipropylamino)phenyl]-acetamide. Purification on a silica-gel column with toluene/acetone (9 : 1). Yield 430 mg (84%); m.p. 202–203°C.

$C_{24}H_{31}N_7O_6$ (513·6)

Calc.	C 56·13	H 6·08	N 19·09	O 18·69%
Found	C 55·80	H 6·24	N 19·07	O 18·63%

N,N-Bis(1-methylethyl)-3-[[4-(diethylamino)phenyl]azo]-4,6-dinitrobenzamide (7h). From 310 mg **3c** and 150 mg N,N-diethylbenzenamine. Purification by recrystallisation from chloroform/hexane. Yield 340 mg (72%); m.p. 212°C.

$C_{23}H_{30}N_6O_5$ (470·5)

Calc.	C 58·71	H 6·43	N 17·86	O 17·00%
Found	C 58·59	H 6·31	N 17·84	O 16·96%

3-[[2-(Acetylamino)-4-(diethylamino)phenyl]azo]-N,N-bis(1-methylethyl)-4,6-dinitro-benzamide (7i). From 310 mg **3c** and 210 mg N-[3-(diethyl-amino)phenyl]acetamide. Purification on a silica-gel column with toluene/acetone/acetic acid (8:1:1). Yield 400 mg (76%); m.p. 159–61°C.

$C_{25}H_{33}N_7O_6$ (527·6)

Calc.	C 56·92	H 6·30	N 18·58	O 18·20%
Found	C 57·37	H 6·28	N 18·27	O 18·55%

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