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Synthesis, ^{1}H-NMR and Electronic Absorption Spectra of 2,6-Disubstituted Derivatives of 2,6-Dihydrobenz [1,2-*c*:4,5-*c*′]dipyrazol-3,7-dione, a New Cross-Conjugated Chromophore

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ABSTRACT

The synthesis of a series of 2,6-substituted 2,6-dihydrobenz[1,2-c:4,5-c′]-dipyrazol-3,7-diones is described and their postulated structures confirmed by means of ^{1}H-NMR and mass spectroscopy. The electronic absorption spectra and the changes of bond and charge orders upon electronic excitation are discussed on the basis of Variable-Electronegativity PPP-CI calculations.

1 INTRODUCTION

Among the approximately one dozen basic chromophoric systems,[1] the indigoid dyes, due to their unconventional molecular structure, have for more than a decade been the special goal of a number of experimental and theoretical investigations. The special properties of the inherent cross conjugation have been recognised as being responsible for the high bathochromicity of these π systems, which has been explained by Klessinger in a simple but straightforward manner in terms of perturbational molecular-orbital (MO) theory.[2]

However, in recent years new chromophores have been developed, which are also classifiable as cross-conjugated, this term describing a π system with two sets of donor-acceptor couples in opposition, conjugating over one or more common π bonds, and which can be derived from their smallest

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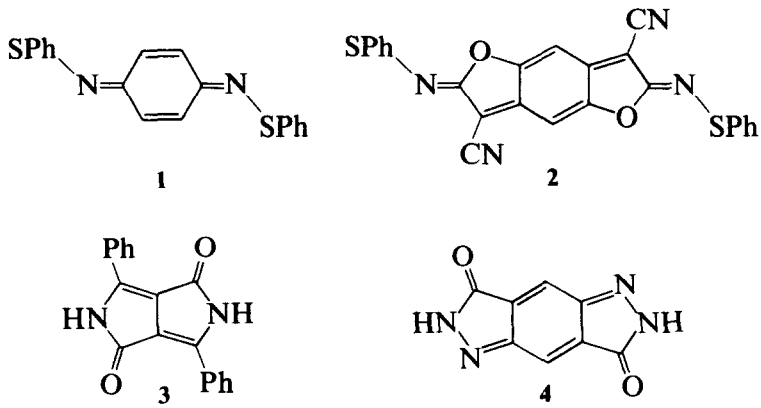


Scheme 1

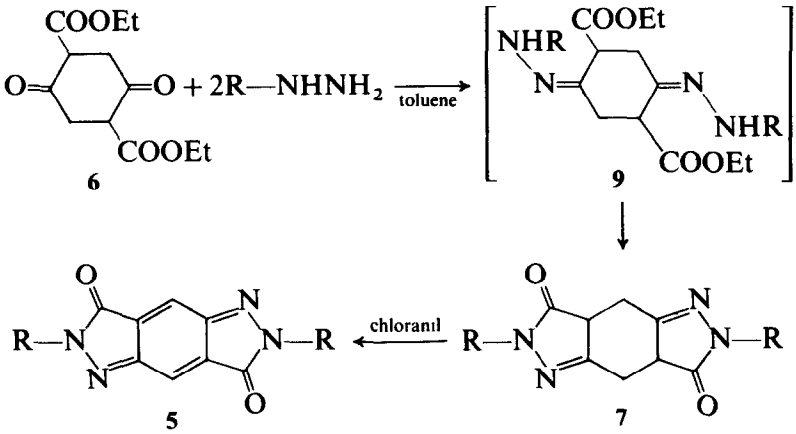
representative glyoxime. Examples are **1**,[3] **2**[4] and, less obviously, **3**[5,6] (Scheme 1).

In the present paper, the synthesis of some derivatives of a further example of a cross-conjugated chromophore, 2,6-dihydrobenz[1,2-*c*:4,5-*c'*]-dipyrazol-3,7-dione (**4**) (Scheme 1), is reported and their structure elucidated by means of ^{1}H-NMR spectroscopy. The electronic absorption spectra will be discussed on the basis of SCF-CI calculations and by means of perturbational MO theory.

2 SYNTHESES

The title compounds (**5**) were obtained in two steps by the reaction of the commercially available diketodiester (**6**) with variously substituted hydrazines[7] and subsequent oxidation of the intermediates (**7**) with chloranil (Scheme 2). Product **8** (Scheme 3), which was claimed to form under slightly different reaction conditions in a patent specification,[8] could be excluded from the ^{1}H-NMR considerations discussed below.

However, the reaction sequence exhibited some limitations. First, the primary condensation products of **6** with the hydrazines, i.e. the dihydrazones (**9**) (Scheme 2), only proceeded to **7** if, except for hydrazine itself, the nucleophilicity of the α-nitrogen in the substituted hydrazines was kept above a certain limit. Thus, reaction of **6** with 4-nitrophenylhydrazine did not result in **7**, but in isolable **9** (with R = 4-nitrophenyl), which resisted all attempts to be cyclised to **7**. Similarly, while 2-naphthylhydrazine did react with **6** to **7**, although in low yield, an analogous product with the parent 1-naphthylhydrazine and its 6-sulphonic-acid derivative as well as 2-naphthylhydrazine-5-sulphonic acid could not be observed. Secondly,

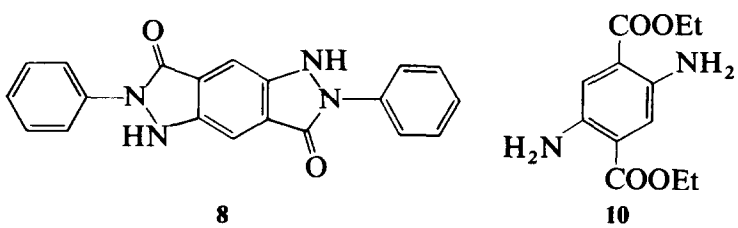


	R
A	CH_3
B	C_2H_5OH
C	$C_2H_5OCOCH_3$
D	phenyl
E	4-methoxyphenyl
F	2-naphthyl

Scheme 2

attempts to increase the generally low yield of the primary reaction step (which was best carried out in boiling toluene without any catalyst) by using acetic acid as a solvent resulted in an unusual intramolecular redox process. Therefore, when phenylhydrazine was condensed with **6** in acetic acid at room temperature, the *p*-phenylenediamine derivative (**10**) (Scheme 3), was isolated in high yield, which can be explained by the elimination of two equivalents of aniline from the corresponding intermediate (**9D**). Thirdly, the final oxidative step to **5** could only be carried out if **7** was soluble enough in organic solvents, which was not the case for **7** ($R = H$)[9] and therefore prevented the synthesis of the unsubstituted title compound.

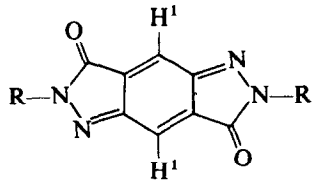
Product **5C** was obtained from **5B** as a by-product of the oxidation of **7B** on prolonged boiling of the acetic-acid solution.

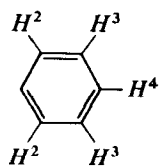
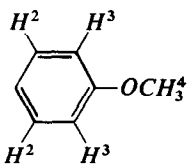


Scheme 3

TABLE 1

Proton Signals of Dyes **5A–5E** from 360-MHz/NMR Measurements in Deuterochloroform



Proton	*Chemical shift (ppm) (multiplicity,[a] number)*				
	5A	***5B***	***5C***	***5D***	***5E***[b]
	$R = CH_3{}^2$	$R = CH_2{}^2CH_2{}^3OH^4$	$R = CH_2{}^2CH_2{}^3OCOCH_3{}^4$	$R =$ 	$R =$ 
1	7·73 (s, 2)	7·76 (s, 2)	7·79 (s, 2)	7·84 (s, 2)	Unresolved
2	3·59 (s, 6)	4·04/4·06/4·08 (t, 4)	4·17/4·19/4·21 (t, 4)	7·86/7·88 (d, 4)	7·75/7·77 (d, 4)
3	—	3·85/3·87/3·89/3·91 (q, 4)	4·39/4·41/4·43 (t, 4)	7·37/7·39/7·41 (t, 4)	7·07/7·09 (d, 4)
4	—	4·54/4·56/4·58 (t, 2)	2·05 (s, 6)	7·22/7·24/7·26 (t, 2)	3·83 (s, 6)

[a] Multiplicities: s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet.

[b] Solvent: perdeutero-dimethylsulphoxide.

3 ^{1}H-NMR SPECTRA

3.1 Method

^{1}H-NMR spectra of compounds **5** were generally recorded on a 360-MHz Fourier NMR spectrometer with deuterochloroform as solvent, except for **5E** where, due to low solubility, perdeutero-dimethylsulphoxide had to be used, and tetramethylsilane as internal standard. **5F** was not soluble enough in any solvent for NMR spectroscopy.

3.2 Results and discussion

In Table 1 the NMR signals of dyes **5A–5E** are collected. Due to the inversion symmetry and the few protons, the method provides only limited information. However, two points should be stressed: in none of the systems was any further signal found that could be ascribed to a hydrazide proton of the reduced analogon of **8**,[8] and the two protons H^1 are shifted to a substantially lower field than the corresponding two aromatic protons in the unexpected product (**10**) which have a similar neighbourhood to those in **8** and absorb at 7·29 ppm. These facts leave little doubt about the correctness of the assumed structure of the dyes.

In order to remove any ambiguity about the oxidation state, mass spectra of **5A**, **5E** and **5F** have been recorded that showed no higher masses than the mass peaks of the molecular ions (i.e. $m/z = 216$, 400 and 440, respectively).

4 ELECTRONIC ABSORPTION SPECTRA

Data of the electronic absorption measurements of dyes **5A–5F** are summarised in Table 2 and compared with results from SCF-CI calculations based on a VEPPPM (Variable-Electronegativity Pariser Parr Pople Mataga) software package (Naef, R., unpublished). It seems evident that the basic chromophore is the 14-centre π system (**4**). However, replacement of the alkyl substituents in **5A–5C** by aryl groups (**5D–5F**) results in a distinct bathochromic shift, which is also reflected in the theoretical results. The next two π–π^* transitions, of which experimentally only the second one with the expected low intensity can be observed, are symmetry-forbidden. These calculations also provide some insight into the electron-rearrangement pattern upon electronic excitation, which is illustrated in examples **4** and **5D** in Figs 1 and 2.

Considering the π-electron density changes (Fig. 1), it is apparent that the nitrogen atoms at positions 2 and 6 lose a substantial amount (about 11%) of

TABLE 2
Experimental and Calculated Visible Absorption Maxima of Dyes **5A–5F**

Dye	*Experimental*[a]		*Calculated*	
	λ_{max} (*nm*)	*log* ε	λ_{max} (*nm*)	f_{osc}
5A	560/541/521[b]	4·28	545	0·88
			487	0·0
	372	3·15	382	0·0
5B	560/541/518[b]	4·28	545	0·88
			487	0·0
	372	3·08	382	0·0
5C	550/534/512[b]	4·30	545	0·88
			487	0·0
	368	3·15	382	0·0
5D	580	4·14	598	1·01
			547	0·0
	400	3·15	389	0·0
5E	614	4·22	609	0·96
			564	0·0
	390	3·64	392	0·0
5F	609	3·99	591	1·13
			539	0·0
	400	3·59	382	0·0

[a] Solvent: chloroform.
[b] Vibrational band structure.

electron density in favour of those at positions 1 and 5 (apart from the carbons at positions 4 and 8), thus showing the typical attributes of a donor-acceptor chromogen. The change of bond orders (Fig. 2) is typical for π systems with highly localised double-bond/single-bond alternation, in that bond orders of bonds with strong double-bond character are decreased and *vice versa*. The fairly high degree of bond-order change (the largest circles in

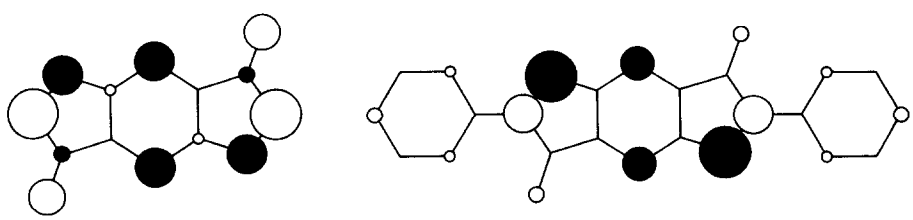


Fig. 1. π-Electron density changes in **4** (left) and **5D** (right) for the electronic S^0–S^1 transition (full circles—increase; empty circles—decrease; radius proportional to value).

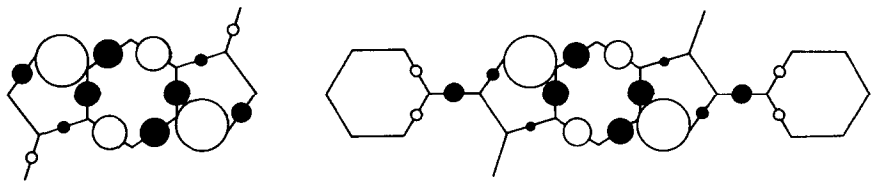


Fig. 2. Bond-order changes in **4** (left) and **5D** (right) for the electronic S^0–S^1 transition (full circles—increase; empty circles—decrease; radius proportional to value).

Fig. 2 represent a value of about −0·14) accounts for the intensity order of the vibrational transitions of 0–1 > 0–0 ≈ 0–2, well resolved in the case of **5A–5C** by their very rigid π frame, and for the broad band width in the larger π systems, **5D–5F**, where the low rotation-energy barrier between chromogen and aryl substituents (bond order in ground state of **5D** between chromogen and phenyl group: 0·30) prevents analogous band resolution.

It is obvious from Figs 1 and 2 that the carbonyl groups only contribute to a minor degree to the electronic transition, and thus essentially seem to have a bridging function.

5 EXPERIMENTAL

5.1 General

Corrected melting points were measured using Dr Tottoli equipment from W. Büchi Glasapparatefabrik, Flawil, Switzerland. The elemental and microanalytical department of Ciba-Geigy AG carried out the micro-elemental analyses. ^{1}H-NMR spectra were recorded on a Bruker AM-360, mass spectra on a Varian CH7, IR spectra on a Perkin-Elmer 983 spectrometer and electronic absorption spectra on a Perkin-Elmer Lambda 9 spectrophotometer at the Physics Department of Ciba-Geigy AG.

Calculations were performed on a Compac Deskpro 386/20e computer with a Brother HL-8e laser printer. For quantum-chemical calculations, a VEPPPM software package (Naef, R., unpublished) was used. Laser printout of some results was performed by a Pizzazz Plus program from Application Techniques Inc., Brooklyn, NY.

5.2 Syntheses

2,4,6,8-Tetrahydrobenzo[1,2-c:4,5-c']dipyrazole-3,7-diones (7)

General procedure. 7·7 g (30 mmol) of **6** was heated for 3–5 h with 66 mmol of hydrazine or correspondingly monosubstituted hydrazine in 100 ml of toluene. The precipitating yellow product was, after cooling, collected and dried under vacuum at 60°C. Low solubility prevented further purification.

Yields: **7** (R = H):[8] 5·7 g (99%), **7A**: 6·6 g (100%), **7B**: 6·0 g (71·4%), **7D**:[6] 2·1 g (20·4%), **7E**: 3·75 g (30·9%), **7F**: 4·9 g (36·8%).

*Benzo[1,2-c:4,5-c']dipyrazole-3,7-diones (**5**)*

General procedure. To a g of **7**, suspended in b ml of acetic acid, c g of chloranil was added and heated for d h under reflux conditions (except for **5B**). The precipitate was filtered from the hot solution and dried under vacuum at 70°C.

*2,6-Dimethylbenzo[1,2-c:4,5-c']dipyrazole-3,7-dione (**5A**).* From **7A**, a = 1·05 (4·8 mmol), b = 50, c = 2·2 (9 mmol), d = 0·5. Yield, 550 mg (53%); m.p., 315–6°C. For $C_{10}H_8N_4O_2$ (216·2), the calculated values were C 55·56, H 3·73, N 25·92, O 14·8%; and the experimental values were C 55·4, H 3·8, N 25·9, O 14·8%.

*2,6-Bis(2-hydroxyethyl)-benzo[1,2-c:4,5-c']dipyrazole-3,7-dione (**5B**).* From **7B**, a = 2·8 (10 mmol), b = 100, c = 4·9 (20 mmol), d = 3·5 (temperature 60°C). Yield, 1·46 g (53%); m.p., 209–10°C. For $C_{12}H_{12}N_4O_4$ (276·3), the calculated values were C 52·17, H 4·38, N 20·28, O 23·17%; and the experimental values were C 52·1, H 4·5, N 19·8, O 23·5%.

*2,6-Bis(2-acetoxyethyl)-benzo[1,2-c:4,5-c']dipyrazole-3,7-dione (**5C**).* From **7B**, a = 2·8 (10 mmol), b = 100, c = 4·9 (20 mmol), d = 10. Yield, 1·95 g (70·7%); m.p., 154–6°C (recrystallised from isopropanol/acetone 9:1). For $C_{16}H_{16}N_4O_6$ (360·3), the calculated values were C 53·33, H 4·48, N 15·55, O 26·64%; and the experimental values were C 53·45, H 4·55, N 15·75, O 26·8%.

*2,6-Diphenylbenzo[1,2-c:4,5-c']dipyrazole-3,7-dione (**5D**).* From **7D**, a = 1·86 (5·4 mmol), b = 50, c = 2·65 (10·8 mmol), d = 1·0. Yield, 660 mg (36%); m.p. 281–2°C (recrystallised from acetic acid). For $C_{20}H_{12}N_4O_2 \cdot 0{\cdot}1\,H_2O$ (342·2), the calculated values were C 70·21, H 3·59, N 16·38, O 9·82%; and the experimental values were C 70·0, H 4·3, N 15·9, O 9·75%.

*2,6-Bis(4-methoxyphenyl)-benzo[1,2-c:4,5-c']dipyrazole-3,7-dione (**5E**).* From **7E**, a = 2·02 (5 mmol), b = 75, c = 2·46 (10 mmol), d = 1·5. Yield, 1·88 g (94%); m.p., 300°C. For $C_{22}H_{16}N_4O_4 \cdot 0{\cdot}2\,H_2O$ (404·0), the calculated values were C 65·41, H 4·09, N 13·87, O 16·63%; and the experimental values were C 65·5, H 4·0, N 14·0, O 16·5%.

*2,6-Bis(2-naphthyl)-benzo[1,2-c:4,5-c']dipyrazole-3,7-dione (**5F**).* From **7F**, a = 1·78 (4 mmol), b = 50, c = 1·96 (8 mmol), d = 1·5. Yield, 1·35 g (77%);

m.p., >330°C (crystallised from *N,N*-dimethylformamide/water). For $C_{28}H_{16}N_4O_2 . 0{\cdot}4\,H_2O$ (447·7), the calculated values were C 75·12, H 3·78, N 12·52, O 8·58%; and the experimental values were C 75·0, H 4·1, N 12·6, O 8·3%.

*2,5-Bis(4-nitrophenylhydrazono)-1,4-cyclohexanedicarboxylic acid, diethylester (**9**, R = 4-nitrophenyl)*

7·7 g (30 mmol) of **6** and 9·2 g (60 mmol) of 4-nitrophenylhydrazine were heated in 150 ml of ethanol for 18 h. The orange precipitate was, after cooling, collected and recrystallised from ethanol/toluene (1:1), yielding 12·9 g (95%) of product with m.p. 228°C (decomposition). For $C_{24}H_{26}N_6O_8$ (526·5), the calculated values were C 54·75, H 4·98, N 15·96, O 24·31%; and the experimental values were C 54·7, H 5·0, N 15·9, O 24·3%.

*2,5-Diamino-1,4-benzenedicarboxylic acid, diethylester (**10**)*

A suspension of 5·12 g (20 mmol) of **6** and 4·76 g (44 mmol) of phenylhydrazine was stirred in 150 ml of acetic acid at room temperature for 2 h. The dark brown solution was then diluted with water and extracted with methylenechloride. After drying the organic phase with sodium sulphate, the solution was concentrated by distillation and the product precipitated with cyclohexane. Purification was accomplished on silica gel with ethylacetate/hexane (3:7), yielding 4 g (79%) of light yellow needles with m.p. 165–7°C (Ref. 10: 168°C). IR (KBr) (cm^{-1}): 3460 s, 3362 s, 1678 s, 1578 s, 1284 s, 1214 s, 1123 m, 1104 s, 1028 m, 900 m, 793 m. ^{1}H-NMR ($CDCl_3$) (ppm): 7·29 (s, 2 H), 5·08 (s, 4 H), 4·37/4·35/4·33/4·31 (q, 4 H), 1·40/1·38/1·36 (t, 6 H).

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