1,1′-Bi-(2-aryl-1,2-dihydrophthalazinylidenes): Potential New Pigments. Relief of Strain by a *trans*-Folded Alkene Linkage

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1-Hydroxy-2-aryl-1,2-dihydrophthalazines are dimerized to give 1,1′-bi-(2-aryl-1,2-dihydrophthalazinylidenes); an *X*-ray crystal structure shows a relief of strain in these compounds by a *trans*-folded alkene linkage and a buckling of the phthalazinyl ring.

Six-membered heterocyclic ylidenes are a remarkably rare class of compounds.[1,2] The lack of examples was earlier ascribed[1] to possible increased steric hindrance between the six-membered rings at each end of the alkene unit relative to the five-membered heterocyclic analogues, such as indigo, which are more common. In strained five-membered ylidenes the double bond is twisted out of planarity (I) and for example the torsional angle in 9,9′-bifluorenylidene is 33°.[3,4] In

Table 1.

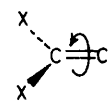
Compound	X	Y	M.p./°C	% Yield	Compound	M.p./°C	% Yield[e]
(2a)	H	MeO	120—121[a]	79	**(3a)**	232—233[c]	58
(2b)	H	Me	85—87	70	**(3b)**	256—257[b]	60
(2c)	H	H	130—131[b]	96	**(3c)**	230—231[b]	48
(2d)	H	Br	149—150[a]	99	**(3d)**	245—246[d]	49
(2e)	Me	H	124—125	79	**(3e)**	232—233[c]	78
(2f)	Br	H	146—148	96	**(3f)**	251	51

[a] From benzene. [b] From MeCN. [c] From chloroform–acetonitrile (1 : 1, v/v). [d] From chloroform. [e] The remainder was starting material recovered.

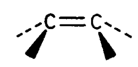
Table 2. U.v.–visible absorptions (nm) in acetonitrile.

Compound	$\lambda_{max.}$ (log ε)	$\lambda_{max.}$ (log ε)	$\lambda_{max.}$ (log ε)	$\lambda_{max.}$ (log ε)	$\lambda_{max.}$ (log ε)	$\lambda_{max.}$ (log ε)
(3a)	597(3.24)	389(3.99)	348(4.14)	290(4.26)	229(4.70)	—
(3b)	595(3.13)	385(3.69)	340(3.97)	268(4.21)	236(4.51)	211(4.59)
(3c)	598(2.84)	389(4.08)	—	270(4.34)	234(4.63)	211(4.68)
(3d)[a]	595(2.50)	380(3.86)	334(4.16)	279(4.30)	230(4.65)	211(4.71)

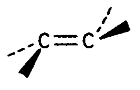
[a] Also $\lambda_{max.}$ 318 nm (log ε, 4.26).



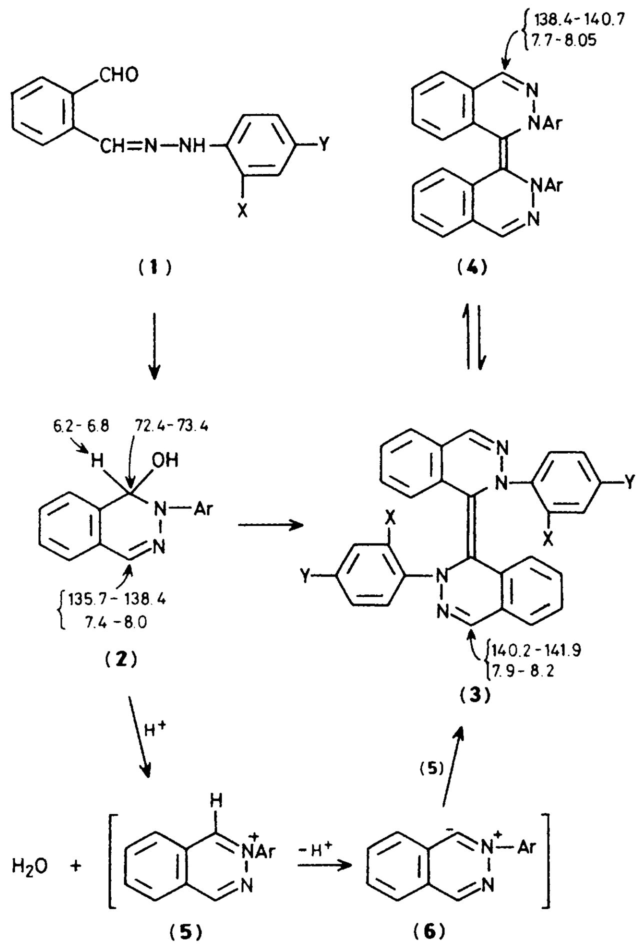
(I)



(II)



(III)



Scheme 1. Some n.m.r. shift ranges are shown.

principle strain could also be relieved in ylidenes by folding rather than torsion as in structures (II) and (III). Many *cis*-bent alkenes involving bridgehead unsaturation with structure (II) are known but it has recently been pointed out that *trans*-bent alkenes (III) are unknown.[5] Herein we describe a simple route to new brightly coloured bi-phthalazinylidenes and illustrate by an *X*-ray crystal structure that steric interactions in these systems are relieved by adopting the *trans*-bent alkene structure (III).

Phthalaldehyde monophenylhydrazones (**1**) are readily cyclised either directly or *in situ*† to give the hydroxydihydrophthalazines (**2**) on being heated or treated with acid.[6] Treatment‡ of the compounds (**2**) with glacial acetic acid in acetonitrile gave good yields of the interesting new bi-phthalazinylidenes (**3**) (Scheme 1) (Table 1).§ The compounds (**3**) always separated as the *trans*-form in the crystalline state but in solution in normal n.m.r. solvents they quickly reached an equilibrium with the *cis*-form (**4**), showing a growth of new signals which were 1—3 p.p.m. and 0.1—0.2 p.p.m. more upfield in the ^{13}C and ^{1}H n.m.r. spectra respectively. An *ortho* substituent in the *N*-aryl ring did not inhibit the formation of these compounds (Table 1). The *X*-ray crystal structure¶ of

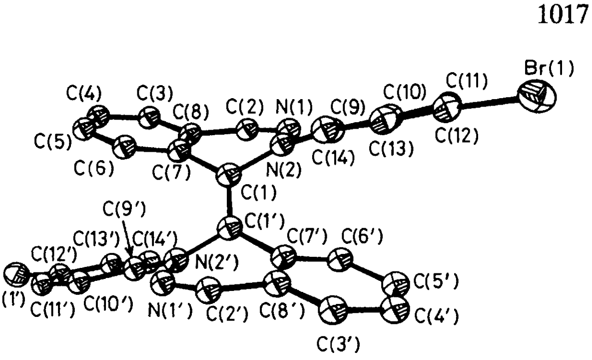


Figure 1. *X*-Ray crystal structure of compound (**3d**).

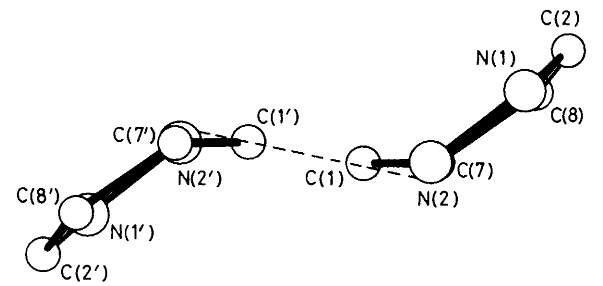
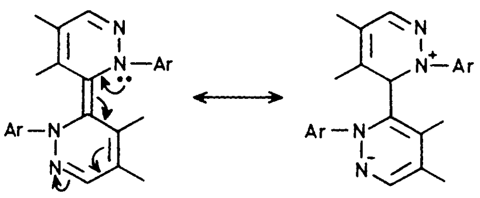


Figure 2. *X*-Ray crystal structure: view of the best plane through C(1), C1') and the atoms to which they are linked; the dotted line joins the centres of C(1) and C(1').



(A)

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† Compounds (**2**): general procedure. A solution of phthalaldehyde (0.5 g, 3.7 mmol) and the phenylhydrazine hydrochloride (3.7 mmol) in water (25 ml) was stirred under reflux for 2 h and treated with an excess of dil. NaOH to give crystals of compounds (**2**).

‡ Compounds (**3**): general procedure. A solution of the hydroxydihydrophthalazine (**2**) (2.2 mmol) in acetonitrile (10 ml) containing glacial acetic acid (0.25 ml) was stirred under reflux for 2 h and filtered hot to remove compound (**3**) which had separated. Remaining starting material (**2**) was recovered by cooling the filtrate in ice.

§ All of the compounds reported gave satisfactory C,H,N microanalyses. Satisfactory cryoscopic molecular weights were also determined on the compounds (**3c**) and (**3d**).

¶ *Crystal data* for (**3d**): $C_{28}H_{18}N_4Br$; $M = 570.27$, monoclinic, space group $P2_1/n$, $a = 5.842$ (2), $b = 14.071$ (3), $c = 14.178$ (3) Å, $\beta = 90.0$ (2)°, $U = 1165.44$ Å^3, $Z = 2$, $F(000) = 568$, $\mu = 34.08$ cm^{-1}. 884 Unique reflections observed with $I > 3\sigma(I)$. [θ–2θ scans over the range $2° < \theta < 24°$, graphite monochromator, $\lambda = 0.71069$ Å, Hilger Y290 diffractometer.] The data were corrected for Lorentz polarization but not for absorption. The structure was solved by direct methods and using SHELX 76. $R = 4.03$, $R_w = 5.08$, $w = 1/(\sigma^2 F_o + 0.0037F^2)$ for 78 refined parameters with hydrogen atoms in calculated positions and all non-hydrogen atoms isotropic except bromine which was refined anisotropically. $\Delta_{p\ \max}$ 0.45 and $\Delta_{p\ \min}$ 0.62 e Å^{-3}. The largest shift/e.s.d. in the final cycle of least squares refinement in any parameter was <0.001 and the goodness of fit was 0.999. The asymmetric unit was one half of a molecule. There is an inversion centre at the mid point of the C_x–C_y bond and thus the molecule has a crystallographically required centre of symmetry. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

compound (**3d**) (Figure 1) showed it to be free of steric interactions around the alkene moiety due to combination of a *trans*-folded alkene linkage and a buckling of the aromatic ring. The ylidene bond length is the normal 1.34 Å and the bond is not stretched. The folding is small with the atoms bonded to the ylidene carbons lying 8.9° from the plane of the C–C line (Figure 2). As far as we are aware this is the first detected case of a *trans*-folded alkene bond.

The compounds showed intense yellow colours in the solid state and solutions ranged in colour from yellow to blue–green. The u.v.–visible absorptions are shown in Table 2. These spectra, which are complex, may arise from an indigo-type[2b] chromogen involving conjugation as in structure (A).

The compounds are probably formed *via* the amino-carbocation (**5**) which is in equilibrium with the key intermediate, the nucleophilic ylide (**6**) (Scheme 1). Attack by the nucleophilic carbene on the precursory cation (**5**) would give the phthalazinylidenes. In agreement with this the qualitative order of reactivity for *para* Y-substituents was MeO > Me > H > Br ≫ NO_2.

A. M. G. acknowledges a State Grant for Research.

Received, 6th March 1987; Com. 283

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