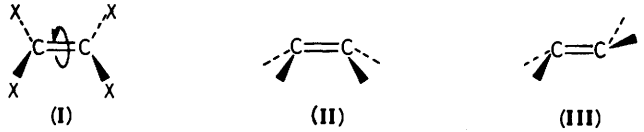
A *trans*-Folded Alkene System: Synthesis, Structure and Isomerization of 2,2'-Diaryl-1,1'-bi(1,2-dihydrophthalazinylidenes)

Richard N. Butler,* Ann M. Gillan, Fiona A. Lysaght, Patrick McArdle and D. Cunningham
Chemistry Department University College, Galway, Ireland

A series of 2,2'-diaryl-1,1'-bi(1,2-dihydrophthalazinylidenes) have been synthesized from 1-hydroxy-2-aryl-1,2-dihydrophthalazines. An X-ray crystal structure showed relief of strain in these new ylidenes by a *trans*-folding of the alkene linkage. The mechanism of their formation was probed with additives such as sulphur, *N*-phenylmaleimide, and dimethyl acetylenedicarboxylate which interacted with intermediates in the reaction and gave further interesting new ylidene structures. The mechanism of *trans-cis* isomerization of the biphthalazinylidenes was studied using 270 MHz ^{1}H NMR spectroscopy to measure the kinetics and activation parameters for the isomerization. X-Ray crystal structures of the following compounds are reported: 2,2'(*p*-bromophenyl)-*trans*-1,1'-bi-[1,2-dihydrophthalazinylidene (**3d**); 3-[2-(*p*-bromophenyl)-1,2-dihydrophthalazin-1-yl]-4-[2-(*p*-bromophenyl)-1,2-dihydrophthalazin-1-ylidene]-1-phenyl-3,4-dihydropyrrole-2,5-dione, (**10d**); dimethyl 3-[2-phenyl-1,2-dihydrophthazin-1-ylidene)-2-oxobutanedioate (**11**), and dimethyl 2-acetoxy-3-(2-phenyl-1,2-dihydrophthazin-1-yl)but-2-ene-1,4-dioate (**12**).

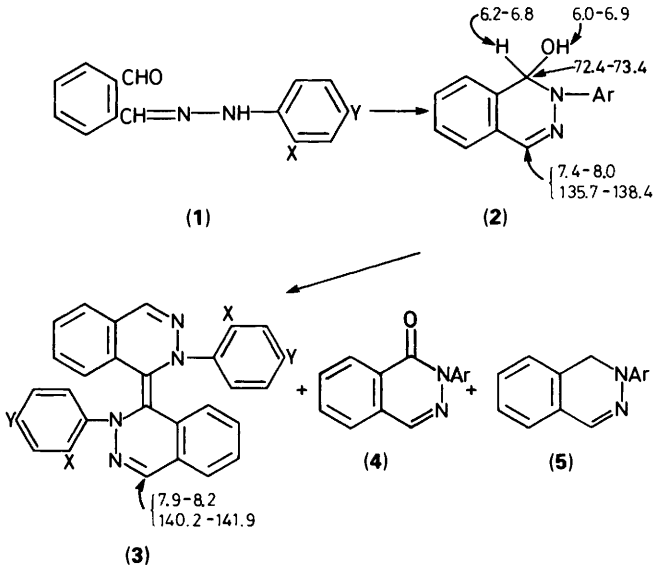
Crowded double bonds exhibiting Prelog-strain effects are of considerable interest.[1–20] The strain features observed involve torsional twisting (**I**) and mixtures of such twisting with *cis*-(**II**) or *trans*-folding (**III**). Pure *cis*-folding (**II**) has been widely observed particularly with fused bridgehead alkene systems.[2–6] In these strained systems the pure sp^2 hybridization of the double bond is distorted towards sp^3 character at the carbons which are no longer planar. A feature of the known *cis*-fold structures (**II**) is that the double bond length remains the normal 1.34 Å.[2–6] With torsionally twisted alkenes (**I**) there is a decrease of p-orbital overlap which is accompanied by a significant stretching of the double bond.[7–12]

The pure *trans*-folded C=C alkene structure (**III**) is unknown.[21,22] Many of these distorted alkene structures are found in ylidene compounds bearing two five-membered rings or a six- and a five-membered ring at each end of the ylidene linkage.[7–12,17,20] Six-membered heterocyclic ylidenes are a remarkably rare[23,24] class of compounds relative to the more ubiquitous five-membered heterocyclic analogues one of the best known examples of which is indigo. Herein we report a study of new biphthalazinylidenes, the first diazinylidenes. These relieve steric interactions by a pure *trans*-folding distortion (**III**), the first[25] such case. Interestingly the C=C bond length in these new compounds was the normal 1.34 Å suggesting that the *trans*-folding distortion (**III**) like the *cis*-folding (**II**) does not stretch the double bond.



Results and Discussion

(*a*) *Synthesis and Structure.*—Phthalaldehyde monophenylhydrazones (**1**) are readily cyclized, either separately or *in situ* when first formed, to give the hydroxydihydrophthalazines (**2**) on being heated or treated with acid. Treatment of compounds (**2**) with glacial acetic acid in acetonitrile gave the interesting



Scheme 1. Some ^{1}H and ^{13}C NMR shift ranges are shown.

new biphthalazinylidenes (**3**) (Scheme 1) (Table 1). The role of the acetic acid in the reaction was catalytic and for molar quantities of HOAc as low as 0.05 the yield of ylidene (**3**) was in the range 27–33%. With 0.01 mol of acetic acid per mol of (**2c**) the yield of ylidene (**3c**) was 14%. Optimum conditions were observed with 2 mol equiv. of HOAc which gave 70% of compound (**3c**). In all the reactions the ylidenes (**3**) were accompanied by low and equal yields of the products (**4**) and (**5**) (5–8%) from a disproportionation of the substrates (**2**). These products (**4**) and (**5**) could be obtained in higher yields (< 40%) by heating the compounds (**2**) for *ca.* 10 min above their melting points to liquefaction. Only trace quantities (< 0.5%) of the ylidenes (**3**) were detected on work-up of these melts. In the ylidene-forming reactions the only other compounds encountered were recovered starting materials (**2**) and in each case the combined products accounted for 95–100% of the reaction. The

Table 1. Phthalazinylidene products and substrates.

Compd.	X	Y	M.p. (°C)	% Yield	Compd.	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
(2g)	H	Cl	144–145[a]	98	**(3g)**	252–253[d]	48

[a] From benzene. [b] From MeCN. [c] From chloroform–acetonitrile (1:1, v/v). [d] From chloroform. [e] Yields are for reactions using 2 mmol of (2) in 10 ml MeCN containing 0.25 ml HOAC.

Table 2. UV–visible absorptions, λ_{max}/nm (log ε), in acetonitrile.

Compd.							
(3a)	597(3.24)	389(3.99)	348(4.14)	312(4.19)	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)	—	310(4.22)	270(4.34)	234(4.63)	211(4.68)
(3d)	595(2.50)	380(3.86)	334(4.16)	381(4.26)	279(4.30)	230(4.65)	211(4.71)
(3e)	591(2.85)	386(3.72)	—	306(3.90)	276(3.98)	236(4.169)	212(4.36)
(3f)	586(3.34)	387(3.91)	—	308(4.13)	274(4.22)	234(4.50)	205(4.66)

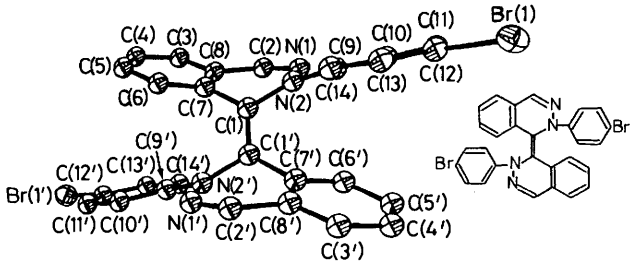


Figure 1. X-Ray crystal structure of compound (**3d**).

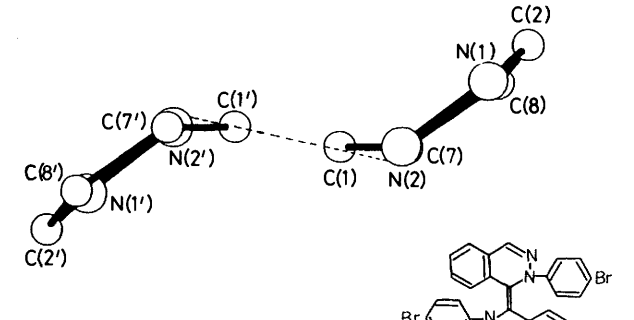


Figure 2. X-Ray crystal structure of (**3d**): view of best plane through C(1) and C(1') and the atoms to which they are linked; the dotted line joins the centres of C(1) and C(1').

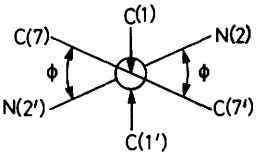


Figure 3. Dihedral angle of the ylidene linkage in (**3d**).

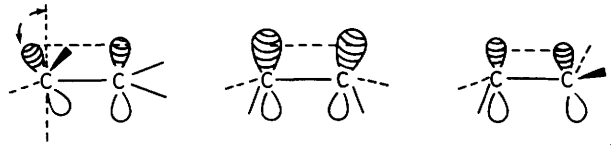
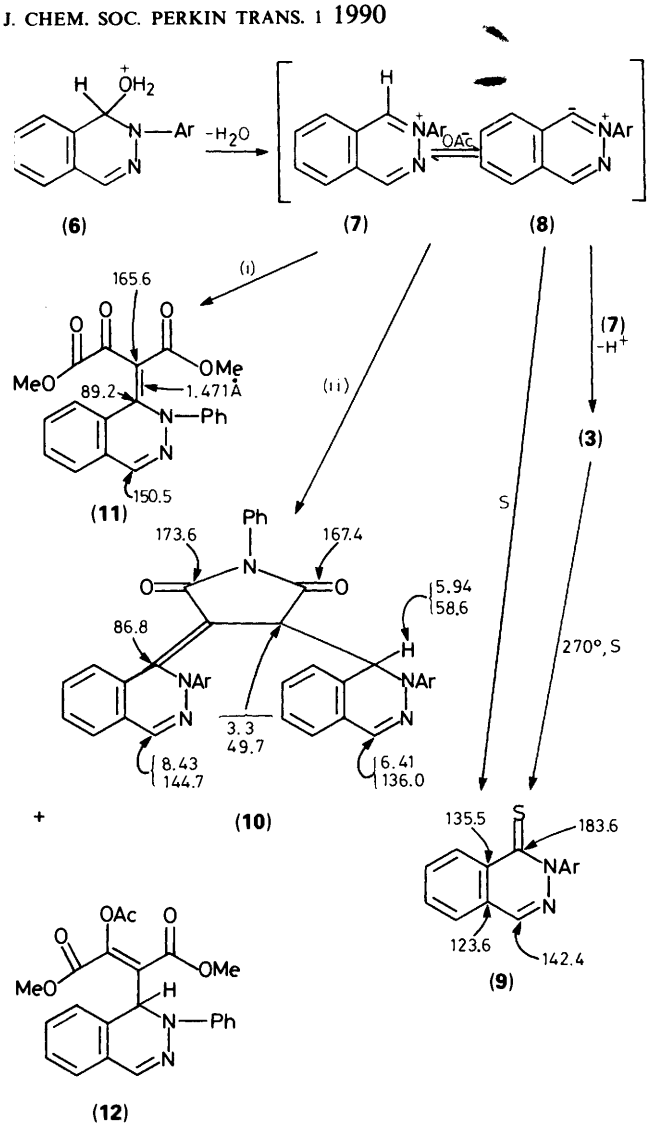


Figure 4. Reduced π-interaction in strained alkenes.

ylidenes (**3**) showed intense yellow colours in the solid state and solutions ranged in colour from yellow to blue–green. Their staining power and bright colours were striking and may indicate pigmentation possibilities. The UV–visible absorptions are shown in Table 2.

The ylidenes crystallized from solution in the *trans*-structure (**3**) but in solution they quickly isomerized to equilibrium mixtures of *cis*- and *trans*-isomers. Hence NMR spectra, showed excessive signals unless they were recorded quickly before the *cis* isomer had grown. The structure was proved by an X-ray crystal structure determination for compound (**3d**) (Figures 1 and 2). This showed that strain around the ylidene linkage was relieved by a *trans*-folding of the alkene bond involving a buckling of the phthalazinyl ring. The folding caused the atoms bonded to the ylidene carbons to lie 8.9° above and below the plane of the C–C line at each end of the bond (Figure 2). The dihedral angles at each end of the C=C bond (for an end-on view Figure 3) were identical at 11.8° confirming a pure *trans*-folded structure with no twisting (which would show up as unequal dihedral angles). The C=C bond length was the normal 1.34 Å. This suggests that for a *trans*-folding of the magnitude observed the sp^3 pyramidalization of the sp^2 carbons (Figure 4) was small with little loss of π-overlap along the C–C axis, much less than would be the case for a torsional twisting. It also indicates that single C–C bonded dipolar or diradical canonical forms such as (**13**) and (**14**) (Scheme 3) do not make important contributions to the ground state of the molecules (**3**).

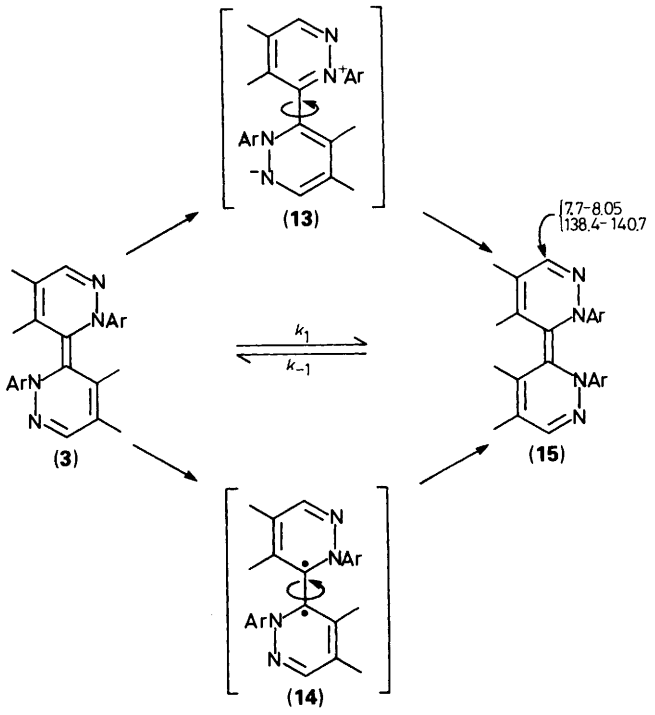
(*b*) *Mechanism.* The reaction is a dimerisation of the substrate (**2**) which probably involves an initial OH protonation to give (**6**) followed by loss of H_2O to give the carbocation (**7**). The qualitative order of reactivity for *para* Y-substituents was MeO > Me > H > Br ≫ NO_2 in agreement with this. Indeed for a *p*-NO_2 substituent no ylidene could be obtained and the chemistry of phthalaldehyde mono-*p*-nitrophenylhydrazone was quite different as we have recently[26] described. The carbocation (**7**) once formed could lose a proton giving the ylide (**8**) which we believe is the key intermediate in the reaction. The trapping of (**8**) by its precursory carbocation (**7**) followed by loss of a proton would give the ylidene (**3**). The possibility that a carbanion could have been generated from unprotonated (**2**)



Scheme 2. Ylidene formation in the presence of additives: (i) $MeO_2CC{\equiv}CO_2Me$ (DMAD); (ii) *N*-phenylmaleimide. Some ^1H and ^{13}C shifts for the **d** series (Y = Br) are shown.

concomitant with the carbocation was discounted when it was found that no hydrogen/deuterium exchange was observed in the recovered substrates (**2**) when CD_3CO_2D was used as the acid.

We attempted to trap the intermediates (**7**) and (**8**) with appropriate additives. Nitrogen ylides (nucleophilic carbenes) have been generated by thermolysis of azolidinylidenes and they have been readily trapped with sulphur to give the corresponding thiones.[27–30] When compound (**3c**) was heated in a melt with sulphur at 270 °C for 10 min. The thione (**9c**) was obtained in 70% yield presumably *via* the species (**8**).[27–30] When compound (**3c**) was heated in acetonitrile containing 2 mol equiv. each of acetic acid and suspended sulphur no reaction occurred and it was recovered unchanged. However when suspended sulphur was present during the conversion to (**2**) into (**3**) with acetic acid in acetonitrile the thione (**9**) was formed in yields of 5–7% along with the normal products (**3**), (**4**), and (**5**) (Table 3). The yield of the ylidene appeared to be reduced relative to its value in the absence of sulphur but owing to the complicated separation involved and contamination of the ylidene with sulphur the yield of (**3**) could not be precisely quantified. Attempted trapping reactions with electron-rich alkenes were not successful but significant results were obtained



Scheme 3. Ylidene isomerization. Some ^1H and ^{13}C NMR shifts for the *cis*-series are shown.

with electron-deficient alkenes. Thus, when *N*-phenylmaleimide was the additive for the reactions of (**2c**) and (**2d**) with acetic acid in acetonitrile the new products (**10c**) (8.1%) and (**10d**) (9%) were isolated along with the normal products; the yield of compounds (**3c**) and (**3d**) were reduced as expected (Table 3). Compounds (**10**) appear to represent a pristine trapping of *both* of the intermediates (**7**) and (**8**). They could readily arise by addition of the nucleophilic carbene (**8**) and the cation (**9**) at opposite ends of the maleimide double bond followed by loss of a proton to generate the new ylidenes (**10**). When dimethyl acetylenedicarboxylate (DMAD) was used as additive the yield of the ylidene (**3**) was reduced and the two products (**11**) and (**12**) were formed (Table 3). The latter can arise by addition of the species (**7**) and acetate ion to DMAD, and the ylidene (**11**) could have arisen from addition of the ylide (**8**) followed by acetolysis of the initial adduct. Taken together, all of these products (**9**)–(**12**) isolated alongside lower yields of the ylidenes (**3**) provide support for the mechanism proposed in Scheme 2.

The structures of the products (**9**)–(**12**) were supported by microanalysis and IR, ^1H NMR, and ^{13}C NMR spectroscopy (Scheme 2). Of interest for compound (**10**) is the unusually high shielding of the CH=N site in the phthalazine entity of the reduced part of the molecule [compare (**10**) with (**2**) Scheme 1]. This exceptional shielding arose because this part of the molecule was held in the shielding region over the plane of the ring current of the other phthalazinyl entity as shown by the X-ray crystal structure of compound (**10d**) (Figure 5B, which contains part of the molecule showing the overlying of the phthalazinyl entities). Compounds (**10**) are interesting new ylidenes also. In them, strain is relieved by a combination of torsional twisting and folding of the C=C bond (Figure 5). The dihedral angle of the twist differed between the two ends of the double bond, the average being 38° (Figure 6). The extent of the fold was 3.02 and 3.64° at each end of the double bond. This was established by generating dummy atoms M(1) midway between C(7) and C(10) and M(2) midway between C(17) and N(3) and then finding the angles M(1)–C(9)–C(18) and M(2)–C(18)–C(9) (Figure 6). The C=C bond length was

Table 3. Reactions with additives.

Substrate	Additive	Compd.	M.p. (°C)	Products (% Yield) Yield %	(3)	(4)	(5)	(2)
(2c)[a]	Nil	—	—	—	65.0	7.1	7.4	
(2d)[a]	Nil	—	—	—	32.0	12.5	12.1	35.0
(2c)[a]	S	(9c)	138	7.1	55–65	7.9	4.5[c]	19.2
(2d)[a]	S	(9d)	179–180	6.2	22–32	13.5	9.2[c]	35.0
(2c)[b]	N-Phenylmaleimide	(10c)	236	8.1	28.0	—[d]	—[d]	—[d]
(2d)[b]	N-Phenylmaleimide	(10d)	246	9.0	28.0	—[d]	—[d]	—[d]
(2c)[b]	DMAD	(11)	251–253	7.5	14.5	—[e]	8.8	39
		(12)	137	15.0				

[a] Under identical conditions with molar proportions of (2):HOAC:S of 1:1:1. [b] Conditions as in Table 1 with 1 mol of additive. [c] Lower yields of reduced product (5) are attributed to preferential reduction of some sulphur to H_2S (odour). [d] Confirmed present in approximately normal proportions not quantified. [e] Oxidised product (4) not detected due to preferential oxidation of compound (12c).

significantly stretched to 1.389 Å owing to the large torsional twist. The structures of compounds (11) and (12) were also proved by X-ray crystal structures (Figures 7 and 8). In the new ylidene (11) the average torsional twist on the ylidene linkage was 61.75° and the >C=C< bond distance was 1.471 Å. These values are remarkable and it seems likely that the major contribution to the ground state of the molecular is a dipolar resonance form with a single bond between the rings and extensive delocalization of negative charge among the three conjugated carbonyl groups at the acyclic end of the ylidene.

Isomerization.—Compounds (3) separated in the *trans*-form in the crystalline state but in solution in normal NMR solvents they rapidly reached an equilibrium with the *cis*-forms (15), showing a growth of new CH=N signals which were 1.3 ppm and 0.1–0.2 ppm more upfield in the ^{13}C and ^{1}H NMR spectra respectively. The kinetics of the isomerization (Table 4) were measured using 270 MHz ^{1}H NMR spectroscopy by following the growth of the new CH=N signal (Scheme 2) as well as *p*-Me and *p*-MeO signals when these were available. The easy isomerization of strained ylidene double bonds relative to normal alkenes[31] has been ascribed[8,31–36] to (i) lower activation barriers owing to ground state destabilization or (ii) well stabilized transition states involving extensive delocalization in diradical or dipolar intermediates or a combination of both. In the case of compounds (3) the kinetic data (Table 4) showed a linear correlation with Hammett σ^+ values giving $\rho = -2.0$ ($r = 0.971$). The strong negative ρ value allied with the σ^+ correlation suggests through-bond resonance to a positive centre in the transition state. No correlation was observed with σ_n values. The ease of isomerization was reflected in the activation parameters, Arrhenius E_{act} = 22.4 kcal mol^{-1} ΔH_{act} = 21.8 kcal mol^{-1}, and $\Delta S_{act} = -4.6$ cal K^{-1} mol^{-1}. Eyring free energy values are also shown in Table 4. These activation data are comparable to those obtained[32–35] for other easily isomerizable ylidene systems. The ylidene bond length in compounds (3) indicated little contribution to the ground state from a dipolar structure such as (13). The kinetic data, however, suggest that the isomerization proceeds through a transition state of type (13) with rotation of the C–C linkage. The stabilization of the species (13) by charge delocalization is the key factor in the facile isomerization of the phthalazinylidenes rather than ground state destabilization. There is no evidence for a diradical intermediate and a transition state such as (14) is unlikely in view of the observed kinetic effects.

Experimental

M.p.s were measured on an Electrothermal apparatus. IR spectra were measured with a Perkin-Elmer 983G spectrophotometer. NMR spectra were measured on a JEOL JNM-GX 270 instrument with tetramethylsilane as internal reference and deuteriochloroform or hexadeuterio dimethyl sulphoxide as solvent. UV–visible absorption spectra were measured with a Shimadzu U.V.-260 spectrophotometer. The substrates (2) (Table 1) were prepared by either of the following procedures, (i) A solution of phthalaldehyde monoarylhydrazone (*ca.* 0.02 mol) in 1,4-dioxane (25 ml) after being heated under reflux for 24 h was evaporated under reduced pressure and the residue compound (2) recrystallized as indicated in Table 1. (ii) An equimolar mixture of phthalaldehyde and the arylhydrazine hydrochloride (*ca.* 4 mmol) was heated under reflux in water (25 ml) for 2 h, after which it was cooled and treated with an excess of dilute aqueous sodium hydroxide to give immediate separation of compound (2). All the compounds described gave satisfactory CHN microanalyses and their structures were confirmed by ^{1}H and ^{13}C NMR spectroscopy. NH and OH signals were confirmed by deuteriation with CD_3CO_2D and carbon-13 assignments were supported by off-resonance and 2D CJ resolve experiments. For compounds (2) the OH proton exchange was slow in [$^{2}H_1$]dimethyl sulphoxide and the >CHOH moiety generally appeared as an AB pair of doublets (J_{AB} 7–9 Hz) (Scheme 1).

(*i*) *2,2′-Diaryl-*1,1′*-bi(1,2-dihydrophthalazinylidenes)* (3).—The following are typical examples.

(*a*) *Synthesis of* (2,2-*diphenyl*-trans-1,1′-*bi*(1,2-*dihydrophthalazinylidene*) (3c). A solution of 1-hydroxy-2-phenyl-1,2-dihydrophthalazine (2c) (0.5 g, 2.2 mmol) in acetonitrile (10 ml) was treated with glacial acetic acid (0.25 ml) and stirred under reflux for 2 h. The title compound (3c) separated during the period under reflux (filtrate A) and was collected as bright yellow needles from acetonitrile (0.22 g, 48%), m.p. 230–231 °C (from acetonitrile) (Found: C, 81.3; H, 5.2; N, 13.7. $C_{28}H_{20}N_4$ requires C, 81.6; H, 4.9; N, 13.6%); δ_H(*trans* configuration only, measured immediately after dissolution) ($CDCl_3$) 6.62–6.67 (1 H, t, phenyl-4′-H), 6.88–7.25 [8 H, m, fused benzene (4 H) and phenyl-2′ and 3′-H (4 H)], and 7.93 (1 H, s, CH=N); δ_C(*trans* configuration only, measured within 30 min after dissolution in $CDCl_3$) 116.20, 118.24, 120.86, 123.44, 125.10, 125.59, 127.79, 128.27, 128.35, 129.91, 141.14, and 143.78 ppm; δ_H(*trans* and *cis* equilibrium mixture; *trans* to *cis* ratio of 59.9:40.1%) ($CDCl_3$) 6.62—7.32 [16 H, m, fused benzene (8 H) and phenyl (8 H)], 7.79 (1 H, s, CH=N *cis*), 7.92 (1 H, s, CH=N) *trans*); δ_C(*trans* and *cis* configurations; *trans* to *cis* ratio 59.9:40.1%) ($CDCl_3$) 115.38, 116.20, 116.74, 118.24, 120.86, 121.81, 123.44, 123.82, 125.10, 125.59, 125.99, 127.37, 127.81, 128.27, 128.35, 128.38, 128.60, 129.90, 139.20, 141.14, 143.42, and 143.78 ppm. δ_C(*cis* configuration obtained by elimination of *trans* signals from the *trans,cis* mixture) ($CDCl_3$) 115.38,

Table 4. Kinetic data at 295 K.

Substrate Compd.	(Y)	(σ^+)	k_{obs} $k_1 + k_{-1}$ (s^{-1}) × 10^5	k_1 (s^{-1}) × 10^5	$\Delta G^{\ddagger}$ [c] (kcal mol^{-1}) [b]	k_{-1} (s^{-1}) × 10^5	$\Delta G^{\ddagger}_{-1}$ [c] (kcal mol^{-1}) [b]
(3a)	MeO	(−0.778)	81.1	40.3	21.8 [c]	40.8	21.8 [c]
(3b)	Me	(−0.311)	20.3	9.6	22.6	10.7	22.6
(3c) [a]	H	(0.0)	4.55	1.82	23.6	2.73	23.35
(3d)	Br	(0.150)	0.87	0.46	24.3	0.413	24.4
(3g)	Cl	(0.114)	1.75	0.905	24.05	0.845	24.1

[a] Arrhenius data; T, 302.7 K, K_{obs}, 13.7 × 10^{-5} s^{-1}; 313 K, 44.0 × 10^{-5} s^{-1}. [b] 4.184 J = 1 cal. [c] Eyring free energies of activation at 295 K.

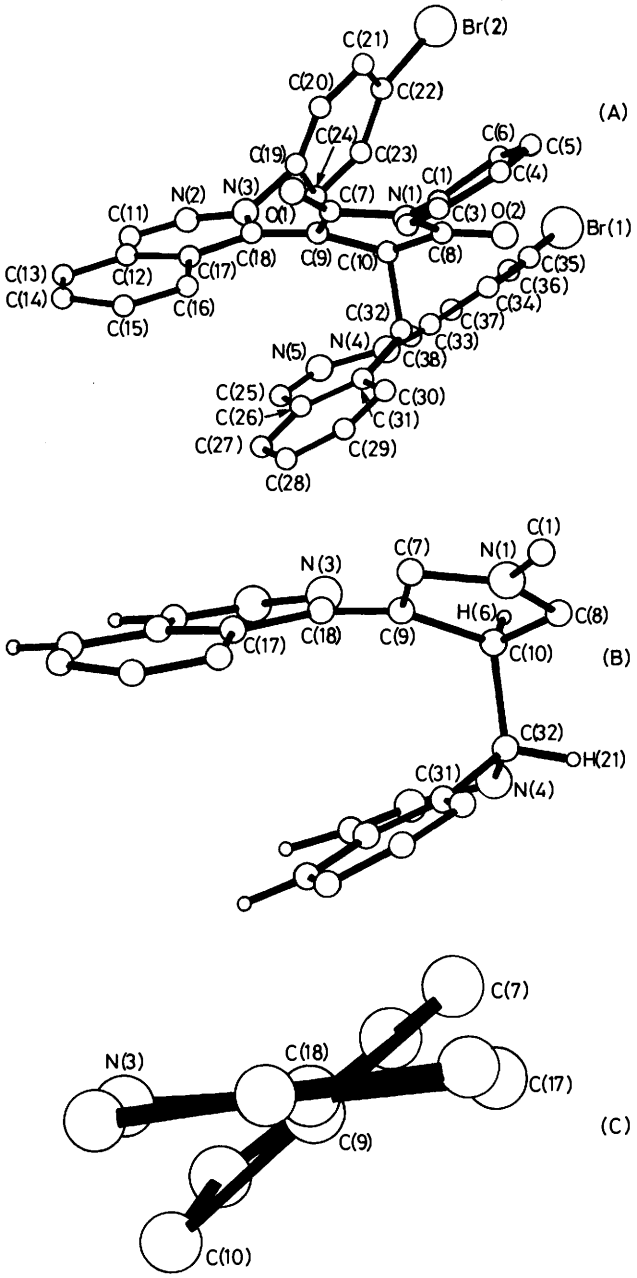


Figure 5. (A) X-Ray crystal structure of compound (**10d**); (B) view showing overlying orientation of the phthalazinyl groups; (C) view along the ylidene linkage showing the twist.

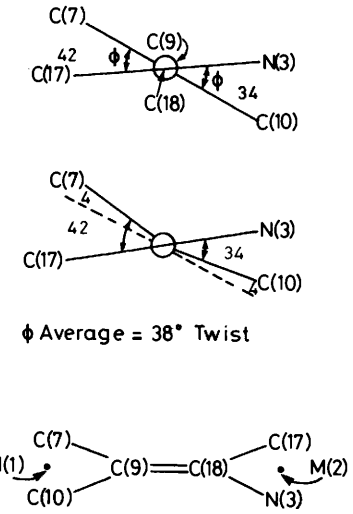


Figure 6. Dihedral angles in (**10d**).

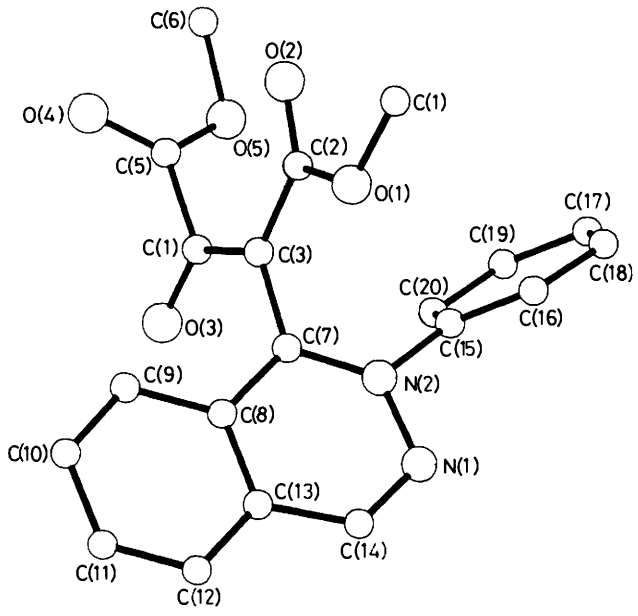


Figure 7. X-Ray crystal structure of compound (**11**).

116.74, 121.81, 123.82, 125.99, 127.37, 128.38, 128.60, 139.20, and 143.42 ppm. Filtrate A contained compounds (**4c**), (**5c**), and unchanged starting material which were separated by flash chromatography as follows. The filtrate was evaporated under reduced pressure and the residue in dichloromethane (2 ml) was placed on a flash column of silica gel (230—400 mesh ASTM) and eluted with dichloromethane. The first product eluted from the column was 2-phenyl-1,2-dihydrophthalazine (**5c**) (0.03 g, 6.5%), m.p. 136–137 °C (from acetonitrile), followed by 2-phenylphthalazin-1-one (**4c**) (0.03 g, 6.1%), m.p. 109–110 °C

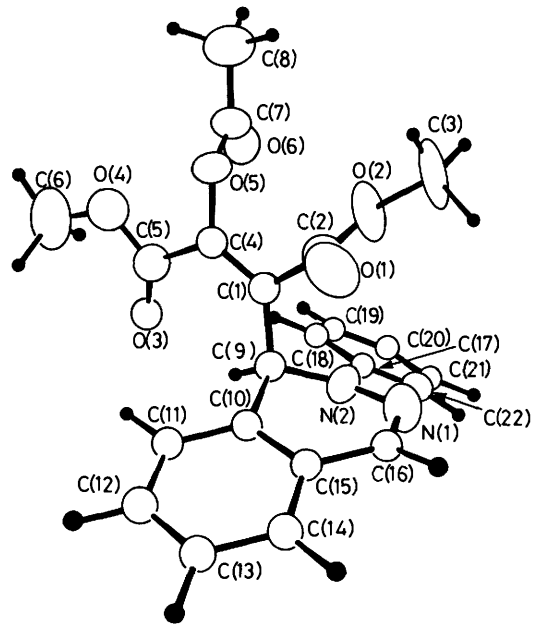


Figure 8. X-Ray crystal structure of compound (**12**).

(from acetonitrile). The last compound eluted was unchanged starting material 1-hydroxy-2-phenyl-1,2-dihydrophthalazine (**2c**) (0.1 g, 20%). Compounds (**4**) and (**5**) could also be obtained in yields of *ca.* 40% by heating compounds (**2**) to liquefaction above their m.p.s for 10 min. Analyses for compounds (**3b**), (**3d**), (**3e**), (**3f**), (**3g**), (**9d**), and (**10d**) were satisfactory and the results are available as a supplementary publication (SUP No. 56776; 2 pp.) *

(*b*) *Bis*-p-*methoxyphenyl*-trans-1,1′-*bi*(1,2-*dihydrophthalazinylidene*) (**3a**).—A solution of 1-hydroxy-2-(*p*-methoxyphenyl)-1,2-dihydrophthalazine (**2a**) (0.5 g, 2.0 mmol) in acetonitrile (10 ml) was treated with acetic acid (0.25 ml) and stirred under reflux for 2 h, during which time precipitation of the product occurred. The precipitate was filtered off (filtrate A) and recrystallized from a (1:1, v/v) mixture of chloroform–acetonitrile to yield the pure title compound (**3a**) (0.27 g, 58%), m.p. 232–233 °C (from chloroform–acetonitrile; 1:1, v/v) (Found: C, 76.1; H, 5.0; N, 11.4. $C_{30}H_{24}N_4O_2$ requires: C, 76.3; H, 5.1; N, 11.9%); δ_H(*trans* configuration measured immediately after dissolution) ($CDCl_3$) 3.65 (3 H, s, MeO), 6.48–6.51 (2 H, d, J_{AB}, 8.9 Hz, H_BH_B', AA'BB' of *p*-MeO C_6H_4), 7.01–7.05 (2 H, d, H_AH_A', AA'BB' of *p*-$MeOC_6H_4$), 6.80–7.30 (4 H, m, fused benzene), 7.87 (1 H, s, CH=N); δ_H(*trans* and *cis* equilibrium mixture with *trans*:*cis* ratio of 50.4:49.6) ($CDCl_3$) 3.65 (3 H, s, MeO *trans*), 3.77 (3 H, s, MeO, *cis*), 6.48–6.51 (2 H, d, J_{AB}, 8.9 Hz, H_BH_B', *trans*, AA'BB' *p*-$MeOC_6H_4$), 6.58–6.62 (2 H, d, *J* 9.0 Hz, H_BH_B', *cis*, AA'BB', *p*-$MeOC_6H_4$), 6.82–6.86 (2 H, d, H_AH_A', *cis*, AA'BB'), 6.80–7.30 (10 H, m, fused benzene rings, *trans* and *cis* and H_AH_A', *trans* AA'BB', *p*-$MeOC_6H_4$), 7.74 (1 H, s, CH=N *cis*), and 7.87 (1 H, s, CH=N *trans*); δ_C(*trans* and *cis* configurations with a *trans* and *cis* ratio of 50.4:49.6) ($CDCl_3$) 55.60, 55.71, 113.30, 113.79, 114.52, 117.50, 117.67, 117.84, 123.10, 123.63, 125.26, 125.77, 125.97, 127.16, 127.68, 127.82, 128.19, 128.71, 129.58, 129.71, 137.44, 137.85, 138.38, 140.28, and 155.02 ppm. A ^{13}C NMR spectrum of the pure *trans* compound could not be obtained because of the speed of the *trans*/*cis* isomerization with the *p*-MeO substituent present. The filtrate (A) contained the compounds (**4a**), (**5a**) and starting material (**2a**) which were separated as follows. The filtrate was evaporated under reduced pressure and the residue in CH_2Cl_2 (2 ml) placed on a flash column of silica gel (230–400 mesh ASTM) and then eluted with dichloromethane. The first compound eluted was 2-(*p*-methoxyphenyl)-1,2-dihydrophthalazine (**5a**) (0.03 g, 6.4%), m.p. 132–133 °C (from acetonitrile), followed by 2-(*p*-methoxyphenyl)phthalazin-1-one (**4a**) (0.03 g, 6.5%), m.p. 129–130 °C (from acetonitrile). The final compound eluted was unchanged starting material, 1-hydroxy-2-(*p*-methoxyphenyl)-1,2-dihydrophthalazine (**2a**) (0.12 g, 24%).

(*ii*) *Experiments with Additives.*—(*a*) *Sulphur.* A mixture of compound (**2c**) (1.48 g, 6.6 mmol), sulphur (0.23 g, 7.17 mmol), glacial acetic acid (0.38 ml, 6.6 mmol), and acetonitrile (30 ml) was stirred under reflux for 2 h, cooled, and filtered (Filtrate A) to give a mixture of compound (**3c**) and sulphur. Filtrate (A) was evaporated under reduced pressure and the residue in dichloromethane (3 ml) was eluted from a flash column of silica gel [230–400 mesh ASTM made up in light petroleum (b.p. 40–60 °C)] with the pure solvents and gradient mixtures (4:1 to 1:4) of toluene progressing to dichloromethane to ethyl acetate to give compounds (**4c**) (from dichloromethane), (**5c**) (toluene), (**2c**) (ethyl acetate) (Table) and (**9c**) (early toluene–dichloromethane), m.p. 137–138 °C (from EtOH) (Found: C, 70.7; H, 4.4; N, 11.3. $C_{14}H_{10}N_2S$ requires, C, 70.6; H, 4.2; N, 11.8%); δ_C 183.3 (C=S); 142.0 (CH=N); 146.2, 135.3, 123.0 (Ar, tertiary-C=); 133.7, 133.4, 131.1, 129.2, 128.6, 126.9, 126.6 (Ar); δ_H($CDCl_3$) 7.41–7.84 (m, 8 H, aromatic, *N*-phenyl and phthazinyl), 8.46 (s, 1 H, CH=N), and 8.96–8.99 (m, 1 H, phthalazinyl, 8-H).

Compound (**9c**) was also obtained in 70.3% yield when a mixture of compound (**3c**) (0.72 g) and sulphur (0.72 g) was heated in a melt at 270 °C under a stream of nitrogen for 20 min. The cooled melt was taken up in dichloromethane from which sulphur was removed and the solution chromatographed as described with dichloromethane as eluant to give compound (**9c**) which was treated with charcoal before recrystallization. Compound (**9c**) was also obtained in yields of 30–40% by prolonged heating of compound (**2c**) under reflux in acetonitrile containing sulphur in the absence of acetic acid. In the presence of acetic acid the ylidene formation was much faster and low yields of (**9c**) formed under these conditions are likely to arise from a sulphur attack on intermediates rather than a separate reaction of sulphur with (**2c**).

N-Phenylmaleimide. N-Phenylmaleimidylphthalazinylidenes (**10**). The following is a typical example. A solution of 1-hydroxy-2-phenyl-1,2-dihydrophthalazine (**2c**) (2.0 g, 8.9 mmol) and *N*-phenylmaleimide (1.54 g, 8.9 mmol) in acetonitrile (40 ml) was treated with glacial acetic acid (0.5 ml) and stirred under reflux for 2 h during which time the colour changed from yellow to red and 2,2′-diphenyl-*trans*-1,1′-bi(1,2-dihydrophthalazinylidene) (**3c**) separated (Filtrate A) (0.52 g, 28%), m.p. 230–231 °C (from acetonitrile). Filtrate (A) was evaporated under reduced pressure and the residue in toluene (3 ml) was placed on a flash column of silica gel (230–400 mesh ASTM) and eluted with the following solvents: (i) light petroleum (b.p. 40–60 °C); (ii) light petroleum (b.p. 40–60 °C)–toluene (1:1 v/v); (iii) toluene; (iv) dichloromethane. The red–purple dichloromethane fractions which contained compounds (**10**) were evaporated under reduced pressure and the residue recrystallized from acetonitrile to yield purple–red plates of compound (**10c**) (0.21 g, 8.1%), m.p. 235–236 °C (from acetonitrile) (Found: C, 77.9; H, 4.7; N, 11.9. $C_{38}H_{27}N_5O_2$ requires C, 77.9; H, 4.7; N, 12.0%); ν_{max}(KBr) 1 660 cm^{-1} (C=O) and 1 712 cm^{-1} (C=O); λ_{max}(CH_3CN) (concentration 2.22 × 10^{-5}M) 237.6 (log ε 4.62), 303 (4.08), 330 (4.03), 367 (3.85), and 485.2 (3.37); δ_H($CDCl_3$) 3.20 (1 H, d, J_{AX} < 0.5 Hz, methine, *N*-phenylmaleimidyl), 5.99 (1 H, d, J_{AX} < 0.5 Hz, methine 1,2-dihydrophthalazinyl), 8.43 (1 H, s,

* For details of the Supplementary Publications Scheme, see 'Instructions for Authors (1990),' *J. Chem. Soc., Perkin Trans. 1*, 1990, Issue 1.

Table 5. X-Ray crystal structures.

	(3d)	(10d)	(11)	(12)
Compound	Monoclinic	Triclinic	Triclinic	Monoclinic
Formula	$C_{28}H_{18}Br_2N_4$	$C_{38}H_{25}Br_2N_5O_2$	$C_{20}H_{16}N_2O_5$	$C_{22}H_{20}N_2O_6$
M	570.285	743.46	364.36	408.41
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a (Å)	5.842(2)	10.541(3)	8.286(2)	10.201(1)
b (Å)	14.071(3)	11.842(3)	8.763(1)	16.444(2)
c (Å)	14.178(3)	13.033(4)	13.452(1)	12.533(1)
α (°)		86.99(3)	96.73(2)	
β (°)	90.0(2)	82.81(4)	90.34(2)	98.79(2)
γ (°)		78.49(3)	114.50(1)	
U (Å^3)	1 165.44	1 580.97	880.99	2 077.8
μ cm^{-1}	34.08	25.28	0.67	0.59
Z	2	2	2	4
D_c g cm^{-3}	1.63	1.56	1.37	1.31
F(000)	568	752	408	856
Radiation Mo-K_α				
Graphite monochromator, λ (Å)	0.710 69	0.710 69	0.7093	0.7093
Diffractometer	Hilger Y290	Hilger Y290	Enraf CAD4F	Enraf CAD4F
Orienting reflections, Range	25, $13 < \theta < 20°$			
Temp. (°C)	22	22	22	22
Scan Method ω–2θ, Data collection range	$2 < 2\theta < 48°$			
No. unique data	1 046	3 865	2 655	3 597
Total $I > 3\sigma I$	884	1 700	1 900	1 264
No. of parameters fitted	78	209	204	191
R^a	4.03%	7.32%	5.05%	6.17%
$R_w{}^b$	5.08%	6.61%	6.22%	5.42%
Weighting factor (g)	0.0037	0.000 02	0.0033	0
Largest shift/esd final cycle	<0.001	<0.001	<0.001	<0.001
Largest positive peak (e/Å^3)	0.45	0.48	0.24	0.11
Largest negative peak (e/Å^3)	−0.62	−0.50	−0.16	−0.10

^{a} $R = [\Sigma \| F_o| - |F_c \|]/\Sigma |F_o|$. ^{b} $R_w = [[\Sigma w(|F_o - F_c|)^2]/[\Sigma w(|F_o|)^2]]^{\frac{1}{2}}$ $w = 1/[(\sigma F_o)^2 - g^* F_o^2]$.

CH=N, of phthalazinylidene) 6.53–6.55 (1 H, d, J 7.3 Hz, phthalazinyl 5-H of phthalazinylidene) 6.98–7.80 (21 H, m, Ar), 8.01–8.04 (1 H, d, J 8.43 Hz, phthalazinyl 5H of dihydrophthalazinyl), 6.36 (1 H, s, CH=N, 1,2-dihydrophthalazinyl ring); δ_C($CDCl_3$) 50.19, 58.87, 86.75, 114.08, 121.04, 124.74, 125.77, 126.01, 126.18, 126.58, 126.97, 127.78, 127.92, 128.06, 128.47, 129.03, 129.55, 130.33, 131.46, 132.06, 132.24, 133.33, 133.66, 135.50, 144.78, 145.48, 146.02, 152.88, 167.65, and 174.09 ppm. The products (**4**) and (**5**) were also obtained in normal yields (8–10%) from these reactions; the only other compounds encountered were recovered *N*-phenylmaleimide and starting material (**2**).

*Dimethyl acetylenedicarboxylate (DMAD).** A solution of compound (**2c**) (1.48 g, 6.6 mmol) and DMAD (0.81 ml, 6.6 mmol) in acetonitrile (30 ml) was treated with glacial acetic acid (0.19 ml, 3.3 mmol) and stirred under reflux for 2 h during which time the colour changed from yellow to deep red and compound (**3c**) (m.p. 230–232 °C from MeCN, 0.197 g, 14.5%) separated (Filtrate A). Filtrate (A) was evaporated under reduced pressure and the residue in chloroform (3 ml) was placed on a flash column of silica gel (230–400 mesh ASTM made up in light petroleum (b.p. 40–60 °C) and eluted with the following solvents: light petroleum (b.p. 40–60 °C), toluene, dichloromethane, ethyl acetate, and finally methanol. The following compounds were eluted: 2-phenyl-1,2-dihydrophthalazine (**5c**) (from toluene fraction) (0.124 g, 8.8%), m.p. 136–137 °C (from MeCN); compound (**12**) (from dichloromethane fractions), m.p. 137–138 °C (from chloroform–hexane) (0.402 g. 15%) (Found: C, 65.1; H, 5.2; N, 6.9. $C_{22}H_{20}N_2O_6$ requires C, 64.7; H, 4.9; N, 6.9%); ν_{max} 1 763 and 1724 cm^{-1} (C=O) and 1 248 and 1 218 cm^{-1} (ester C–O); δ_H(CDCl) 2.05, 3.59, and 3.93 (each 3 H, s, Ac, MeO, MeO), 6.98–7.55 (m, Ar and C=C–CH–N), and 7.59 (s, CH=N); δ_C 19.65; 51.92; 52.3 (MeC, MeO); 52.68 (CHN); 114.9, 126.0; 124.36; 130.75; 134.55 (Ar): 145.75; 114.9, 128.6, 121.4 (N-Ph, C-1′, C-2′, C-3′, C-4′ respectively) 135.57 (CH=N); 161.88.

A small quantity of an unidentified product was also obtained from the later dichloromethane fractions. It had m.p. 120–122 °C and molecular formula $C_{22}H_{20}N_2O_6$; limited spectra data suggest it may be the *Z*-isomer of compound (**12**); compound (**2c**) recovered (0.574 g, 39%) (from the ethyl acetate fraction; compound (**11**) (from methanol fraction) (0.180 g, 7.5%), m.p. 251–253 °C (from methanol) (Found: C, 66.0; H, 4.6; N, 7.6. $C_{20}H_{16}N_2O_5$ requires C, 65.9; H, 4.4; N, 7.7%); ν_{max} 1 727 and 1 673 cm^{-1} (C=O) and 1 216 cm^{-1} (ester C–O) δ_H($CDCl_3$) 3.34 (s, 3 H, OMe), 3.82 (s, 3 H, OMe), 7.49–8.70 (m, 9 H, aromatic), and 9.33 (s, 1 H, CH=N); δ_C 50.2 (MeO); 89.2 (ylidene =C–N); 144.9, 124.7, 128.9, 127.5 (*N*-phenyl, C-1′, C-2′, C-3′, C-4′ respectively) 130.05, 131.1 (phthalazinyl 4a,8a); 132.0, 135.0, 137.3 (phthalazinyl C-5, C-6, C-7, C-8); 165.62 (ylidene, =C); 164.1, 168.2 (ester C=O); 179.0 (ketone C=O).

(*iii*) *Kinetic studies.* For an equilibrium system the equi-

$$trans(T) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} cis(C)$$

librium constant $K = k_1/k_{-1} = [cis]/[trans]$ at equilibrium. The value of $(k_1 + k_{-1})$, *i.e.* k_{obs} (Table 4) was determined[37] from equation (1) by plotting $\ln m/(m - f)$ *versus* t which gave a straight line with slope $(k_1 + k_{-1})$.

$$\ln \frac{m}{(m - f)} = (k_1 + k_{-1}) \cdot t \qquad (1)$$

for $m = \dfrac{k_1}{k_1 + k_{-1}}$ and $f = \dfrac{I_C}{I_C + I_T}$

I = intensity of the signal at time t

* We thank Mr. F. Quinn for assistance with these reactions.

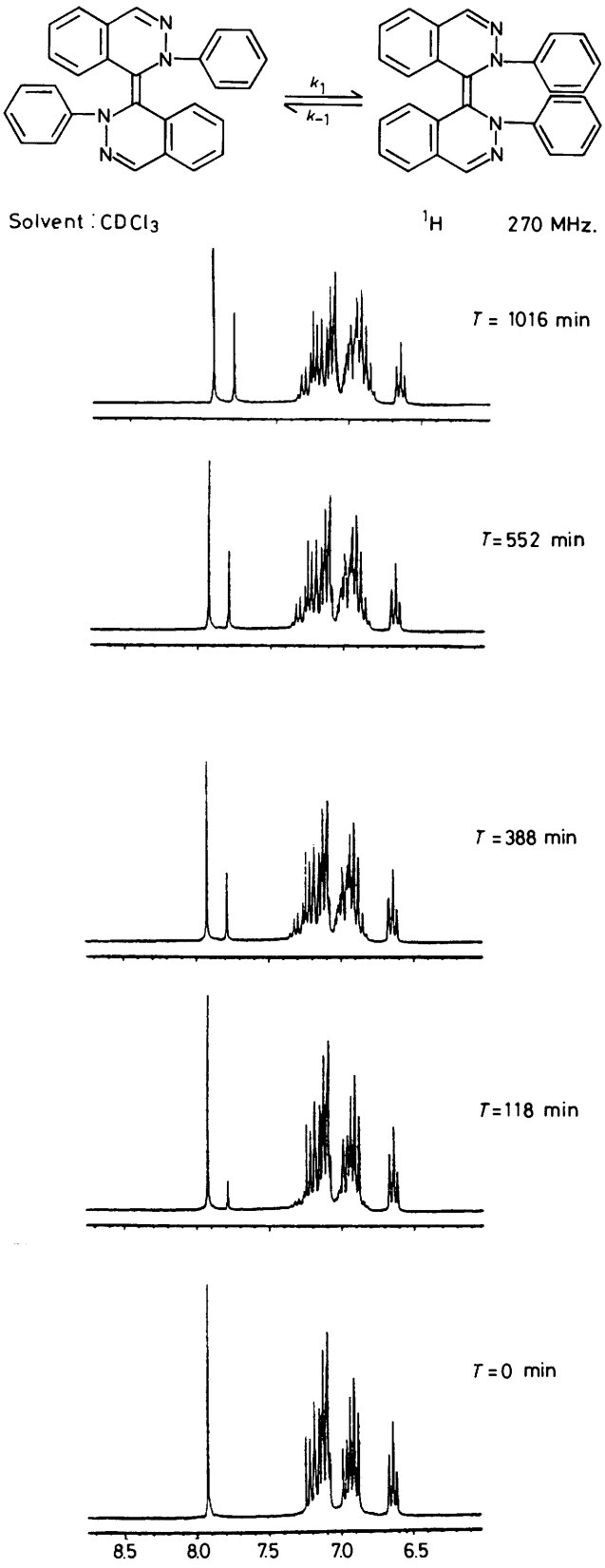


Figure 9. Kinetics of isomerization of compound (**3c**).

For example, for compound (**3c**) the equilibrium mixture of (**15c**) and (**3c**) was 40.1% *cis* (**15c**) and 59.9% *trans* (**3c**) hence giving $k_1/k_{-1} = 0.669$ and $m = 0.401$. For this compound I_T and I_C were taken as the intensities of the phthalazinyl CH=N

Table 6. Fractional atomic co-ordinates for (**3d**)

Atom	*x*	*y*	*z*
Br(1)	0.654 80(14)	0.377 57(6)	0.549 79(5)
N(1)	0.225 2(10)	0.123 5(3)	0.623 6(4)
N(2)	0.417 2(8)	0.067 7(3)	0.608 8(3)
C(1)	0.487 4(9)	0.045 3(4)	0.513 9(4)
C(2)	0.161 0(11)	0.176 4(5)	0.554 5(4)
C(3)	0.258 3(12)	0.268 2(5)	0.407 8(5)
C(4)	0.410 1(12)	0.285 1(5)	0.336 2(5)
C(5)	0.604 0(12)	0.229 7(4)	0.326 3(5)
C(6)	0.640 0(11)	0.152 2(4)	0.384 3(4)
C(7)	0.483 1(10)	0.131 3(4)	0.454 7(4)
C(8)	0.296 1(10)	0.191 8(4)	0.469 7(4)
C(9)	0.523 3(10)	0.031 1(4)	0.689 6(4)
C(10)	0.406 6(11)	0.028 8(4)	0.775 4(4)
C(11)	0.504 0(11)	−0.015 8(4)	0.854 4(5)
C(12)	0.714 3(11)	−0.057 2(4)	0.846 1(4)
C(13)	0.836 0(10)	−0.052 9(4)	0.763 5(4)
C(14)	0.744 5(10)	−0.007 5(4)	0.685 5(4)

Table 7. Fractional atomic co-ordinates for (**10d**)

Atom	*x*	*y*	*z*
Br(1)	0.108 5(2)	0.145 1(1)	0.512 8(2)
Br(2)	−0.053 3(2)	−0.037 9(2)	0.821 6(2)
O(1)	0.652 3(9)	−0.461 9(7)	0.988 5(7)
O(2)	0.608 9(10)	−0.097 2(7)	0.841 8(7)
N(1)	0.652 5(10)	−0.274 0(9)	0.928 5(8)
N(2)	0.321 7(11)	−0.532 5(9)	0.724 4(8)
N(3)	0.381 2(10)	−0.454 0(8)	0.768 9(8)
N(4)	0.546 7(10)	−0.259 7(8)	0.585 3(8)
N(5)	0.534 1(11)	−0.362 7(10)	0.544 6(8)
C(1)	0.727 9(13)	−0.244 1(11)	1.003 8(10)
C(2)	0.835 0(14)	−0.324 5(12)	1.028 7(11)
C(3)	0.908 2(17)	−0.297 6(14)	1.105 3(13)
C(4)	0.871 7(17)	−0.190 8(14)	1.146 6(13)
C(5)	0.767 7(17)	−0.113 6(14)	1.124 7(13)
C(6)	0.689 1(16)	−0.138 9(13)	1.053 2(12)
C(7)	0.625 2(13)	−0.389 0(12)	0.923 5(11)
C(8)	0.599 9(13)	−0.197 5(12)	0.852 7(10)
C(9)	0.552 5(10)	−0.386 1(9)	0.833 0(9)
C(10)	0.542 4(12)	−0.266 8(9)	0.781 4(9)
C(11)	0.379 7(13)	−0.639 1(11)	0.735 6(10)
C(12)	0.495 5(12)	−0.678 6(10)	0.777 4(10)
C(13)	0.552 5(14)	−0.797 6(12)	0.782 4(10)
C(14)	0.668 5(14)	−0.830 5(13)	0.816 6(11)
C(15)	0.741 1(15)	−0.751 8(12)	0.838 5(11)
C(16)	0.686 5(14)	−0.633 7(11)	0.833 9(10)
C(17)	0.562 0(12)	−0.596 3(10)	0.809 6(10)
C(18)	0.497 2(12)	−0.476 4(10)	0.806 0(9)
C(19)	0.284 9(12)	−0.347 1(10)	0.782 7(11)
C(20)	0.246 1(14)	−0.305 1(11)	0.878 7(12)
C(21)	0.145 9(15)	−0.209 7(12)	0.889 2(13)
C(22)	0.091 1(13)	−0.161 0(11)	0.802 3(12)
C(23)	0.133 4(13)	−0.199 3(11)	0.707 7(12)
C(24)	0.232 7(13)	−0.296 3(11)	0.694 7(12)
C(25)	0.625 5(13)	−0.448 9(11)	0.554 4(10)
C(26)	0.739 4(13)	−0.449 7(10)	0.603 7(10)
C(27)	0.845 5(13)	−0.540 6(12)	0.597 0(11)
C(28)	0.955 4(15)	−0.534 9(12)	0.640 9(11)
C(29)	0.956 4(14)	−0.441 5(11)	0.697 9(11)
C(30)	0.852 7(13)	−0.349 4(11)	0.705 3(10)
C(31)	0.745 5(13)	−0.354 6(11)	0.658 8(10)
C(32)	0.623 9(11)	−0.258 9(10)	0.672 2(9)
C(33)	0.450 4(12)	−0.161 4(11)	0.565 0(10)
C(34)	0.431 5(11)	−0.062 8(9)	0.621 6(9)
C(35)	0.331 0(13)	0.029 1(11)	0.604 9(10)
C(36)	0.251 3(13)	0.020 9(11)	0.531 7(11)
C(37)	0.270 6(14)	−0.074 1(11)	0.473 3(11)
C(38)	0.368 8(12)	−0.165 9(11)	0.488 2(10)

Table 8. Fractional atomic co-ordinates for (**11**)

Atom	*x*	*y*	*z*
O(1)	0.356 6(3)	0.963 1(2)	0.302 6(1)
O(2)	0.314 9(3)	0.761 5(2)	0.401 5(1)
O(3)	0.127 4(3)	0.402 5(3)	0.149 3(2)
O(4)	0.329 2(3)	0.409 6(3)	0.340 8(2)
O(5)	0.062 7(3)	0.400 6(3)	0.372 7(2)
N(1)	0.069 1(3)	0.877 3(3)	0.043 7(2)
N(2)	0.097 6(3)	0.806 2(3)	0.124 7(2)
C(1)	0.420 7(6)	1.087 7(4)	0.389 7(3)
C(2)	0.302 8(3)	0.799 2(3)	0.319 1(2)
C(3)	0.240 3(3)	0.684 2(3)	0.227 5(2)
C(4)	0.188 1(4)	0.510 4(3)	0.225 5(2)
C(5)	0.205 0(4)	0.440 4(3)	0.320 2(2)
C(6)	0.077 1(6)	0.342 8(5)	0.467 6(3)
C(15)	−0.030 0(4)	0.796 4(4)	0.199 6(2)
C(16)	−0.034 8(4)	0.943 5(4)	0.244 7(2)
C(17)	−0.167 0(5)	0.929 4(5)	0.311 7(3)
C(18)	−0.287 1(5)	0.770 6(6)	0.331 1(3)
C(19)	−0.277 8(4)	0.626 9(5)	0.284 1(3)
C(20)	−0.149 2(4)	0.638 8(4)	0.217 5(3)
C(7)	0.221 4(3)	0.747 4(3)	0.133 6(2)
C(8)	0.328 1(4)	0.751 4(3)	0.050 8(2)
C(9)	0.469 7(4)	0.701 3(3)	0.054 4(2)
C(10)	0.570 6(4)	0.711 4(4)	−0.027 3(2)
C(11)	0.533 4(4)	0.768 1(4)	−0.113 8(3)
C(12)	0.399 2(4)	0.820 6(4)	−0.117 9(2)
C(13)	0.296 8(4)	0.814 1(3)	−0.035 1(2)
C(14)	0.164 0(4)	0.876 6(3)	−0.031 6(2)

Table 9. Fractional atomic co-ordinates for (**12**)

Atom	*x*	*y*	*z*
O(1)	0.186 2(6)	−0.127 3(3)	0.878 7(4)
O(2)	0.347 1(5)	−0.040 6(3)	0.943 1(5)
O(3)	0.034 8(7)	0.163 4(4)	0.739 4(5)
O(4)	−0.017 1(5)	0.175 6(3)	0.901 6(4)
O(5)	0.121 3(5)	0.055 2(3)	0.985 2(4)
O(6)	0.261 6(5)	0.161 4(3)	1.013 1(4)
N(1)	0.349 9(6)	−0.087 2(4)	0.664 1(5)
N(2)	0.305 0(6)	−0.010 8(3)	0.676 0(4)
C(2)	0.233 7(9)	−0.061 3(5)	0.885 1(6)
C(3)	0.413 7(8)	−0.105 6(5)	1.005 8(7)
C(5)	0.040 8(8)	0.139 7(5)	0.826 8(7)
C(6)	−0.093 3(7)	0.248 7(5)	0.869 2(6)
C(7)	0.202 1(9)	0.110 0(6)	1.048 7(7)
C(8)	0.197 2(8)	0.091 0(5)	1.163 2(6)
C(1)	0.171 9(6)	0.010 4(4)	0.819 7(5)
C(4)	0.116 6(7)	0.066 8(4)	0.875 1(6)
C(9)	0.173 1(7)	0.009 6(4)	0.699 2(5)
C(10)	0.073 3(7)	−0.050 9(4)	0.640 8(5)
C(11)	−0.058 2(7)	−0.030 3(4)	0.614 2(5)
C(12)	−0.144 6(7)	−0.086 7(4)	0.560 3(5)
C(13)	−0.101 9(7)	−0.161 1(4)	0.530 2(5)
C(14)	0.028 4(7)	−0.182 0(5)	0.555 7(5)
C(15)	0.117 9(8)	−0.127 0(4)	0.612 5(5)
C(16)	0.260 6(8)	−0.140 9(5)	0.636 5(6)
C(17)	0.401 2(7)	0.051 9(4)	0.677 7(5)
C(18)	0.378 3(7)	0.131 3(4)	0.705 7(5)
C(19)	0.470 0(7)	0.191 9(4)	0.696 0(5)
C(20)	0.585 4(8)	0.173 0(5)	0.660 5(6)
C(21)	0.609 2(9)	0.094 0(5)	0.632 6(6)
C(22)	0.517 6(7)	0.033 1(5)	0.641 3(5)

signals in compounds (**3c**) and (**15c**) respectively and a plot of ln 0.401/(0.401-*f*) against *t* gave a straight line with slope (k_1 + k_{-1}). A typical kinetic run is shown in Figure 9. The series of rates were measured in this manner and double checked with *p*-Me or *p*-MeO signals where these were available. All rates were measured at least three times and were reproducible to ±2%. Probe temperatures which are accurate to ±0.5 °C, were measured before and after each rate using a standard methanol sample.

X-Ray Crystal Structures (*Tables* 5–9).—The X-ray crystal structure of compound (**3d**) has been reported previously.[25] Listings of the bond angles and bond lengths together with the thermal parameters for compounds (**3d**), (**10d**), (**11**), and (**12**) are available, on request from the Cambridge Crystallographic Data Centre.*

The structure of compound (**10d**) was solved by Patterson methods and the structures of (**11**) and (**12**) were solved by direct methods, SHELX86.[38] The three structures were refined by full matrix least-squares using SHELX76.[39] Data were corrected for Lorentz and polarization effects but not for absorption. Hydrogen atoms were included in calculated positions with fixed thermal parameters (μ = 0.05). The following atoms were refined anisotropically, for (**3d**) bromine, for (**10d**) bromine and oxygen, for (**11**) oxygen, nitrogen, and carbons C(1–6) and C(15–20), and for (**12**) the nitrogen, oxygen, and carbons C(2), C(3), and C(5–8) were refined anisotropically.

The atomic scattering factors for non-hydrogen and hydrogen atoms and the anomalous dispersion correction factors for non-hydrogen atoms were taken from the literature.[40–42] All calculations were performed on a VAX 8700 computer. The ORTEP program was used to obtain the drawings.[43]

* For details see 'Instructions for Authors (1990)', *J. Chem. Soc., Perkin Trans. 1*, 1990, Issue 1.

References

1 For a review *cf.* K. B. Wiberg, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 312.
2 N. M. Weinshenker and F. D. Greene, *J. Am. Chem. Soc.*, 1968, **90**, 506.
3 R. L. Viavattene, F. D. Greene, L. D. Cheung, R. Majeste, and L. M. Trefonas, *J. Am. Chem. Soc.*, 1974, **96**, 4342.
4 J. P. Hagenbuch, P. Vogel, A. A. Pinkerton, and D. Schwarzenbach, *Helv. Chim. Acta*, 1981, **64**, 1818.
5 R. Greenhouse, W. T. Borden, K. Hirotsu, and J. Clardy, *J. Am. Chem. Soc.*, 1977, **99**, 1664.
6 J. R. Wiseman and W. A. Pletcher, *J. Am. Chem. Soc.*, 1970, **92**, 956.
7 N. A. Bailey and S. E. Hull, *Chem. Commun.*, 1971, 960; also *Acta Crystallogr., Sect. B*, 1978, **34**, 3289.
8 I. R. Gault, W. D. Ollis, and I. O. Sutherland, *Chem. Commun.*, 1970, 269.
9 W. E. Thiessan, H. A. Levy, W. G. Dauben, G. H. Beasley, and D. A. Cox, *J. Am. Chem. Soc.*, 1971, **93**, 4312.
10 S. C. Piessard, J.-M. Leger, G. LeBaut, J.-C. Colleter, and J.-D. Brion, *J. Chem. Res.*, 1987, (*S*), 34; (*M*), 368.
11 H. L. Ammon and G. L. Wheeler, *J. Am. Chem. Soc.*, 1975, **97**, 2326.
12 H. L. Ammon, G. L. Wheeler, and I. Agranat, *Tetrahedron*, 1973, **29**, 2695.
13 W. L. Mock, *Tetrahedron Lett.*, 1972, 475; L. Rodom, J. A. Pople, and W. L. Mock, *ibid.*, p. 479.
14 G. A. Olah and G. K. Surya Prakash, *J. Org. Chem.*, 1977, **42**, 580.
15 J. E. Murray and M. P. Fleming, *J. Am. Chem. Soc.*, 1974, **96**, 4708.
16 D. H. R. Barton, F. S. Guziec, Jr., and I. Shahak, *J. Chem. Soc., Perkin Trans. 1*, 1974, 1794.
17 T. C. Back, D. H. R. Bargon, M. R. Britten-Kelly, and F. S. Guziec, Jr., *J. Chem. Soc., Perkin Trans. 1*, 1976, 2079.
18 J. Dannheim, W. Grahn, H. Kopf, and C. Parodi, *Chem. Ber.*, 1987, **120**, 871.
19 J. R. Wiseman, *J. Am. Chem. Soc.*, 1967, **89**, 5966.
20 T. Pilati and M. Simonetta, *J. Chem. Soc., Perkin Trans. 2*, 1977, 1435.
21 C. Wentrup, 'Reactive Molecules. The Neutral Reactive Intermediates in Organic Chemistry,' Wiley Interscience, New York, 1984, p. 270.

22 A. Greenberg and J. F. Liebman, 'Strained Organic Molecules,' A.P., New York, 1978, pp. 90–91.
23 A. Albert, 'Heterocyclic Chemistry,' Oxford University Press, New York, 1968, p. 150.
24 'Comprehensive Heterocyclic Chemistry,' eds. A. R. Katritzky and C. W. Rees, Pergamon Press, Oxford 1984, no six-membered (di-, tri-, or tetra-azine) ylidenes listed.
25 Part of this work has been published in preliminary communication form: R. N. Butler, A. M. Gillan, P. McArdle, and D. Cunningham, *J. Chem. Soc., Chem. Commun.*, 1987, 1016.
26 R. N. Butler, A. M. Gillan, J. P. James, P. McArdle, and D. Cunningham, *J. Chem. Res.*, 1989, (*S*), 62; (*M*), 0523.
27 H.-W. Wanzlick, B. Lachmann, and E. Schikora, *Chem. Ber.*, 1965, **98**, 3170, and other papers in the series.
28 H.-W. Wanzlick and B. Koenig, *Chem. Ber.*, 1964, **97**, 3513.
29 H.-W. Wanzlick and H. J. Kleiner, *Angew. Chem.*, 1963, **75**, 1204.
30 H.-W. Wanzlick, F. Esser, and H. J. Kleiner, *Chem. Ber.*, 1963, **96**, 1208 and 3024.
31 H. Kessler, *Angew. Chem., Int. Ed. Engl.*, 1970, **9**, 230 and 233.
32 M. Rabinovitz, I. Agranat, and A. Weitzen-Dagan, *Tetrahedron Lett.*, 1974, 1241.
33 I. Agranat, M. Rabinovitz, A. Weitzen-Dagan, and I. Gosnay, *J. Chem. Soc., Chem. Commun.*, 1972, 732.
34 I. Agranat and Y. Tapuhi, *J. Am. Chem. Soc.*, 1976, **98**, 615.
35 I. Agranat, M. Rabinovitz, I. Gosnay, and A. Weitzen-Dagan, *J. Am. Chem. Soc.*, 1972, **94**, 2889.
36 I. Belsky, H. Dodiuk, and Y. Shvo, *J. Org. Chem.*, 1977, **42**, 2734.
37 W. J. Moore, 'Physical Chemistry,' Longmans, Green and Co., Toronto, 1957, p. 537.
38 G. M. Sheldrick, SHELX86 a computer program for crystal structure determination, University of Goetingen 1986.
39 G. M. Sheldrick, SHELX76 a computer program for crystal structure determination, University of Cambridge (Cambridge, England) 1976.
40 D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 1968, **24**, 321.
41 R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.
42 D. T. Cromer and D. J. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.
43 C. K. Johnson, ORTEP, Oak Ridge Natl. Lab. (Rep.) ORNL (US), 1965–3794 revised (1971).

Paper 9/01790I
Received 27*th April* 1989
Accepted 6*th July* 1989