Regioselectivity and *endo*/*exo* selectivity in the cycloadditions of the phthalazinium dicyanomethanide 1,3-dipole with unsymmetrical alkene and alkyne dipolarophiles. Unexpected reversals of regiochemistry: a combined experimental and DFT theoretical study

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Received (in Cambridge, UK) 5th February 2001, Accepted 20th April 2001
First published as an Advance Article on the web 25th May 2001

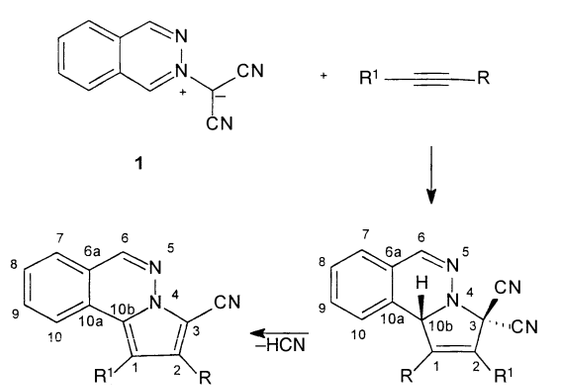
In the reactions of phthalazinium dicyanomethanide 1,3-dipole with electron-poor monosubstituted alkene and alkyne dipolarophiles the dicyanomethanide terminus bonds to the unsubstituted carbon giving 1-substituted pyrrolo[2,1-*a*]phthalazines. With electron-rich dipolarophiles the regiochemistry is reversed and the products are 2-substituted pyrrolo[2,1-*a*]phthalazines. An unexpected reversal of regiochemistry occurred with methyl methacrylate, due to a steric effect of the C–Me group, and the main product was 2-*exo*-methyl-2-*endo*-methoxycarbonyl-3,3-dicyano-1,2,3,10b-tetrahydropyrrolo[2,1-*a*]phthalazine, **17**. *endo* Cycloadditions were strongly favoured with alkene dipolarophiles containing π bonds in substituents on the alkene unit. With *N*-substituted maleimides *endo* products were formed exclusively even when the *N*-substituent was ^{t}Bu or adamantyl. Only with alkoxyvinyl ethers were *exo*-cycloadducts encountered. The mechanisms are discussed in conjunction with DFT calculations. An X-ray crystal structure is reported on *endo*-*N*-*tert*-butyl-3,3-dicyano-1,2,3,10b-tetrahydropyrrolo[2,1-*a*]phthalazine-1,2-dicarboximide, **25**.

There has been widespread recent interest in the cycloaddition reactions of azinium ylide 1,3-dipoles,[1–15] with much focus on pyridinium systems,[1,4,5–10] diazinium systems[2,3,11] and isoquinolinium substrates.[12–15] Our interest in azolium ylide 1,3-dipoles[16–18] led us to explore some azinium ylide systems also for comparison purposes and we focused on the phthalazinium ylide structure. We have recently reported on the reactions of phthalazinium methanide 1,3-dipoles with symmetrical alkene and alkyne dipolarophiles[19] and with thiones.[20] Much of the interesting vagaries of these types of dipoles remain to be uncovered and there are few reports of the reactive categories into which these dipoles fit. Some substituted pyridazinium dicyanomethanide dipoles have recently been found[3] to react mainly as dipole-LUMO controlled entities. Herein we report the synthetic regiochemistry and *endo*–*exo* selectivity of the phthlazinium 2-dicyanomethanide dipole **1** with a range of unsymmetrical alkene and alkyne dipolarophiles. The results, as well as theoretical calculations and a kinetic study,[21] show that for the phthalazinium case where the pyridazinium unit has a fused benzo ring the 1,3-dipole is a classic Sustmann Type II case. The reactions are dipole-HOMO controlled with electron deficient dipolarophiles and dipole-LUMO controlled with electron rich dipolarophiles. The regiochemistry switches over with the mechanistic switch.

Results and discussion

(i) Alkynes

When the dipole **1** was treated with monosubstituted alkynes containing CO_2R substituents in acetonitrile the products arose from bonding of the dicyanomethanide terminus to the unsubstituted alkyne carbon (Scheme 1, Table 1). Replacement of the alkyne H-atom by a D atom did not affect the regiochemistry.



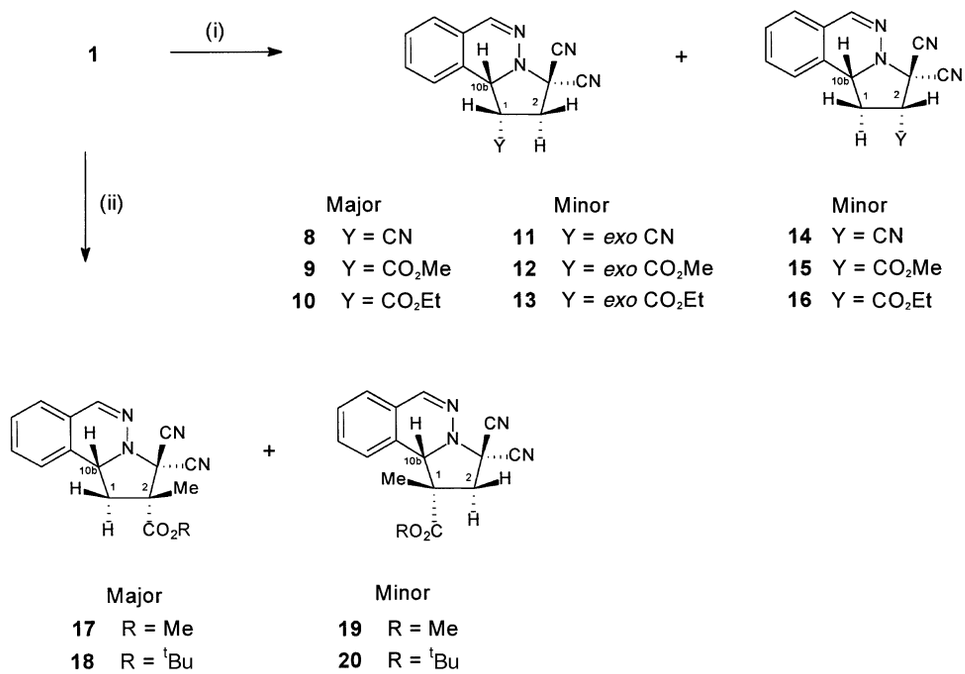
Scheme 1

With acidic dipolarophiles such as these monosubstituted alkynes we have examined the possibility that an early H-bonding of the dipolarophile to the dipole could influence the regiochemical outcome but to date there was no indication of a significant effect. For alkyl propiolates reactions occurred readily at ambient temperatures and the immediate cycloadducts **3** and **4** were stable products. For phenyl- and benzylacetylene the reactions required heat and the initial cycloadduct lost HCN *in situ* to give the isolated products **5**, **6** and **7** (Scheme 1). Interestingly in these cases the regiochemistry was reversed and the dicyanomethanide terminus was bonded to the substituted alkyne carbon. The 1-CH signal of compound **5** stood out as a strong singlet at 7.5 δ and this was

Table 1 Products

Entry	Compound	Mp/°C[a]	Yield (%)[c]	Minor products[e]			
				Compound	Yield	Compound	Yield
1	**3**	110–112	81	—	—	—	—
2	**4**	119–121	81	—	—	—	—
3	**5**	210–212[b]	82	—	—	—	—
4	**6**	213–214[b]	86	—	—	—	—
5	**7**	191–193[b]	70	—	—	—	—
6	**8**	212–213	60	**11**	0	**14**	8
7	**9**	132–133	58	**12**	7	**15**	2
8	**10**	130–131	60	**13**	9	**16**	4
9	**17**	138–139	62	**19**	13	—	—
10	**18**	119–120	62	**20**	17	—	—
11	**21**	137–138	85	—[f]	—	—	—
12	**22**	140–141	86	—[f]	—	—	—
13	**23**	233–235	87	—	—	—	—
14	**24**	205–207	81	—	—	—	—
15	**25**	212–214	80	—	—	—	—
16	**26**	229–230	52[d]	—	—	—	—

[a] Recrystallised from EtOH unless stated otherwise. [b] From MeCN. [c] Isolated yield of pure product. Some resins from decomposition of **1** were also obtained. [d] Starting materials recovered, 30%. [e] Isolated as gums; characterized by proton and carbon-13 NMR spectra. [f] A trace, <1%, of the *endo* isomer was detected by NMR in the residual gums.



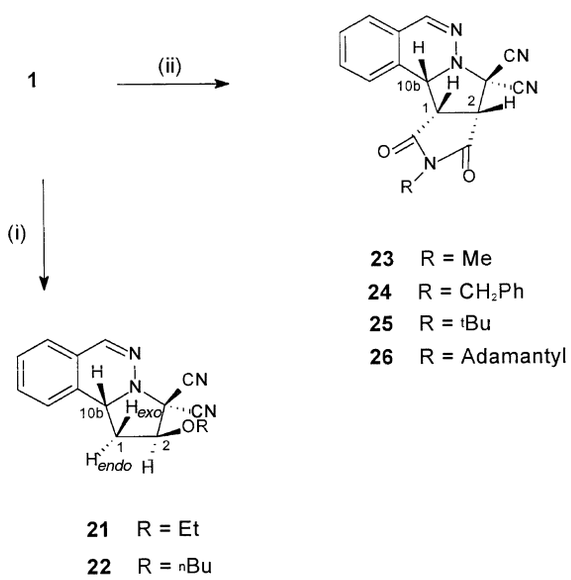
Scheme 2

completely absent in the deuterio product **6**. Location of the D-atom at C-1 in compound **6** was further confirmed by the ^{13}C NMR spectrum with the C-1 signal, strongly reduced. The regiochemistry of the products was readily established by proton and carbon-13 NMR spectra which showed all of the expected signals including NOE enhancement between the aromatic H-10 and H-1 and between H-1 and the 2-phenyl substituent. The former enhancement could not arise if the H-atom were located at C-2 and it did not occur in products with structure **2**.

(ii) Alkenes

(a) Monosubstituted and 1,1-disubstituted alkenes. In the reactions with unsymmetrical alkene dipolarophiles the number of possible products is increased by the possibility of *endo*- and *exo*- stereoisomers of the regioisomeric products. The regioproducts could be identified from the multiplicity of the CH-10b proton signal which was a doublet when C-1 carried a single proton, as in compounds **8**–**10** (Scheme 2) and a doublet of doublets when C-1 carried two protons as in structures **14**–**16**. The *endo* or *exo* stereochemistry might have been expected to reflect the magnitude of the *J* value between the 1-CH and 10b-CH, being larger when these were *cis* (*endo*-isomer) than when they were *trans* (*exo*-isomer) in accordance with the expected dihedral angle. However these *J* values were found to be unreliable indicators of the stereochemistry. The *endo* or *exo* stereochemistry was determined from NOE effects across the face of the fused pyrrole ring. Strong enhancement (5–10%) was observed between H-10b and *cis* H-atoms or Me groups at C-1. Little NOE enhancement (>0.5%) was observed between H-10b and H-1 when these were *trans* on the opposite face of the pyrrole ring. Enhancements were also observed between H-10b and H-2 when these were on the same face of the molecule and no enhancement was observed when they were *trans*. The cycloadditions of **1** with monosubstituted alkenes bearing electron withdrawing groups gave *endo* products with the dicyanomethanide terminus of the dipole bonded to the unsub-

stituted terminus of the alkene. Thus the major products were compounds **8**, **9** and **10** (Scheme 2). The *exo*-isomers **12** and **13** were also isolated and the *endo* : *exo* ratio was in the range 5–6 : 1 (Table 1, Scheme 2). The other regio-isomers **14**, **15** and **16** were also isolated or detected in the residual resinous products in low yields (Table 1, Scheme 2). When methyl methacrylate was used as dipolarophile an unexpected reversal of regio-chemistry occurred and this was also observed with *tert*-butyl methacrylate (Scheme 2, Table 1). In these cases the major products were compounds **17** and **18** and the minor products were compounds **19** and **20** (Table 1 entries 9 and 10). In the former pair the bridgehead H-10b proton signal was a doublet of doublets and in the latter pair it was a sharp singlet. NOE enhancements were observed between H-10b and the C–Me groups in compounds **17**–**20** thereby placing the carboxy groups in the *endo*-orientation. A complete reversal of regio-chemistry also occurred with the electron rich dipolarophiles alkyl vinyl ethers (Scheme 3). These gave the sole products **21**



Scheme 3 (i) CH_2=CH–OR (ii) *N*-substituted maleimide.

and **22** in high yields, (Table 1, entries 11 and 12). For these products H-10b was a doublet of doublets confirming the regiochemistry. Strong NOE effects (5–11%) were observed between H-10b and *exo*-H-1 and between *endo*-H-1 and H-2 which is also *endo*, thereby placing the alkoxy group at C-2 in the *exo*-position. The NOE effects observed between *endo*-H-2 and *exo*-H-1 and between *endo*-H-2 and H-10b both of which are on opposite faces of the plane were only 0.2–0.3%. All of the expected couplings for structures **21** and **22** were confirmed with COSY and single proton decoupled spectra.

(b) *N*-Substituted maleimides. In a recent study[19] of the reactions of the dipole **1** with symmetrical alkenes we established a strong preference for *endo*-cycloaddition with *N*-substituted maleimides except in the case of *N*-*tert*-butylmaleimide for which we obtained a cycloadduct with mp 157–159 °C in 80% yield. This was clearly the *exo*-isomer. It did not display an NOE effect between the H-atoms at C-10b and those at C-1 and C-2 which were on the opposite face of the fused 5,5-ring system. We assumed that the *tert*-butyl substituent had changed the *endo–exo* selectivity due to a steric effect. In the present work when we increased the steric effect by using *N*-adamantylmaleimide we were surprised to obtain as the sole product compound **26**, the *endo*-cycloadduct. This showed all of the characteristics of the *endo* structure and in particular the NOE effects. We then prepared the series of products **23**–**25**, repeating the reaction with *N*-*tert*-butylmaleimide and in each case we obtained exclusively the *endo* product (Table 1) (Scheme 3).

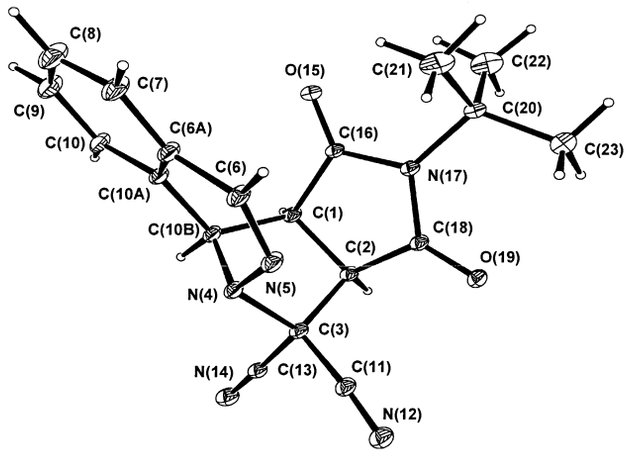


Fig. 1 X-Ray crystal structure of **25**.

Compound **25** had mp 212–214 °C and was clearly different to the cycloadduct of mp 157–159 °C which we obtained previously.[19] The reaction with *N*-*tert*-butylmaleimide has now been repeated many times in the temperature range, −20 °C, 0 °C, 25 °C and in each case we obtained compound **25**, the *endo*-isomer. Its structure was indicated as *endo*- by the NMR NOE data. The X-ray crystal structure is shown in Fig. 1 and confirms the *endo* structure. We have not been able to regain the *exo*- isomer, mp 157–159 °C which we isolated four years ago.[19] Re-examination of the retained NMR spectra of the original compound confirmed that it was indeed the *exo*-isomer. The spectra suggested that there may have been a low-level acidic impurity present in the samples of *N*-*tert*-butylmaleimide used since very weak signals due to *N*-*tert*-butylmaleamic acid were present. Despite numerous reactions in the temperature range −20 °C to ambient temperatures with the addition of varying quantities and mixtures of acetic acid, *N*-*tert*-butylmaleamic acid and water we have not been able to regain the *exo*-isomer. The *endo*-isomers are stable and do not rearrange to the *exo*-forms and the phenomenon was not due to a kinetic effect. Indeed the *exo*-isomer would not be an expected kinetic product since such isomers are usually the thermodynamic products. At present we do not know what caused the *exo*-isomer to be isolated from our earlier reactions but it was not a steric effect and we wish to correct our previous conclusion. Steric effects, as exhibited by the *tert*-butyl and adamantyl groups on the *N*-atom of maleimides do not change the preferred *endo* selectivity of the cycloaddition with the phthalazinium dicyanomethanide 1,3-dipole.

Discussion and theoretical calculations

Ongoing kinetic studies, which will be reported separately,[21] suggest that the dipole **1** is an example of a Sustmann Type II dipole where the cycloaddition reaction may be HOMO dipole or LUMO dipole controlled depending on the dipolarophile used. Thus for the electron deficient dipolarophiles used herein the reaction is a HOMO dipole–LUMO dipolarophile process. The regiochemistry observed agrees with this insofar as the negative terminus of the dipole (HOMO, highest atomic orbital coefficient set) bonds to the unsubstituted terminus of the dipolarophile (LUMO, highest atomic orbital coefficient set). The reversal of regiochemistry with the electron rich dipolarophiles alkyl vinyl ethers and benzyl- and phenylacetylenes which give the exclusive products **21**, **22** and **5**–**7**, respectively results from the switchover to a LUMO dipole controlled reaction where the HOMO of the dipolarophile mixes with the LUMO of the dipole in the transition state. The orbital coefficients now result in the C–$(CN)_2$ terminus of the dipole (smaller orbital coefficient in LUMO) connecting with monosubstituted terminus of dipolarophile (smaller orbital coefficient in HOMO). Density

Table 2 DFT calculations, Frontier orbital coefficients and energies

No. from Table 1	Substituents	HOMO C-1	HOMO C-2	LUMO C-1	LUMO C-2	HO-π	LUMO	LU**d**-HO**p** [h]	LU**p**-HO**d** [h]	ΔE_{rel} [i]/ kJ mol^{-1}
11	H,OCH_3 [a]	0.2723	0.4005	−0.4763	0.3867	−0.2151	0.0447	0.1135	0.2515	21.6
6	H,CN [b]	0.3109	0.3516	−0.3202	0.4147	−0.2892	−0.0563	0.1876	0.1505	−10.8
7	H,CO_2H [c]	0.3706	0.3661	−0.262	0.3885	−0.287	−0.0494	0.1854	0.1574	−4.1
9	CH_3,CO_2H [d]	0.3554	0.3763	−0.2585	0.3723	−0.2696	−0.042	0.168	0.1648	1.1
3	Ph [e]	0.2187	0.3191	−0.1409	0.2569	−0.2311	−0.0284	0.1295	0.1784	13.1
1	CO_2Me [f]	0.3967	0.3969	−0.1899	0.335	−0.2995	−0.0443	0.1979	0.1625	−8.6
—	Dipole **1** [g]	0.3869	−0.2545	0.1687	0.2926	−0.2068	−0.1016			

[a] Methyl vinyl ether (representing ethyl vinyl ether). [b] Acrylonitrile. [c] Acrylic acid (representing methyl acrylate). [d] Methacrylic acid (representing methyl methacrylate). [e] Phenylacetylene. [f] Methyl propiolate. [g] C-1 represents $C^-(CN)_2$ terminus; C-2 represents CH-10b-terminus (**d** dipole; **p** dipolarophile). [h] Frontier orbital energy gaps (Ha). [i] ΔE_{rel}, difference in transition state energies; negative indicates dipolarophile substituent at CH-10b dipole terminus and positive indicates dipolarophile substituent at $C^-(CN)_2$ dipole terminus.

functional theory (DFT) calculations agree with the observed experimental results. A number of computational methods incorporated into the Gaussian98A7 series of programs were used in this study.[22] All geometry optimisations were carried out with the RB3LYP[23] DFT method. The standard split valence plus polarisation 6-31G(d) basis set was used in all cases. Normal mode analysis was performed to ascertain the nature of some of the structures identified as stationary points on the potential energy surfaces. In all cases, optimised lower level basis set geometries including force constants were used as starting points for the 6-31G(d) transition state optimisations. All results reported here are for the 6-31G(d) set.

Table 2 gives the coefficient of the $2p_z$ AO for the π-HOMO and LUMO for C-1 (with substituent) and C-2 (unsubstituted) of the isolated dipolarophiles (symbol **p**) and the CH-10b and $C^-(CN)_2$ termini of the dipole (symbol **d**). There are $3p_z$ and d_{xz} and d_{yz} coefficients which enter the π system with the 6-31G(d) basis set but their relative weights follow the $2p_z$ results. Thus arguments based on single AO ratios are valid here. The π-HOMO and LUMO orbital energies are reported for the dipole and dipolarophiles as well as the energy gaps (Ha) between the LUMOd − πHOMOp and LUMO**p** − HOMO**d**. It was verified that the HOMO and LUMO of the dipole **1** is composed mainly of the AO coefficients from the three dipole atoms and not a lone pair for example. Lastly relative energies (kJ mol^{-1}) of the transition states are given. Those with positive values are for the regiochemistry where substituents are favoured over the $C^-(CN)_2$ terminus of the dipole, and those with negative values are when the dipolarophile substituent is favoured over CH-10b of the dipole.

In every case the relative energies follow experimental findings. Whichever HOMO–LUMO gap is smaller corresponds to the major isomer found, as well as for the AO coefficient relationships. In the case of methacrylate positive relative energy indicates a preference for the isomer with the dipolarophile substituents at the $C^-(CN)_2$ terminus as in experiment for the methyl ester and in reverse to the results for the acrylate case. The HOMO–LUMO gaps for methacrylate are nearly equal and the change in relative weights of the HOMO coefficients between acrylate and methacrylate are indicative of the change in isomer preference.

Experimental

Mps were measured on an electrothermal apparatus. IR spectra were measured with a Perkin-Elmer Spectrum 1000 spectrophotometer and microanalysis on a Perkin-Elmer Model 240 CHN analyser. NMR spectra were measured on a JEOL GXFT 400 instrument with tetramethylsilane as internal reference and either deuteriochloroform or hexadeuteriomethyl sulfoxide as a solvent. ^{1}H NMR assignments were supported by selective proton decoupling and COSY spectra. *J* values are given in Hz. C-13 NMR assignments were supported by DEPT spectra. The dipole **1** was prepared as previously described.[19] The *N*-adamantylmaleimide was prepared according to a literature procedure.[24] The other dipolarophiles were from Aldrich.

Alkyne dipolarophiles: phenylacetylene, benzylacetylene (3-phenylpropyne), methyl propiolate and ethyl propiolate

1-Methoxycarbonyl-3,10b-dihydro-3,3-dicyanopyrrolo[2,1-*a*]-phthalazine 3. A suspension of dipole **1** (0.30 g, 1.54 mmol) in acetonitrile (20 cm^3) was treated with an excess of methyl propiolate (0.27 cm^3, 3.08 mmol), stirred at ambient temperature for 24 hours giving a pale yellow solution, from which the solvent was removed under reduced pressure to give the compound **3** (81%); white crystalline solid; mp 110–112 °C (EtOH) (Found: C, 64.7; H, 3.60; N, 20.1. $C_{15}H_{10}N_4O_2$ requires C, 64.7; H, 3.4; N, 20.1%); ν_{max}(mull)/cm^{-1} 2226 (C≡N), 1739 (C=O); δ_H($CDCl_3$) 3.98 (s, 3H, OMe), 5.44 (s, 1H, H-10b), 6.86 (s, 1H, H-2), 7.37–7.52 (m, 4H, H-7 to H-10), 7.87 (s, 1H, H-6); δ_C($CDCl_3$) 53.2 (C-3), 60.7 (OMe), 110.7, 112.0 (C≡N), 124.1 (C-2), 126.6 (C-1), 128.8, 131.3, 132.3 (C-6a to C-10), 146.5 (C-6), 163.5 (C=O); similarly isolated was compound **4**.

1-Ethoxycarbonyl-3,10b-dihydro-3,3-dicyanopyrrolo[2,1-*a*]-phthalazine 4. (86%); mp 119–121 °C (EtOH) (Found: C, 65.5; H, 4.0; N, 19.3. $C_{16}H_{12}N_4O_2$ requires C, 65.7; H, 4.1; N, 19.1%); ν_{max}(mull)/cm^{-1} 2223 (C≡N), 1718 (C=O); δ_H($CDCl_3$) 1.42 (t, 3H, *J* 7.0, CH_3), 4.43 (q, 2H, CH_2), 5.43 (s, 1H, H-10b), 6.88 (s, 1H, H-2), 7.26–7.49 (m, 4H, H-7 to H-10), 7.86 (s, 1H, H-6); δ_C($CDCl_3$) 14.0 (CH_3), 40.7 (CH_2), 62.5 (C-10b), 110.5, 110.8 (C≡N), 124.0 (C-2), 126.5 (C-1), 127.9, 128.7, 128.9, 130.9, 132.3 (C-6a–C-10), 146.4 (C-6), 162.0 (C=O).

2-Phenyl-3-cyanopyrrolo[2,1-*a*]phthalazine 5. A suspension of dipole **1** (0.30 g, 1.54 mmol) in acetonitrile (20 cm^3) was treated with an excess of phenylacetylene (1.69 cm^3, 15.4 mmol), stirred under reflux in an anhydrous atmosphere for 24 hours, cooled to ambient temperature and filtered to give **5** (82%), white needles, mp 210–212 °C (CH_3CN) (Found: C, 80.0; H, 4.0; N, 15.4. $C_{18}H_{11}N_3$ requires C, 80.2; H, 4.1; N, 15.6%); ν_{max}(mull)/cm^{-1} 2214 (C≡N); δ_H([$^2H_6$]DMSO, 60 °C) 7.41–7.45 (m, 1H, Ph H-4′), 7.51–7.57 (m, 2H, Ph H-3′), 7.57 (s, 1H, H-1), 7.71–7.75 (m, 1H, H-9), 7.85–7.87 (m, 2H, Ph H-2′), 7.90–7.92 (m, 1H, H-8), 8.06 (d, 1H, *J* 7.7, H-10), 8.31 (d, 1H, *J* 8.1, H-7), 8.90 (s, 1H, H-6); δ_C([$^2H_6$]DMSO, 60 °C) 99.2 (C-1), 113.5 (C≡N), 120.6 (C-2), 122.5 (PhC-4′), 125.9 (C-3), 127.7 (C-10b), 128.4, 128.6, 128.9, 129.0 (C-8 to C-10 and PhC-2′ and PhC-3′), 131.8 (C-1′), 133.5 (C-7), 133.9 (C-6a), 146.2(C-6). Products **6** and **7** were similarly obtained.

1-Deuterio-2-phenyl-3-cyanopyrrolo[2,1-*a*]phthalazine 6. 6 (86%); white needles, mp 213–214 °C (CH_3CN) (Found: C, 79.6; H, 3.5; N, 15.6. $C_{18}H_{10}N_3D$ requires C, 79.9; H, 3.7; N, 15.5%); ν_{max}(mull)/cm^{-1} 2215 (C≡N); δ_H([$^2H_6$]DMSO, 60 °C) 7.43 (t, 1H, *J* 6.3, Ph H-4′), 7.51–7.57 (m, 2H, Ph H-3′), 7.71–7.75 (m,

1H, H-9), 7.85–7.87 (m, 2H, Ph H-2′), 7.90–7.92 (m, 1H, H-8), 8.06 (d, 1H, *J* 7.7, H-10), 8.31 (d, 1H, *J* 8.1, H-7), 8.90 (s, 1H, H-6), the H-1 signal at 7.57 for **5** was absent; δ_C([$^2H_6$]DMSO, 60 °C) 113.5 (C≡N), 120.6 (C-2), 122.5 (C-4′), 125.9 (C-3), 127.7 (C-10b), 128.4, 128.6, 128.9, 129.0 (C-8 to C-10 and C-2′ and C-3′), 131.8 (C-1′), 133.5 (C-7), 133.9 (C-6a), 146.2 (C-6), the C-1 signal at 99.2 ppm was reduced almost to zero.

2-Benzyl-3-cyanopyrrolo[2,1-*a*]phthalazine 7. 7 (70%), white crystalline solid, mp 191–193 °C (CH_3CN) (Found: C, 80.9; H, 4.5; N, 14.8. $C_{19}H_{13}N_3$ requires C, 80.5; H, 4.6; N, 14.8%); ν_{max}(mull)/cm^{-1} 2216 (C≡N); δ_H([$^2H_6$]DMSO, 70 °C), 4.12 (s, 2H, CH_2 benzyl), 7.06 (s, 1H, H-1), 7.22–7.32 (m, 5H, Ph H-2′, H-3′, H-4′), 7.66–7.68 (m, 1H, H-9), 7.84–7.88 (m, 1H, H-8), 8.02 (d, 1H, *J* 7.7, H-10), 8.20 (d, 1H, *J* 8.1, H-7), 8.87 (s, 1H, H-6); δ_C([$^2H_6$]DMSO) 32.5 (CH_2), 100.7 (C-1), 112.5 (C≡N), 120.4 (C-2), 122.3, 125.9, 128.5 (C-8 to C-10 and C-2′ to C-3′), 126.3 (C-10b), 133.4 (C-7), 133.8 (C-4′), 135.2 (C-6a), 139.5 (C-1′), 145.6 (C-6).

(ii) Alkene dipolarophiles: acrylonitrile, methyl acrylate, ethyl acrylate, methyl methacrylate, *tert*-butyl methacrylate, *n*-butyl vinyl ether and ethyl vinyl ether

***endo*-1,3,3-Tricyano-1,2,3,10b-tetrahydropyrrolo[2,1-*a*]-phthalazine 8 and *endo*-2-cyano isomer 14.** A suspension of dipole **1** (0.30 g, 1.54 mmol) in acetonitrile (20 cm^3) was treated with acrylonitrile (0.53 cm^3, 7.7 mmol), stirred at ambient temperature for 24 hours and the solvent was removed under reduced pressure. Treatment of the residue with dichloromethane (4 cm^3) gave **8**.

Compound **8** yield 60%; mp 212–213 °C (EtOH) (Found: C, 68.0; H, 3.6; N, 28.0. $C_{14}H_9N_5$ requires C, 68.0; H, 3.7; N, 28.3%); ν_{max}(mull)/cm^{-1} 2248 (C≡N); δ_H([$^2H_6$] DMSO) 3.26–3.38 (m, 2H, H-2), 4.31–4.34 (m, 1H, H-1), 4.73 (d, 1H, *J* 4.8, H-10b), 7.40 (m, 1H, H-10), 7.47–7.57 (m, 2H, H-8-H-9), 7.58–7.62 (m, 1H, H-7), 7.60 (s, 1H, H-6); δ_C([$^2H_6$] DMSO) 29.9 (C-2), 59.4 (C-10b), 114.8, 115.3 (C≡N on C-3), 119.7 (C≡N on C-1), 125.5 (C-10a), 127.8, 130.2, 133.3 (C-8, C-9, C-10), 131.4 (C-6a), 133.2 (C-7), 144.7 (C-6).

The filtrate was placed on a flash column of silica gel (230–400 mesh ASTM) and eluted with a mixture of petroleum spirit (bp 40–60 °C) and dichloromethane in the gradient 1 : 1 to 0 : 1. To give **14** as a gummy residue

Compound **14** yield 8%; gum (re-columned crude sample); ν_{max}(CCl_4 liquid cell)/cm^{-1} 2228 (C≡N); δ_H(CD_3CN) 3.31–3.33 (m, 2H, H-1), 3.76 (m, 1H, H-2), 4.17 (dd, 1H, *J* 8.6, 8.4, H-10b), 7.42–7.80 (m, 4H, H-7 to H-10), 7.86 (s, 1H, H-6), the only other products were intractable resins and the *exo*-isomer **11** was not detected.

***endo*-1-Methoxycarbonyl-3,3-dicyano-1,2,3,10b-tetrahydro-pyrrolo[2,1-*a*]phthalazine 9 and *exo*-1-methoxycarbonyl isomer 12 and *endo*-2-methoxycarbonyl-3,3-dicyano-1,2,3,10b-tetra-hydropyrrolo[2,1-*a*]phthalazine 15.** A suspension of the dipole **1** (0.30 g, 1.54 mmol) in acetonitrile (20 cm^3) was treated with methyl acrylate (0.69 cm^3, 7.7 mmol), stirred at ambient temperature for 12 h, giving a pale yellow solution from which the solvent was removed under reduced pressure. The residue was dissolved in dichloromethane (4 cm^3). This was placed on a flash column of silica gel (230–400 mesh ASTM) and eluted with a gradient mixture of dichloromethane and petroleum spirit (bp 40–60 °C) in the range 1 : 1 to 1 : 0. The products from the column were isolated in the following order:

Compound **15** yield 2%; gum (re-columned crude sample); ν_{max}(CCl_4 liquid cell)/cm^{-1}, 1742 (C=O); δ_H($CDCl_3$) 2.53–2.98 (m, 2H, H-1), 3.96 (s, 1H, OMe), 3.90–3.96 (m, 1H, H-2$_{exo}$), 4.34 (dd, 1H, *J* 8.6, 8.5, H-10b), 7.13–7.53 (m, 4H, H-7 to H-10), 7.81 (s, 1H, H-6).

Compound **12** yield 7%; gum (re-columned crude sample); ν_{max}(CCl_4 liquid cell)/cm^{-1}, 1751 (C=O); δ_H($CDCl_3$) 3.00–3.22 (m, 2H, H-2), 3.86 (s, 3H, OMe$_{exo}$), 3.54–3.59 (m, 1H, H-1$_{endo}$), 4.46 (d, 1H, *J* 8.8, H-10b), 7.40–7.61 (m, 4H, H-7 to H-10), 7.89 (s, 1H, H-6); δ_C($CDCl_3$) 42.3 (OMe), 58.7 (C-10b), 113.2, 113.5 (C≡N), 123.4, 124.9, 126.0, 128.8 (C-7 to C-10), 131.5 (C-6a), 145.8 (C-6), 170.8 (C=O).

Compound **9** yield 58%; white crystalline solid, mp 132–133 °C (EtOH) (Found: C, 63.9; H, 4.3; N, 19.9. $C_{15}H_{11}N_4O_2$ requires C, 63.4; H, 4.3; N, 19.9%); ν_{max}(mull)/cm^{-1} 1742 (C=O); δ_H($CDCl_3$) 3.03–3.68 (m, 1H, H-2$_{exo}$), 3.55 (s, 3H, OMe$_{endo}$), 3.94–4.05 (m, 1H, H-2$_{endo}$), 3.63–3.68 (m, 1H, H-1$_{exo}$), 4.82 (d, 1H, *J* 6.6, H-10b), 7.26–7.45 (m, 4H, H-7 to H-10), 7.66 (s, 1H, H-6); δ_C($CDCl_3$) 39.2 (C-2), 42.9 (OMe), 52.4 (C-1), 55.8 (C-3), 59.2 (C-10b), 113.3, 113.9 (C≡N), 124.7 (C-10a), 125.1, 126.1 (C-9, C-8), 129.7 (C-7), 130.2 (C-6a), 144.4 (C-6), 170.6 (C=O).

Similarly obtained from the column in the following order were compounds **16**, **13** and **10**.

***endo*-2-Ethoxycarbonyl-3,3-dicyano-1,2,3,10b-tetrahydropyr-rolo[2,1-*a*]phthalazine 16.** Yield 4%, gum (re-columned crude sample); ν_{max}(CCl_4 liquid cell)/cm^{-1} 1743 (C=O); δ_H($CDCl_3$) 1.34 (t, 3H, *J* 6.9, CH_3), 2.96–3.05 (m, 1H, H-1), 3.18–3.23 (m, 1H, H-1), 3.51–3.56 (m, 1H, H-2), 4.31 (q, 2H, CH_2), 4.45 (dd, 1H, *J* 10.8, 6.9,H-10b), 7.40–7.60 (m, 4H, H-7 to H-10), 7.78 (s, 1H, H-6).

***exo*-1-Ethoxycarbonyl-3,3-dicyano-1,2,3,10b-tetrahydropyr-rolo[2,1-*a*]phthalazine 13.** Yield 9%, gum (re-columned crude sample); ν_{max}(CCl_4 liquid cell)/cm^{-1} 1752 (C=O); δ_H($CDCl_3$) 1.42 (t, 3H, *J* 6.9, CH_3), 2.51–2.57 (m, 1H, H-2), 2.92–2.99 (m, 1H, H-2), 3.83–3.89 (m, 1H, H-1), 4.36 (q, 2H, CH_2), 4.46 (d, 1H, *J* 9.2, H-10b), 7.13–7.15 (d, 1H, *J* 6.6, H-10), 7.26–7.53 (m, 3H, H-7 to H-9), 7.80 (s, 1H, H-6); δ_C($CDCl_3$) 14.0 (CH_3), 38.2 (CH_2), 58.8 (C-10b), 62.5 (C-2), 112.6, 113.2 (C≡N), 128.7, 128.9, 133.1 (C-7 to C-10), 148.8, (C-6), 170.4 (C=O).

***endo*-1-Ethoxycarbonyl-3,3-dicyano-1,2,3,10b-tetrahydropyr-rolo[2,1-*a*]phthalazine 10.** Yield 60%, 130–131 °C (from ethanol) (Found: C, 65.7; H, 4.4; N, 19.2. $C_{16}H_{14}N_4O_2$ requires C, 65.3; H, 4.7; N, 19.1%); ν_{max}(mull)/cm^{-1} 1753 (C=O); δ_H($CDCl_3$) 1.07 (t, 3H, *J* 6.9, CH_3), 2.90–3.03 (m, 1H, H-2), 3.13–3.17 (m, 1H, H-2), 3.60–3.64 (m, 1H, H-1), 4.00 (q, 2H, CH_2), 4.85 (d, 2H, *J* 6.2, H-10b), 7.20–7.43 (m, 4H, H-7 to H-10), 7.60 (s, 1H, H-6); δ_C($CDCl_3$) 13.8 (CH_3), 39.2 (CH_2), 39.5 (C-2), 55.0 (C-3), 59.2 (C-10b), 61.8 (C-2), 113.9 (C≡N), 124.7 (C-7), 125.5 (C-6a), 126.6 (C-9), 129.4 (C-7), 131.4 (C-10), 144.1 (C-6), 170.1 (C=O).

***endo*-2-Methoxycarbonyl-*exo*-2-methyl-3,3-dicyano-1,2,3,10b-tetrahydropyrrolo[2,1-*a*]phthalazine 17 and *endo*-1-methoxy-carbonyl-*exo*-1-methyl-3,3-dicyano-1,2,3,10b-tetrahydropyrrolo-[2,1-*a*]phthalazine 19.** A suspension of the dipole **1** (0.30 g, 1.54 mmol) in acetonitrile (20 cm^3) was treated with an excess of methyl methacrylate (0.82 cm^3, 7.7 mmol), stirred at ambient temperature for 24 h and the solvent was removed under reduced pressure. The residue in dichloromethane (3 cm^3) was then placed onto a flash column of silica gel (230–400 mesh ASTM) and eluted with a petroleum spirit (bp 40–60 °C) dichloromethane mixture in the range 1 : 1 to 0 : 1. The products were eluted in the following order:

Compound **17** yield 62%, white crystalline solid, mp 138–139 °C (EtOH) (Found: C, 65.0; H, 4.4; N, 18.7. $C_{16}H_{14}N_4O_2$ requires C, 65.2; H, 4.7; N, 19.0%); ν_{max}(mull)/cm^{-1} 1738 (C=O), 2234 (C≡N); δ_H([$^2H_6$]DMSO) 2.70–2.79 (m, 2H, H-1), 3.35 (s, 3H, CH_{3exo}), 3.78 (s, 3H, OMe$_{endo}$), 4.73 (dd, 1H, *J* 9.9, 6.5, H-10b), 7.24 (d, 1H, *J* 7.2, H-10), 7.48–7.58 (m, 3H, H-7 to H-9), 7.93 (s, 1H, H-6); δ_C([$^2H_6$]DMSO) 21.4 (CH_3), 37.2 (C-1), 53.4 (C-2), 54.3 (OMe), 54.7 (C-3), 64.1 (C-10b), 111.8, 112.9 (C≡N), 123.5 (C-10a), 123.9 (C-6a), 128.5 (C-8), 129.2 (C-9), 132.0 (C-7), 132.5 (C-10), 145.1 (C-6a), 170.7 (C=O).

Compound **19** yield 13%, gum (re-columned crude sample), ν_{max}(CCl_4 liquid cell/cm^{-1} 1739 (C=O); δ_H($CDCl_3$) 1.64 (s, 3H, CH_3), 2.72 (d, 1H, *J* 14.6, H-2$_{exo}$), 3.27 (d, 1H, *J* 14.6, H-2$_{endo}$), 4.52 (s, 1H, H-10b), 7.43–7.61 (m, 4H, H-7 to H-10), 7.80 (s, 1H, H-6).

Similarly isolated from the column were compounds **18** and **20.**

***endo*-2-*tert*-Butyloxycarbonyl-*exo*-2-methyl-3,3-dicyano-1,2,3,10b-tetrahydropyrrolo[2,1-*a*]phthalazine 18 and *endo*-1-*tert*-butyloxycarbonyl-*exo*-1-methyl-3,3-dicyano-1,2,3,10b-tetrahydropyrrolo[2,1-*a*]phthalazine 20**

Compound **18** yield 62%, 119–120 °C (EtOH) (Found: C, 67.3; H, 5.8; N, 16.3. $C_{19}H_{20}N_4O_2$ requires C, 67.5; H, 5.9; N, 16.6%); ν_{max}(mull)/cm^{-1} 1743 (C=O); δ_H($CDCl_3$) 1.52 (s, 9H, ^{t}Bu), 1.78 (s, 3H, CH_3), 2.53 (dd, 1H, *J* 12.8, 6.6, H-1$_{exo}$), 2.90 (dd, 1H, *J* 12.8, 9.9, H-1$_{endo}$), 4.69 (dd, 1H, *J* 9.9, 6.6, H-10b), 7.04 (d, 1H, *J* 7.3, H-10), 7.25–7.49 (m, 3H, H-7 to H-9), 7.69 (s, 1H, H-6); δ_C($CDCl_3$) 21.9 (CH_3), 27.6 ((CH_3)$_3$), 37.6 (C-1), 54.2 (C-10b), 55.0 (C-2), 64.4 (C-3), 84.6 (C(CH_3)$_3$), 111.8, 113.0 (C≡N), 123.5 (C-10a), 123.9 (C-6a), 126.2, 128.6, 131.2 (C-7 to C-9), 132.4 (C-10), 144.4 (C-6), 169.4 (C=O).

Compound **20** yield 17%; gum (re-columned crude sample); ν_{max}(mull)/cm^{-1} 1742 (C=O); δ_H($CDCl_3$) 1.15 (s, 9H, ^{t}Bu), 1.63 (s, 1H, CH_3), 2.55 (d, 1H, *J* 14.2, H-2 $_{exo}$), 3.27 (d, 1H, *J* 13.9, H-2$_{endo}$), 4.49 (s, 1H, H-10b), 7.24–7.44 (m, 4H, H-7 to H-10), 7.58 (s, 1H, H-6).

***exo*-2-Butoxy-3,3-dicyano-1,2,3,10b-tetrahydropyrrolo[2,1-*a*]-phthalazine 22.** A solution of dipole **1** (0.30 g, 1.54 mmol) in acetonitrile (20 cm^3) was treated with *n*-butyl vinyl ether (1.47 cm^3, 15.4 mmol), stirred under reflux for 12 hours, and the solvent was removed under reduced pressure to give the compound **22**.

Compound **22** yield 86%, white crystalline solid, mp 140–141 °C (EtOH) (Found: C, 69.3; H, 6.2; N, 19.0. $C_{17}H_{18}N_4O$ requires C, 69.1; H, 6.1; N, 18.9%); δ_H($CDCl_3$) 0.96 (t, 3H, *J* 6.8, CH_3), 1.42–1.49 (m, 2H, CH_2), 1.65–1.70 (m, 2H, CH_2), 2.39–2.45 (m, 1H, H-1$_{exo}$), 2.64–2.72 (m, 1H, H-1$_{endo}$), 3.65–3.71 (m, 1H, H-1 ^{n}Bu), 3.83–3.89 (m, 1H, H-1 ^{n}Bu), 4.44 (dd, 1H, *J* 8.3, 8.1, H-10b), 4.58–4.61 (m, 1H, H-2), 7.07 (d, 1H, *J* 7.3, H-10), 7.28–7.50 (m, 3H, H-7 to H-9), 7.72 (s, 1H, H-6); δ_C($CDCl_3$) 13.6 (CH_3), 18.8 (CH_2), 31.7 (CH_2), 32.9 (C-1), 55.2 (C-10b), 61.6 (C-3), 72.2 (CH_2), 83.8 (C-2), 110.2, 113.9 (C≡N), 123.4 (C-10), 124.7 (C-10a), 126.1, 128.5, 125.9 (C-8 to C-10), 132.1 (C-7), 134.2 (C-6a), 146.3 (C-6).

Similarly obtained was compound **21**.

***exo*-2-Ethoxy-3,3-dicyano-1,2,3,10b-tetrahydropyrrolo[2,1-*a*]-phthalazine 21.** Compound **21** yield 85% mp 137–138 °C (EtOH) (Found: C, 67.6; H, 5.3; N, 21.2. $C_{15}H_{13}N_4O$ requires C, 67.7; H, 5.3; N, 21.0%); δ_H($CDCl_3$) 1.35 (t, 3H, *J* 6.9, CH_3), 2.41–2.47 (m, 1H, H-1$_{exo}$), 2.65–2.73 (m, 1H, H-1$_{endo}$), 3.74–3.78 (m, 1H, CH_2), 3.90–3.94 (m, 1H, CH_2), 4.42 (dd, 1H, *J* 8.4, 8.3, H-10b), 4.60 (dd, 1H, *J* 9.1, 2.9, H-2$_{endo}$), 7.06 (d, 1H, *J* 7.7, H-10), 7.26–7.50 (m, 3H, H7 to H-10), 7.74 (s, 1H, H-6); δ_C($CDCl_3$) 14.9 (CH_3), 33.0 (CH_2), 55.0 (C-10b), 61.5 (C-3), 67.7 (C-1), 83.7 (C-2), 110.1, 113.8 (C≡N), 123.3 (C-10), 124.7 (C-10a), 125.9, 126.1, 128.6, (C-8 to C-10), 132.1 (C-7), 134.1 (C-6a), 146.4 (C-6).

(iii) Maleimide dipolarophiles: *N*-*tert*-butylmaleimide, *N*-methylmaleimide, *N*-benzylmaleimide, *N*-adamantylmaleimide

***endo*-*N*-*tert*-Butyl-3,3-dicyano-1,2,3,10b-tetrahydropyrrolo-[2,1-*a*]phthalazine-1,2-dicarboximide 25.** A suspension of dipole **1** (0.30 g, 1.54 mmol) in acetonitrile (20 cm^3) was treated with *N*-*tert*-butylmaleimide (0.24 cm^3, 1.54 mmol), stirred at ambient temperature for 24 h and the solvent was removed under reduced pressure to give compound **25**.

Compound **25** yield 80%, white crystalline solid; mp 212–214 °C (EtOH) (Found: C, 65.5; H, 5.0; N, 19.8. $C_{19}H_{17}N_5O_2$ requires C, 65.7; H, 4.9; N, 20.2%); ν_{max}(mull)/cm^{-1} 2263 (C≡N), 1774 (C=O), 1702; δ_H([$^2H_6$]DMSO) 1.35 (9H, s, ^{t}Bu protons), 3.92–3.95 (1H, dd, *J* 7.7, 8.0, H-1), 4.29 (1H, d, *J* 8.0, H-2), 4.93 (1H, d, *J* 7.7, H-10b), 7.44–7.57 (3H, m, H-7 to H-9), 7.67 (1H, d, *J* 7.3, H-10), 7.87 (1H, s, H-6); δ_C([$^2H_6$]DMSO) 27.3 (^{t}Bu CH_3), 44.4 (C-2), 50.8 (C-1), 58.2 (Bu^t C(CH_3)$_3$), 59.2 (C-1), 59.5 (C-3), 110.8, 112.4 (C≡N), 123.6 (C-10a), 126.9, 127.6, 129.1 (C-8 to C-10), 129.8 (C-6a), 131.7 (C-7), 146.5 (C-6), 171.6 and 173.8 (C=O); X-ray crystal structure, Fig. 1. Similarly obtained were compounds **23**, **24**, and **26**.

***endo*-*N*-Methyl-3,3-dicyano-1,2,3,10b-tetrahydropyrrolo-[2,1-*a*]phthalazine-1,2-dicarboximide 23.** Compound **23** yield 87%; 233–235 °C (EtOH) (Found: C, 68.5; H, 3.6; N, 19.7. $C_{16}H_{11}N_5O_2$ requires C, 68.7; H, 3.5; N, 19.9%); ν_{max}(mull)/cm^{-1} 2300 (C≡N), 1785, 1716 (C=O); δ_H([$^2H_6$] DMSO) 2.78 (s, 3H, CH_3), 4.18 (dd, 1H, *J* 7.3, 7.7, H-1), 4.45 (d, 1H, *J* 7.7, H-2), 4.85 (d, 1H, *J* 7.3, H-10b), 7.45–7.55 (m, 3H, H-7 to H-9), 7.77 (d, 1H, *J* 7.7, H-10), 7.91 (s, 1H, H-6); δ_C([$^2H_6$] DMSO) 25.4 (CH_3), 43.4 (C-2), 50.0 (C-1), 57.4 (C-3), 58.7 (C-10b), 110.9, 112.1 (C≡N), 124.0 (C-10a), 127.0, 127.7, 129.0 (C-8 to C-10), 130.2 (C-6a), 131.7 (C-7), 147.6 (C-6), 171.2, 173.2 (C=O).

***endo*-*N*-Benzyl-3,3-dicyano-1,2,3,10b-tetrahydropyrrolo-[2,1-*a*]phthalazine-1,2-dicarboximide 24.** Compound **24** yield 81%, 205–207 °C (from EtOH) (Found: C, 69.3; H, 4.0; N, 18.6. $C_{22}H_{15}N_5O_2$ requires C, 69.3; H, 4.0; N, 18.4%); ν_{max}(mull)/cm^{-1} 2254 (C≡N), 1785, 1715 (C=O); δ_H([$^2H_6$] DMSO) 4.25 (dd, 1H, *J* 7.7, 7.5, H-1), 4.49 (d, 2H, *J* 7.3, CH_2), 4.57 (d, 1H, *J* 7.7, H-2), 4.92 (d, 1H, *J* 7.5, H-10b), 7.09–7.10 (m, 2H, H-2′), 7.22–7.30 (m, 3H, H-3′ and H-4′), 7.39–7.55 (m, 3H, H-7 to H-9), 7.63 (s, 1H, H-6), 7.72 (d, 1H, *J* 7.7, H-10); δ_C([$^2H_6$] DMSO) 44.0 (C-2), 42.4 (CH_2), 50.5 (C-1), 58.0 (C-3), 58.1 (C-10b), 110.8, 112.2 (C≡N), 123.7 (C-10a), 127.0, 127.5, 127.6, 127.7, 128.4, 129.0, 129.9 (C-8 to C-10 and C-2′ to C-4′), 134.8 (C-1′), 147.1 (C-6), 170.9, 172.0 (C=O).

***endo*-*N*-Adamantyl-3,3-dicyano-1,2,3,10b-tetrahydropyrrolo-[2,1-*a*]phthalazine-1,2-dicarboximide 26.** Compound **26** yield 52%; 229–230 °C (EtOH) (Found: C, 70.9; H, 5.2; N, 16.2. $C_{25}H_{23}N_5O_2$ requires C, 70.6; H, 5.4; N, 16.5%); ν_{max}(mull)/cm^{-1} 2260 (C≡N), 1773 (C=O), 1698; δ_H([$^2H_6$] DMSO) 1.98–3.52 (m, 15H, adamantyl ring), 3.96 (1H, dd, *J* 7.7, 8.1, H-1), 4.27 (1H, d, *J* 8.1, H-2), 4.92 (1H, d, *J* 7.7, H-10b), 7.45–7.54 (3H, m, H-7 to H-9), 7.67 (1H, d, *J* 5.9, H-10), 7.90 (1H, s, H-6); δ_C([$^2H_6$] DMSO) 28.9, 35.3, 38.0, 38.2, 44.0 (adamantyl), 50.7 (C-2), 54.9 (C-1), 59.3 (C-10b), 59.5 (C-3), 110.8, 112.4 (C≡N), 123.7 (C-10a), 127.0, 127.7, 129.1 (C-8 to C-10), 129.9 (C-6a), 131.7 (C-7), 146.7 (C-6), 171.7, 173.7 (C=O).

X-Ray crystal structure determination of compound 25†

Good quality colorless crystals of compound **25** were grown from acetone at ambient temperature. The crystal used for data collection had the approximate dimensions 0.65 × 0.53 × 0.32 mm. The crystal was triclinic with the space group $P\bar{1}$ and had unit cell parameters a = 10.755(1), b = 13.375(2), c = 13.425(1) Å, α = 112.95(1), β = 93.05(1), γ = 99.40(1)°. Reflections were collected on a Enraf-Nonius CAD4F four circle diffractometer, using graphite monochromated Mo-Kα radiation, λ = 0.71069 Å. The criterion which qualified a reflection for observation was $I > 2\sigma(I)$ and 4843 reflections satisfied this condition. The calculated density was 1.326 Mg m^{-3} and Z = 4. The absorption

† CCDC reference number(s) 157788. See http://www.rsc.org/suppdata/p1/b1/b101150m/ for crystallographic files in .cif or other electronic format.

coefficient was 0.090 mm^{-1} and the theta range for data collection was 2.30 to 23.98°. The total number on independent reflections was 3379 [R(int) = 0.0412]. The structure was solved by direct methods SHELXS-86,[25] and refined by full matrix least squares using SHELXL-97.[26] SHELX operations were automated using ORTEX which was also used to obtain the drawings.[27] Data were corrected for Lorentz and polarisation effects but not for absorption. Hydrogen atoms were included in calculated positions with thermal parameters 30% larger than the atom to which they were attached. The non-hydrogen atoms were refined anisotropically. There are two molecules per asymmetric unit which are chemically identical. To test the lattice type and unit cell used for data collection several different starting positions for random reflection search were used with two different indexation methods. The indexation methods used were the standard Nonius software and the program BRVCEL.[28] After full matrix refinement the final R indices [$I > 2\sigma(I)$] were $R_1 = 5.84\%$ and $wR_2 = 18.25\%$ and R indices (all data) were $R_1 = 7.5\%$ and $wR_2 = 19.72\%$> the maximum and minimum excursions in the final $F_o - F_c$ difference map were 0.63 and -0.26 $eÅ^{-3}$. All calculations were performed on a Pentium PC.

Acknowledgements

A. G. C. acknowledges support from the Government Agency, Enterprise Ireland and from the Higher Education Authority. L. A. B. acknowledges the National Science Foundation for a computer equipment grant MRI 9871088.

References

1 I. T. Druta, M. A. Andrei, C. I. Ganj and P. S. Aburel, *Tetrahedron*, 1999, **55**, 13063.
2 K. Elender, H. Noth, P. Riebel, A. Weber and J. Sauer, *Tetrahedron*, 2000, **56**, 5463.
3 K. Elender, P. Riebel, A. Weber and J. Sauer, *Tetrahedron*, 2000, **56**, 4261.
4 M. Caprosu, I. Mangalagiu, D. S. Maftei, I. Olariu and M. Petrovanu, *An. Stiint. "Univ. Al. I. Cuza" Iasi, Chim.*, 1997, **5**, 95 (*Chem. Abstr.*, 2000, **132**, 207816k).
5 K. Matsumotu and T. Uchida, *J. Chem. Soc.*, *Perkin Trans. 1*, 1981, 73.
6 O. Tsuge, S. Kanemasu and J. Takenaka, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 2513.
7 U. Bergstrasser, A. Hoffmann and M. Regitz, *Tetrahedron Lett.*, 1992, **33**, 1049.
8 A. F. Khlebniknov, E. I. Kostik, R. R. Kostikov and V. Ya. Bespotlav, *Khim. Geterotsikl.*, *Soedin.*, 1990, 355 (*Chem. Abstr.*, 1990, **113**, 131933f).
9 A. M. Shestopalov, Yu. A. Sharanin, V. N. Nesterov, L. A. Rodinovskaya, V. E. Shklover, Yu. T. Struchkov and V. P. Litinor, *Khim. Geterotsikl. Soedin.*, 1991, 1248 (*Chem. Abstr.*, 1992, **116**, 214313s).
10 Y. Miki, H. Hachiken and S. Takemura, *Heterocycles*, 1984, **22**, 701.
11 T. Itoh, Y. Matsuya, K. Nagata, M. Okada and A. Ohsaura, *J. Chem. Soc.*, *Chem. Commun.*, 1995, 2067; Y. Ikemi, K. Matsumoto and T. Uchida, *Heterocycles*, 1983, **20**, 1009.
12 R. Huisgen, H. Hauck, R. Grashey and H. Seidl, *Chem. Ber.*, 1969, **102**, 736.
13 W. J. Linn, O. W. Webster and R. E. Benson, *J. Am. Chem. Soc.*, 1965, **87**, 3651.
14 N. Basketter and A. O. Plunkett, *J. Chem. Soc.*, *Chem. Commun.*, 1971, 1578.
15 Y. Kobayashi, T. Kutsuma and Y. Sekine, *Tetrahedron Lett.*, 1972, 3325.
16 For a review see: R. N. Butler and D. F. O'Shea, *Heterocycles*, 1994, **37**, 571; R. N. Butler, M. O. Cloonan, P. McArdle and D. Cunningham, *J. Chem. Soc.*, *Perkin Trans. 1*, 1999, 1103.
17 R. N. Butler, F. A. Lysaght and L. A. Burke, *J. Chem. Soc.*, *Perkin Trans. 2*, 1992, 1103.
18 R. N. Butler, J. P. Duffy, D. Cunningham and P. McArdle, *J. Chem. Soc.*, *Perkin Trans. 1*, 1992, 147; R. N. Butler, P. McDonald, P. McArdle and D. Cunningham, *J. Chem. Soc.*, *Perkin Trans. 1*, 1996, 1617.
19 R. N. Butler, D. M. Farrell and C. S. Pyne, *J. Chem. Res.* (*S*), 1996, 418; R. N. Butler and D. M. Farrell, *J. Chem. Res.* (*S*), 1998, 214.
20 R. N. Butler, D. M. Farrell, P. McArdle and D. Cunningham, *J. Chem. Soc.*, *Perkin Trans. 1*, 1998, 869.
21 R. N. Butler, A. G. Coyne and L. A. Burke, *unpublished work.*
22 Gaussian 98, Revision A.7, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1998.
23 A. D. Becke, *Phys. Rev. A At. Mol. Opt. Phys.*, 1988, **38**, 3098; C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B Condens. Matter Mater. Phys.*, 1988, **37**, 785.
24 P. Cava, A. A Deana, K. Muth and M. J. Mitchell, *Org. Synth.*, *Collect. Vol. 5*, 1973, 944.
25 G. M. Sheldrick, *Acta Crystallogr.*, *Sect. A*, *Fundam. Crystallogr.*, 1990, **46**, 467.
26 G. M. Sheldrick, SHELXL-97 a computer program for crystal structure determination, University of Göttingen, 1997.
27 P. McArdle, *J. Appl. Crystallogr.*, 1995, **28**, 65.
28 T. Higgins, R. Dark, P. McArdle, J. Simmie, *Comput. Chem.*, 1990, **14**, 33.