1,2,3-Triazolium-1-unsubstituted methanides, carbon analogues of triazole-*N*-oxides: a 1,3-dipole cascade from 1,2,3-triazolium-1-methanide to 1,2,4-triazinium-4-methanide: new routes to pyrrolo[1,2-*c*][1,2,3]triazoles, pyrrolo[1,2-*d*][1,2,4]triazines and substituted 1-aminopyrroles. Azolium 1,3-dipoles

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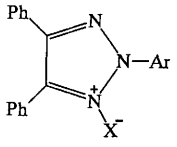
A 1,2,3-triazolium-1-methanide species has been generated and trapped in cycloadditions with alkyne dipolarophiles. The triazolium-1-methanide, a direct carbon analogue of the triazole-*N*-oxide, is an unstable intermediate prone to ring-opening and re-cyclisation to a 1,2,4-triazine system. New routes to substituted pyrrolo[1,2-*c*][1,2,3]triazoles, pyrrolo[1,2-*d*][1,2,4]triazines and substituted 1-aminopyrroles have resulted from this work. X-Ray crystal structures are described for 1,3,3a-triphenyl-4,5-diethoxycarbonyl-3a,6-dihydropyrrolo[1,2-*c*][1,2,3]triazole 6a, 1-*N*-anilino-2-phenyl-3,4-diethoxycarbonylpyrrole 9a and 3-(*p*-methoxyphenyl)-1,8a-diphenyl-8-*exo*-ethoxycarbonyl-3,4,6,7,8,8a-hexahydropyrrolo[1,2-*d*][1,2,4]triazine 15d.

The general azole *N*-oxide structure of type **A** is ubiquitous and heavily studied in the azole series.[1] The direct carbon analogue, the unsubstituted methanide structure **C** is unknown among the azoles but examples containing two stabilizing electron withdrawing groups, C=O or C≡N, bonded to the C^- atom are known among the lower azoles.[2–6] The wide synthetic scope of the cycloaddition–rearrangement reactions of 1,2,3-triazolium-1-oxides A,[7,8] and -1-aminides **B**,[9] prompted a search for the analogous methanide systems **C**. We now



A X = O
B X = NR
C X = CH_2

report[10] the trapping and behaviour of the structure **C**, *i.e.* compounds **3**, the first direct carbon analogue of an azole *N*-oxide. It has provided new synthetic routes to pyrrolo-[1,2-*c*][1,2,3]triazoles, pyrrolo[1,2-*d*][1,2,4]triazines and substituted 1-aminopyrroles.

Results and discussion

(*a*) Alkyne dipolarophiles

The 1,2,3-triazolium-1-methanides **3** were generated by trimethylsilylmethylation of the triazoles **1** to the salts **2** followed by desilylation with CsF following a literature[11,12] procedure. In a previous attempt[13] to produce the species **3** the products **10** and **11** only were encountered *via* electrocyclisations in **4**, the ring-opened isomer of **3** which is the thermodynamically stable form (the reverse of the *N*-oxide case where the cyclic form is thermodynamically favoured[13]) and we thought the species **3** did not exist.[13] A critical factor, not previously realised, proved to be the unexpectedly high lability of the $SiMe_3$ group in **2** which precluded any attempt to isolate and purify the salts **2**. Indeed it was necessary to introduce the trapping dipolarophile before the alkylation of **1** was fully complete, *i.e.* before all of **1** had disappeared. The products **10** and **11** could be seen to be appearing at this point and if the dipolarophile was introduced too late or not at all only these products were encountered.[13] Thus with careful monitoring, after the alkylation of the 1,2,3-triazoles **1** in trimethylsilylmethyl trifluoromethanesulfonate as solvent at 100 °C for 5 h, the system was cooled and, without isolation of the products **2**, two mol of dialkyl acetylenedicarboxylate in dichloromethane was introduced followed by CsF[11,12] and the mixture stirred at ambient temperatures. After removal of salts, chromatographic separation of the products on a silica gel 60 column gave the products **5** or **6** accompanied by **10** and **11** (Table 1). The compounds **5** and **6** arise from a direct trapping of the species **3** while **10** and **11** are formed *via* electrocyclisations in **4** from the rapid ring-opening of the triazolium methanide **3** which cannot be completely avoided. The structures of the products **5** and **6** were established from microanalyses, IR, ^1H and ^{13}C NMR spectra which showed all of the expected signals, some key shifts being shown in Scheme 1. An X-ray crystal structure (Fig. 1) determination on **6a** further supported the structure of the adduct. These results confirm the existence of the triazolium-1-methanide species **3** as an unstable intermediate prone to ring-opening and the antithesis of the triazole-*N*-oxide system.

The products **5** and **6** represent the first example where the fused 5,5-cycloadduct from any exocyclic azolium ylide type 1,3-dipole did not rearrange or fragment *in situ*. Since the adducts had been expected to rearrange their thermal behaviour in toluene was examined. Heating resulted in extrusion of benzonitrile followed by 1,3-H migration in **7** giving the 1-aminopyrroles **8** and **9** in 85–90% yields (Table 1) in a new route to substituted 1-aminopyrroles. The intermediates **7** were shortlived and were not trapped when the thermolysis was carried out in the presence of alkyne dipolarophiles. The structures of the products **8** and **9** were supported by IR and NMR spectra and an X-ray crystal structure of compound **9a** (Fig. 2).

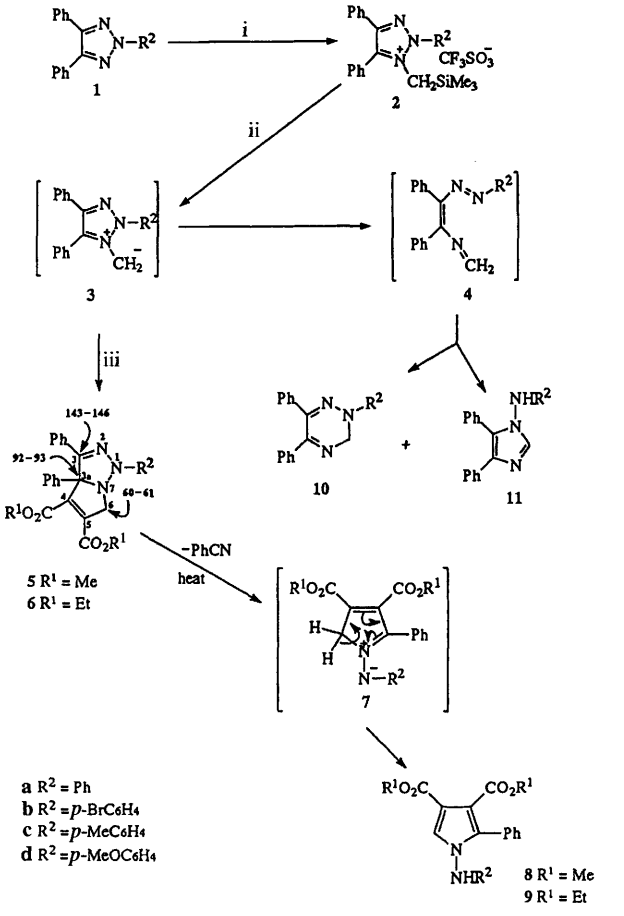
(*b*) Alkene dipolarophiles: a reaction cascade

Kinetic studies[14] of the reactions of triazolium-1-imide systems **B** with alkyne and alkene dipolarophiles showed that dimethyl acetylenedicarboxylate reacted 500–1500 times faster than

Table 1 Products

Entry No.	Compound	Mp (T°/c)	Yield (%)	Microanalysis Found % (Required %) C	H	N	**10** Yield
1	**5a**	129–130[a]	50	71.4 (71.5)	5.2 (5.1)	9.1 (9.3)	23.5[e]
2	**5b**	142–144[a]	49.5	61.2 (60.9)	4.2 (4.1)	7.7 (7.9)	25[e]
3	**5c**	171–173[a]	52.5	71.7 (72.0)	5.4 (5.4)	8.9 (9.0)	21[e]
4	**5d**	154–156[a]	47.5	69.2 (69.6)	5.1 (5.2)	8.6 (8.7)	22.5[e]
5	**6a**	123–125[a]	40[c]	72.1 (72.4)	5.7 (5.6)	8.5 (8.7)	9.5[e]
6	**6b**	108–110[a]	39.5[c]	61.2 (61.5)	4.2 (4.4)	7.6 (7.7)	17[e]
7	**6c**	126–128[a]	34[c]	72.4 (72.7)	5.7 (5.9)	8.3 (8.5)	17.5[e]
8	**6d**	124–125[a]	36[c]	70.4 (70.5)	5.8 (5.7)	8.1 (8.2)	16[e]
9	**8a**	158–160[b]	87	68.3 (68.6)	5.1 (5.2)	7.8 (8.0)	—
10	**8b**	191–193[b]	89	55.9 (55.9)	3.9 (4.0)	6.5 (6.5)	—
11	**8c**	177–178[b]	92	68.8 (69.2)	5.4 (5.5)	7.5 (7.7)	—
12	**8d**	152–154[b]	91	65.9 (66.3)	5.4 (5.3)	7.2 (7.4)	—
13	**9a**	137–139[b]	93	69.9 (69.8)	5.8 (5.8)	7.2 (7.4)	—
14	**9b**	124–126[b]	92	57.9 (57.8)	4.5 (4.6)	5.9 (6.1)	—
15	**9c**	118–120[b]	87	70.3 (70.4)	6.3 (6.1)	7.1 (7.1)	—
16	**9d**	122–124[b]	76	68.0 (67.7)	5.9 (5.9)	6.9 (6.9)	—
17	**14a**	159–161[a]	42 (24)[d]	79.6 (79.4)	5.7 (5.8)	14.5 (14.8)	22[f]
18	**15a**	117–119[a]	45 (21)[d]	75.9 (76.2)	6.4 (6.4)	10.0 (9.9)	17[f]
19	**15b**	162–164[a]	41	64.3 (64.3)	5.5 (5.2)	8.2 (8.3)	22[f]
20	**15d**	160–162[a]	42	73.8 (73.9)	6.2 (6.4)	8.9 (9.2)	18.5[f]
21	**16a**	112–114[a]	28.5	76.8 (77.1)	5.1 (5.2)	11.1 (11.3)	25[f]

[a] From pentane. [b] From ethanol. [c] Low yields (1–3%) of another product, which appeared to be isomeric with **6**, were also encountered but it could not be characterised. [d] Yields starting from **10** rather than **1**. [e] Compound **11** (4–8%) was also encountered. [f] Extensive decomposition resins also encountered.



Scheme 1 Some ^{13}C shift ranges shown. *Reagents:* i, trimethylsilylmethyl trifluoromethanesulfonate; ii, CsF; iii, dialkyl acetylenedicarboxylate

alkene dipolarophiles such as acrylonitrile and ethyl acrylate. This factor proved critical in attempts to extend the cycloaddition chemistry of the species **3** with alkenes since the cycloadditions proved to be slower than the ring opening.

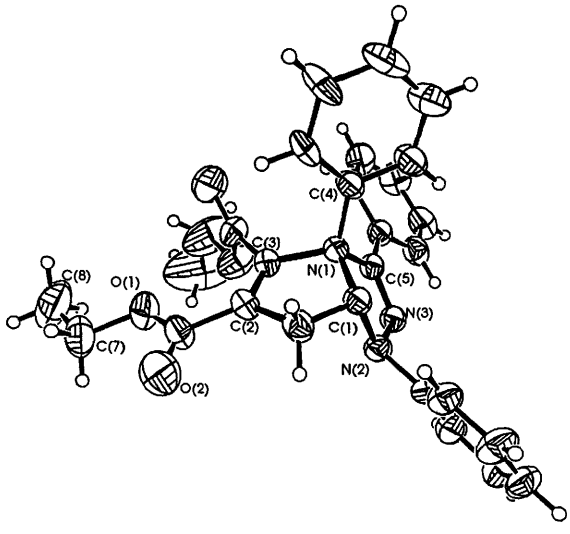


Fig. 1 X-ray crystal structure of compound **6a**

However, an interesting cascade of reactions occurred when some alkene dipolarophiles were introduced in place of the alkynes at the appropriate time during the trimethylsilylation of **1** with 1.5–2 mol of trimethylsilyltriflate. A possible cycloaddition with the alkene did not occur and instead ring opening gave rise to the triazine **10** which was alkylated *in situ*, followed by desilylation giving the species **13** (Scheme 2). These then underwent cycloaddition with the alkenes giving the products **14–16**. In these reactions the alkenes are present in 3–5 molar excess in dichloromethane as solvent and their presence facilitates the *in situ* trimethylsilylmethylation of the triazines **10** since this does not occur in the absence of the alkenes despite the excess of the alkylating agent. The best yields of the products **14–16** were 40–45% (Table 1, entries 17–21) and the reaction was not clean since these products were accompanied by some resins. The products **14–16** were also produced by starting with the triazines **10**, but this approach was less effective and yields were significantly lower (Table 1, entries 17 and 18) testifying to the beneficial effect of the presence of the

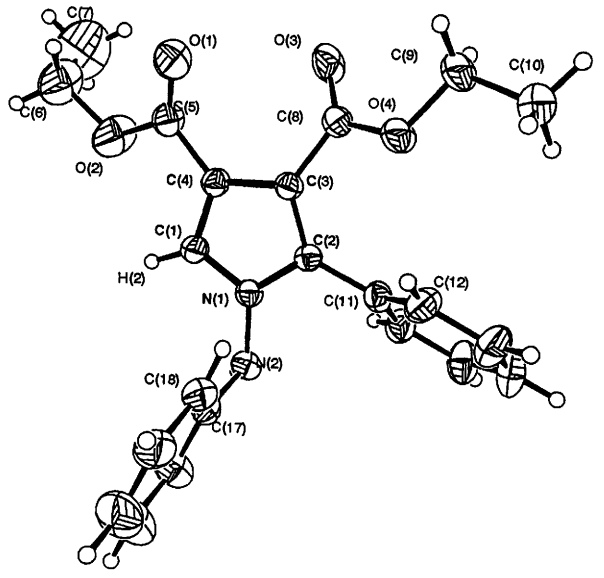
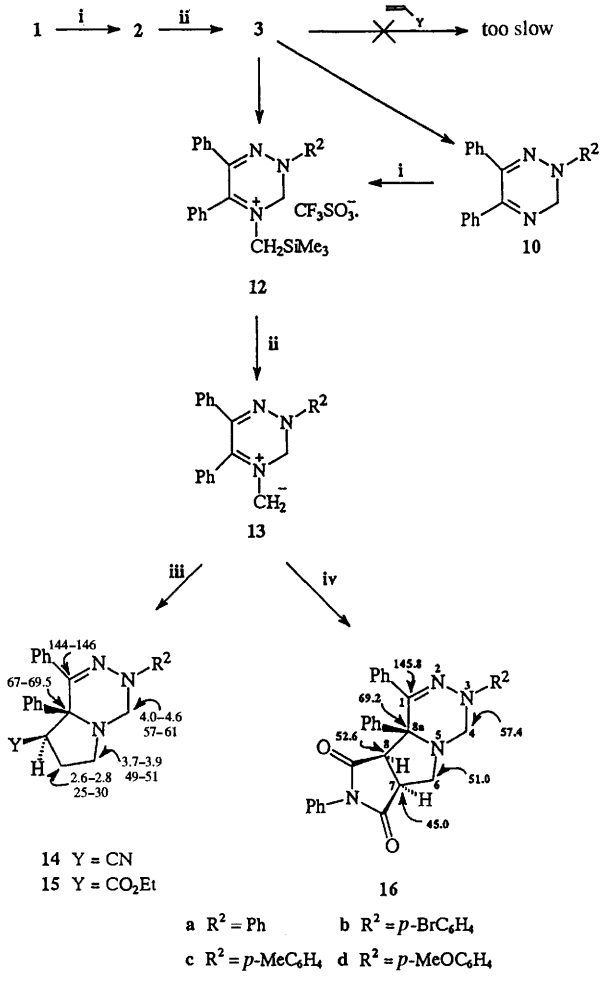


Fig. 2 X-ray crystal structure of compound **9a**



Scheme 2 *Reagents:* i, trimethylsilylmethyl trifluoromethanesulfonate; ii, CsF; iii, CH_2=CH–Y; iv, *N*-phenylmaleimide, some ^{1}H and ^{13}C NMR shifts shown

alkene on the overall cascade. This effect could be a solvent effect or there may be some more complicated manner in which the alkylation of **10** is facilitated by the presence of the alkene. In separate alkylation studies of the series **10**, which will be reported elsewhere, the *N*-alkyl quaternisation site was confirmed to be N-4. The structures of the products **14–16** were supported by microanalyses, IR, ^{1}H and ^{13}C NMR spectra. Some key shifts are shown in Scheme 2. An X-ray crystal

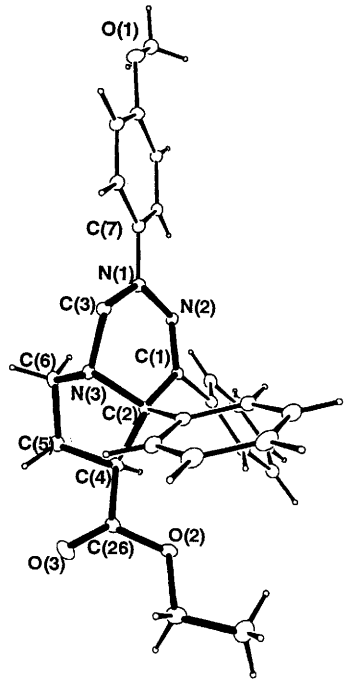


Fig. 3 X-ray crystal structure of compound **15d**

structure determination on compound **15d** showed the substituent Y to be in *exo* site (Fig. 3). An *endo*-cycloaddition might have been expected for the dipole **13** and the *exo* orientation of the products does not necessarily preclude this since the reactions required heat and a rearrangement of the CN bond in the adduct could have occurred under the reaction conditions.

Experimental

Mps 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 hexadeuteriodimethyl sulfoxide as solvent. ^{1}H NMR assignments were supported by decoupled spectra and ^{13}C assignments were supported by off-resonance decoupled spectra. Microanalyses were measured on a Perkin-Elmer model 240 CHN analyser. The substrates **1** were prepared as previously described.[13] The products **10** and **11** have been described and characterised previously.[13] The following are typical examples:

(i) Pyrrolo[1,2-*c*][1,2,3]triazoles 5 and 6. A solution of **1a** (0.50 g, 1.68 mmol) in trimethylsilylmethyl trifluoromethanesulfonate (0.44 cm^3, 2.02 mmol) was heated to 100 °C and stirred for 5 h, cooled to ambient temperature, and then treated with dry dichloromethane (20 cm^3) and dimethyl acetylenedicarboxylate (0.41 cm^3, 3.36 mmol) followed by CsF (0.38 g, 2.52 mmol) and the mixture stirred at ambient temperature for 8 h. The solution was filtered to remove insoluble salts and the solvent removed under reduced pressure. The residue was dissolved in dichloromethane (3 cm^3) and was placed on a silica gel-60 column (230–400 mesh ASTM) and the product **5a** was eluted using a gradient mixture of light petroleum (bp 40–60 °C)–dichloromethane (1:0–1:1.5 v/v), mp 129–130 °C (from pentane) (50%) (Found: C, 71.4; H, 5.2; N, 9.1. $C_{27}H_{23}N_3O_4$ requires: C, 71.5; H, 5.1; N, 9.3%); ν_{max}(Nujol)/cm^{-1} 1735 and 1724 (ester C=O); δ_H($CDCl_3$) 3.3 (s, 3 H, OMe), 3.8 (s, 3 H, OMe), 4.2 (s, 2 H, CH_2N) and 7.1–7.6 (m, ArH); δ_C 52.2 and 52.4 (OMe), 60.8 (CH_2N), 165.6 and 162.6 (ester C=O), 146.3, 143.4, 142.1, 139.0, 135.6 and 130.2 (quaternary C), 92.0 (bridgehead C), 129.4, 128.9, 128.7, 128.3, 127.7, 127.2, 126.7, 123.2 and 117.5 (aromatic CH). The other products recovered

Table 2 Crystal data and structure refinement

Compound	**15d**
Empirical formula	$C_{28}H_{27}N_3O_3$
Formula weight	453.53
Temperature	293(2) K
Wavelength	0.710 69 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 10.899(2) Å
	b = 13.1106(12) Å β = 96.786(14)°
	c = 17.090(3) Å
Volume	2425.0(7) Å^3
Z	4
Density (calculated)	1.242 Mg m^{-3}
Absorption coefficient	0.082 mm^{-1}
F(000)	960
Crystal size	0.38 × 0.44 × 0.22 mm
Theta range for data collection	2.11 to 24.97°
Index ranges	$0 <= h <= 12$; $0 <= k <= 15$; $-20 <= l <= 20$
Reflections collected	4631
Independent reflections	4254 [R(int) = 0.0221]
Reflections observed ($> 2\sigma$)	2033
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4254/0/309
Goodness-of-fit on F^2	0.475
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0648 wR_2 = 0.2461
R indices (all data)	R_1 = 0.1245 wR_2 = 0.3713
Largest diff. peak and hole	0.496 and −0.216 e Å^{-3}

R indices; $R_1 = [\Sigma||F_o| - |F_c||]/\Sigma|F_o|$ (based on F)
$wR_2 = [[\Sigma_w(|F_o - F_c|)^2]/[\Sigma_w(|F_o|)^2]]^{\frac{1}{2}}$ (based on F^2)
$w = q/[(\sigma F_o)^2 + (a^*P)^2 + b^*P + d + e^*\sin(\theta)]$
Goodness-of-fit = $[\Sigma_w(|F_o^2| - |F_c^2|)^2/(N_{obs}\text{-}N_{parameters})]^{\frac{1}{2}}$

from the column were **10a** (24%), **11a** (9%), **1a** (5%) and some intractable resins.

(ii) 1-Aminopyrroles 8 and 9. A solution of **5a** (150 mg, 0.331 mmol) in dry toluene (10 cm^3) was stirred under reflux for 46 h, cooled and then the solvent removed under reduced pressure. The residue was crystallized from EtOH giving compound **8a** (87%), mp 158–160 °C (from EtOH) (Found: C, 68.3; H, 5.1; N, 7.8. $C_{20}H_{18}N_2O_4$ requires C, 68.6; H, 5.2; N, 8.0%); ν_{max}(Nujol)/cm^{-1} 3318 (NH) and 1719 and 1694 (ester C=O); δ_H([$^2H_6$]DMSO) 3.65 (s, 3 H, OMe), 3.77 (s, 3 H, OMe), 7.70 (s, 1 H, pyrrole 5-H), 9.54 (s, 1 H, NH), 6.48 (d, 2 H, H_{ortho} N–Ph) and 6.8–7.5 (m, Ar-H); δ_C 51.5 and 51.8 (MeO), 165.2 and 162.9 (ester C=O), 147.7, 135.5, 129.3, 113.7 and 112.5 (quaternary C), 120.2 (pyrrole C-5), 129.5, 129.2, 128.5, 128.4, 128.0 and 127.8 (aromatic CH).

(iii) Pyrrolo[1,2-*d*][1,2,4]triazines 14–16. (*a*) A solution of **1d** (0.75 g, 2.29 mmol) in trimethylsilylmethyl trifluoromethane sulfonate (0.92 cm^3, 4.59 mmol) was stirred at 100 °C for 5 h, cooled, treated with dry dichloromethane (20 cm^3), followed by ethyl acrylate (1.38 cm^3, 12.7 mmol) and CsF (3.23 g, 15.2 mmol), stirred at 25 °C for 8 h and at 60 °C for 12 h, filtered to remove insoluble salts. The filtrate was evaporated under reduced pressure and the residue was dissolved in dichloromethane (3 cm^3), placed on a silica gel-60 column (230–400 mesh ASTM) and eluted with gradient mixtures of light petroleum (bp 40–60 °C)–dichloromethane (1:0–1:1.5 v/v) to yield 3-(*p*-methoxyphenyl)-1,8a-diphenyl-8-*exo*-ethoxycarbonyl-3,4,6,7,-8,8a-hexahydropyrrolo[1,2-*d*][1,2,4]triazine, **15d**, mp 160–162 °C (pentane) (42%); ν_{max}(Nujol mull)/cm^{-1} 1731, (ester, C=O); δ_H($CDCl_3$) 0.88 (3 H, t, EtO, CH_3), 2.77 (2 H, m, 7-CH_2), 3.24 (1 H, t, 8-C*H*CO_2Et), 3.62 and 3.75 (2 H, m, 6-CH_{ax} and 8-$CO_2CH_AH_B$-Me), 3.76 (3 H, s, *p*-MeO), 3.80 and 3.89 (2 H, m, 6-CH_{eq} and 8-$CO_2CH_AH_B$-Me), 4.12 and 4.54 (2 H, ds, 4-H_{ax} and 4-H_{eq}, J_{AB} 12.3), 6.87 and 8.0 (AA′ BB′, ds, J_{AB} 8.6, *p*-anisyl), 7.2 (10 H, m, C-8a-Ph and C-1-Ph); δ_C($CDCl_3$) 13.5 (CO_2CH_2-CH_3), 25.7 (C-7), 49.1 (C-6), 51.7 (C-8), 55.7 (MeO), 58.4 (CO_2-CH_2CH_3), 60.7 (C-4), 69.2 (C-8a), 140.4, 129.2, 114.6 and 154.3 (C-1′, C-2′, C-3′, C-4′; 3-C_6H_4-OMe-4′), 138.4 and 138.5 (C-1′ of 8a-C-Ph and 1-C-Ph), 145.8 (1-C=N), 173.1 (C=O) remaining aromatic 127.0, 127.2, 128.0 and 128.1 (one signal overlapped at 127–128 ppm). X-ray crystal structure, Fig. 3. Dichloromethane eluted **10d** (18.5%) and intractable resins from the column.

(*b*) A mixture of **1a** (0.75 g, 2.53 mmol) in trimethylsilylmethyl trifluoromethanesulfonate (1.1 cm^3, 5.06 mmol) was stirred at 100 °C for 5 h, cooled, dissolved in dry dichloromethane (20 cm^3), treated with *N*-phenylmaleimide (2.19 g, 12.7 mmol) followed by CsF (2.32 g, 15.2 mmol) stirred at 25 °C for 8 h and at 60 °C for 12 h, filtered to remove salts and the filtrate evaporated under reduced pressure. The residue in CH_2Cl_2 (3 cm^3) was placed on a silica gel-60 column (230–400 mesh ASTM) and eluted with gradient mixtures of light petroleum (bp 40–60 °C)–dichloromethane (1:0–1:1.5 v/v) to give 1,3,-8a-triphenyl-7,8-(*exo*-dicarboxy-*N*-phenylimido)-3,4,6,7,8,8a-hexahydropyrrolo[1,2-*d*][1,2,4]triazine **16a**, mp 112–114 °C (pentane) (28.5%); ν_{max}/cm^{-1} 1715 (C=O); δ_H($CDCl_3$) 3.11 and 3.34 (m, 2 H, 6-$CH_{ax}H_{eq}$), 3.72 (m, 1 H, 7-H), 4.28 (d, 1 H, *J* 9.0, 8-H), 4.12 and 4.64 (ds, 2 H, J_{AB} 12.6, 3-$CH_{ax}H_{eq}$), 7.23 (m, 18 H, Ar), 8.01 (m, 2 H, Ar); δ_C($CDCl_3$) 45.0 (C-7), 51.0 (C-6), 52.6 (C-8a), 57.4 (C-4), 69.2 (C-8a), 140.9, 113.6, 128.4 and 121.3 (C-1′, C-2′, C-3′, C-4′, resp.; 3-N-Ph), 134.2, 137.0 and 137.7 (C-1′ of 1-C-Ph and 8a-C-Ph, N-phenylimido resp.), 174.7 and 177.8 (C=O), remaining aromatic 126.0, 127.2, 127.7, 127.8, 128.9, 129.2 and 129.3 (two signals overlapped). Dichloromethane eluted **10a** (25%) and intractable resins from the column.

X-Ray crystal structure determination of compound 6a

Good quality yellow crystals of compound **6a** were grown from pentane at ambient temperature. The crystal used for data collection had the approximate dimensions 0.5 × 0.55 × 0.48 mm and reflections were collected on an Enraf-Nonius CAD4F four circle diffractometer using a graphite monochromated Mo-K radiation, λ = 0.710 69 Å. The crystal was triclinic with space group $P\bar{1}$ and had unit cell parameters a = 9.4784(10); b = 11.5639(10); c = 12.8436(10) Å; α = 80.414(8); β = 68.821(8); γ = 78.283(8)°. The criterion which qualified a reflection for observation was $I > 2\theta I$ and 8061 reflections

satisfied this condition. The structure was solved by direct methods, SHELXS-86,[15] and refined with 330 variable parameters using SHELXL-93.[16] Data were corrected for Lorentz and polarisation effects but not for absorption. Hydrogen atoms were included in calculated positions with fixed thermal parameters. The non-hydrogen atoms were refined anisotropically. The atomic scattering factors for non-hydrogen atoms were taken from the literature.[17] After full matrix refinement; $R_1 = 7.04\%$ and $wR_2 = 22.20\%$. The maximum and minimum excursions in the final $F_o - F_c$ difference map were 0.533 and -0.333 e Å^{-3}. All calculations were performed on a VAX 6610 computer. The ORTEX programme was used to obtain the drawings.[17],†

X-Ray crystal structure determination of compound 9a

Colourless crystals of 1-aminopyrroles **9a** were grown from ethanol at ambient temperature. A good quality crystal of approximate dimensions 0.69 × 0.48 × 0.41 mm was used for data collection on an Enraf-Nonius CAD4F four circle diffractometer. The crystal was monoclinic with space group $P2_1/n$ and had unit cell parameters of (a) = 8.706(2); (b) = 13.191(2); (c) = 17.818(2) Å; $\beta = 100.88°$. Reflections were collected using monochromated Mo-Kα radiation, λ = 0.710 69A°. The criterion which qualified a reflection for observation was $I > 2\sigma I$ and 7283 reflections satisfied this condition. The structure was solved by direct methods, SHELXS-86,[15] and refined with 259 variable parameters using SHELXL-93.[16] Data were corrected for Lorentz and polarisation effects but not for absorption. Hydrogen atoms were included in calculated positions with fixed thermal parameters and non-hydrogen atoms were refined anisotropically.[17] After full matrix refinement; $R_1 = 7.10\%$ and $wR_2 = 22.2\%$. The maximum and minimum excursions in the final $F_o - F_c$ difference map were 0.784 and -0.537 e Å^{-3}. All calculations were calculated on a VAX 6610 computer and the ORTEX[17] programme was used to obtain the drawings.†

X-Ray crystal structure determination of compound 15d

The structure was solved by direct methods, SHELXS-86,[15] and refined by full matrix least squares using SHELXL-93.[16] Data were corrected for Lorentz and polarization 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. The C(27)-C(28) bond is foreshortened by librational motion involving C(28). No attempt was made to treat disorder in C(28). All calculations were performed on a VAX 6610 computer. The ORTEX program was used to obtain the drawings.[17],†

† Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 207/9.

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