Aromatic azapentalenes: 1*H*- and (mesoionic) 2*H*-pyrrolotetrazoles. Part 2.[1] Reaction with electrophiles

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Protonation, acetylation, benzoylation, carbamoylation, formylation, bromination, azo coupling, nitrosation and addition to DMAD were studied. Monosubstitution occurred as a rule (bromination excepted), the preferred site of attack being C(5) if both the 5 and 7 positions were free. A number of observations point to a slightly higher reactivity of the mesoionic isomers **2**; this is consistent with AM1 calculations. 1,3-Dipolar cycloaddition behaviour of **2** towards DMAD, a conceivable process, could not be detected; only linear addition was observed. Nitroso derivatives of the series **3**, **4** and **8** were not isolated as such but as the ring-opened nitrile oxides **11** and **12**; at elevated temperature analogous valence isomers arise also from the nitroso derivative **7e** and the azo compounds **3e** and **4e**.
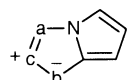
Introduction

In the preceding Part[1] we showed that pyrrolotetrazoles **1** and **2**—new classes of aromatic azapentalenes—are accessible in a straightforward manner. These compounds were characterised by physical methods; for completion, we investigate the behaviour towards electrophilic agents.[2] Reactivity is anticipated from the properties of related systems such as **IA–C**
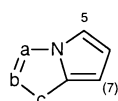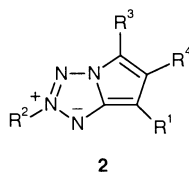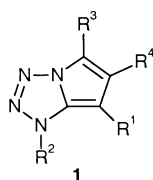
IA a = b = CH, c = NR or S   **II** a = b = CH, c = NR or S
IB a = CH, b = N, c = NR
IC a = N, b = CH, c = NR

1	R¹	R²	R³	R⁴	2
a	H	Me	H	H	a
b	H	Me	H	Me	
	H	Ph	H	Me	b
c	H	Me	H	Ph	c
d	H	Ph	H	Ph	d
e	H	Me	Me	Ph	e
f	Ac	Me	H	Me	
	Ac	Ph	H	Me	f
g	Ac	Me	H	Ph	
	Ac	Ph	H	Ph	g
h	CO₂Me	Me	H	Ph	h

including 4*H*-pyrrolo[1,2-*a*]benzimidazole (**I**; ab = CC of benzo, c = NR).[3,4] The ample material demonstrates that protonation, S_E-reactions and additions to activated multiple

Table 1 AM1 atomic charges for **1a** and **2a**

	1a		**2a**	
	Total	π	Total	π
N(1)	−0.199	1.669	−0.061	1.269
N(2)	0.017	1.126	−0.067	1.444
N(3)	0.020	1.175	−0.046	1.362
N(4)	−0.135	1.543	−0.048	1.417
C(5)	−0.099	1.124	−0.181	1.220
C(6)	−0.159	1.065	−0.119	1.022
C(7)	−0.197	1.166	−0.199	1.165
C(7a)	−0.024	1.110	−0.079	1.105

bonds occur uniformly at C(5) [*i.e.* C(1) of the pyrrolobenzimidazole], whereas C(7) [C(3)] reacts only in the case of 5-[1-]substituted derivatives.[5] Such selectivity is consistent with semiempirical calculations which, in addition, show that C(6) [C(2)] is electronically disfavoured.[6] Hence, the presence of a substituent at this position, which is encountered with practically all substrates **I** studied, does not detract from the above orientation rule. Azapentalenes of type **II** with a free pyrrolic half-ring are represented by a derivative having c = NR; here H–D exchange experiments[7] suggest that class **2** will be primarily attacked at C(5), too. This view is supported by AM1 computations which we performed with the pyrrolotetrazoles **1a** and **2a** (Table 1).
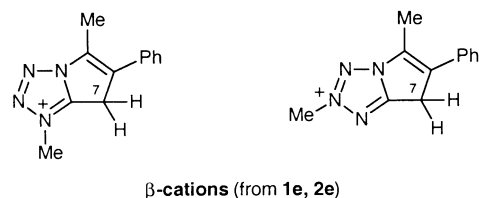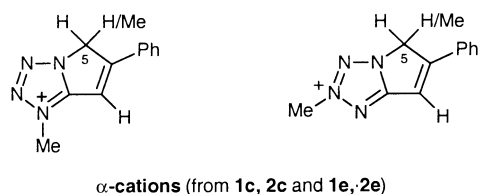
Results

As expected, derivatives **1** and **2** are capable of forming stable salts with strong acids, exemplified by the picrate of **1b**[1] and the perchlorates of **1c** and **2c**. The site of protonation with both classes is C(5) (Table 2: 'α-cation'). This follows, for **1**, from an NOE experiment with **1c·HClO₄** (enhancement between the one-proton singlet at δ 7.38 and the three-proton singlet at δ 4.43), and for **2**, from the similarity of the spectrum of **2c·HClO₄** with that of the aforementioned substance. The same set of NMR signals was obtained from solutions of the bases **1c** and **2c** in trifluoroacetic acid, confirming that on preparation of the above perchlorates species that might have eluded isolation were not formed. In contrast to **1c** and **2c**, the 5-methyl deriv-

Table 2 Protonation of the pyrrolotetrazoles **1c,e** and **2c,e** [a]

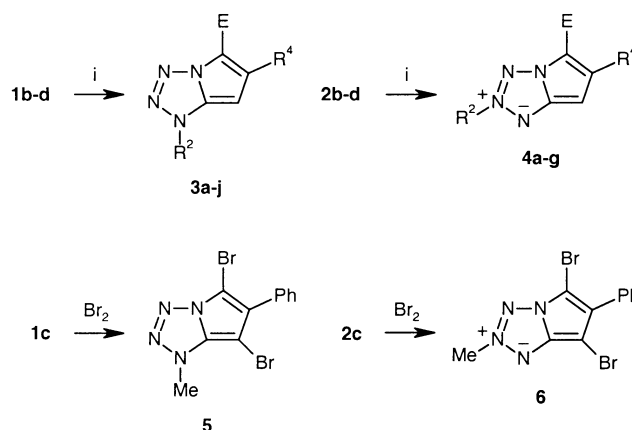| Compound | α-Cation | | | β-Cation | | Percentage | |
	5-H₂/5-*H*Me	7-H	Me	7-H₂	Me	α-Cation	β-Cation
1c·HClO₄	5.84[b]	7.38[b]	4.43			100	0
1c	5.86	7.36	4.43			100	0
2c·HClO₄	5.87	7.26	4.71			100	0
2c	5.89	7.30	4.74			100	0
1e	6.13 (q, *J* 7.2)	7.31	1.98 (d, *J* 7.2), 4.46	4.57 (br)	2.78 (t, *J* 1.7), 4.54	67	33
2e	6.16 (dq, *J* 7.2, 1.0)	7.21 (d, *J* 1.0)	1.95, 4.74	4.47 (q, *J* 1.9)	2.75 (t, *J* 1.9), 4.77	20	80

[a] NMR study in CF₃CO₂H [δ_H values; unspecified signals are singlets. *Cf.* δ_H of bases in CDCl₃ (5-H/7-H/Me and 7-H/Me, respectively): 7.46/5.78/3.97 (**1c**),[2] 7.42/6.17/4.25 (**2c**),[1] 5.60/2.64, 3.99 (**1e**),[1] 6.00/2.61, 4.32 (**2e**)[1]]. [b] Assignment by means of an NOE experiment.

α-cations (from **1c, 2c** and **1e,·2e**)

β-cations (from **1e, 2e**)

5

6

3	(from)	E	R²	R⁴	**4**	(from)
a	(**1b**)	Ac	Me	Me		
		Ac	Ph	Me	**a**	(**2b**)
b	(**1c**)	Ac	Me	Ph	**b**	(**2c**)
c	(**1c**)	CHO	Me	Ph	**c**	(**2c**)
d	(**1c**)	CY=CHY[a]	Me	Ph	**d**	(**2c**)
e	(**1c**)	N=NPh	Me	Ph	**e**	(**2c**)
f[b]	(**1c**)	NO	Me	Ph	**f**[b]	(**2c**)
g[b]	(**1d**)	NO	Ph	Ph	**g**[b]	(**2d**)
h[b]	(**1b**)	NO	Me	Me		
i	(**1b**)	Bz	Me	Me		
j	(**1c**)	CONHPh	Me	Ph		

[a] Y = CO₂Me; (*E*)- and/or (*Z*)-isomer obtained (see text).
[b] Isolated as the respective valence-isomeric nitrile oxide **11** (*cf.* ref. 2) and **12** (Scheme 3, eqns. 1 and 2).

Scheme 1 *Reagents*: i, Ac₂O (for **3a,b** and **4a,b**), DMF–POCl₃ for **3c** and **4c**), DMAD (for **3d** and **4d**), PhN₂Cl (for **3e** and **4e**), NaNO₂–AcOH (for **3f–h** and **4f,g**), Bz₂O (for **3i**), PhNCO (for **3j**).

atives **1e** and **2e** are protonated also at C(7), the 2*H*-isomer† **2e** to an even greater extent ('β-cation'). While the results concerning **1c,e** and **2c** match findings with congeners of **I**[3,4c–f] and **II**,[7] the behaviour of **2e** has no direct precedent.

As substrates for S_E-reactions we chose the pyrrolotetrazoles **1b–h** and **2b–h**. These compounds were transformed as shown in Schemes 1 and 2 to give, depending on starting material and reagent, four categories of substitution products, *i.e.* **3/4**, **5/6**, **7/8** and **9/10**. The derivatives of type **3/4** demonstrate the preferential attack of the electrophile at position 5 as evidenced by NMR (δ_{7-H} 5.5–6.5, $\delta_{C(7)}$ 78–87; data to be compared with those of the substrates collected in Part 1[1]). Double substitution was observed only on bromination (**5/6**). Although the substrates **1f–h** and **2f–h** bear a deactivating substituent at C(7), they proved sufficiently reactive to afford products of type **7/8**. Compound **8f** was envisaged as a potential monobromo derivative of series **4**, but efforts to remove the ester group without affecting the bromo function remained unrewarded.[8] Finally, the derivatives of class **9/10** serve to illustrate the rule that C(7) is attacked only if position 5 is occupied. Except for bromination, all of the reactions performed with the acceptor-free 1*H*-pyrrolotetrazoles **1b–e** have a precedent with azapentalenes **I**.[3,4a,b,5a]

The influence of both the starting bicycle (type **1** or **2**) and the substituent R⁴ on reactivity became apparent in certain cases: thus, acetylation of **2c** proceeded distinctly faster compared to that of **1c**, and **1f**—in contrast to **2f**—reacted only in the presence of sodium acetate;[9] also the conversion of **2h** with DMAD (see later) occurred more rapidly than that of **1h**. These observations are consistent with the calculations of Table 1 [higher electron density at C(5) for **2a**]. Regarding the effect of R⁴, the derivative **1b** having the electron-releasing 6-methyl group underwent acetylation considerably faster than did **1c**;
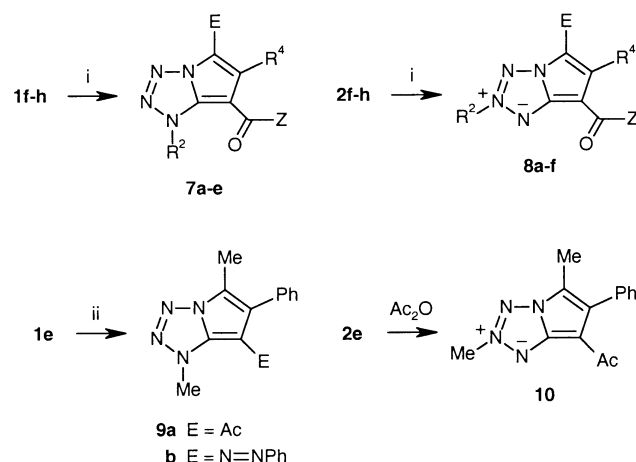
the same is true of benzoylation.[10] Finally, comparing acetylation of the 6-methyl compounds **1f/2f** to that of the 6-phenyl congeners **1g/2g**, the latter couple (including **2g**!) failed to react at all.

A remarkable finding, already reported,[2] concerns nitrosation: substitution products of class **3/4** such as **3f–h** and **4f,g** once formed are converted into the valence-isomeric nitrile oxides **11a–c** and **12a,b** [Scheme 3, eqns. (1) and (2)]. Pyrrole ring opening is impeded by an acceptor group at C(7) so as to allow isolation of the derivatives **7d,e**.[2] With this in view, we attempted to prepare the isomers **8d,e** but found that the materials isolated exist under the same conditions predominantly as the nitrile oxides **12e,f** [Scheme 3, eqn. (5); see also Table 3]. Here obviously the 'stabilising' effect of the acceptor substituent is offset by the less nucleophilic N(4) atom of a (monocyclic) 2*H*-tetrazole ring.[11] The differing stabilities of the 1*H*- and 2*H*-systems have recently been described for isomeric

† The term '2*H*-pyrrolotetrazole' is used to accord with established literature practice. See ref. 5 of Part 1.[1]

Table 3 Equilibrium between the nitroso derivative **8e** and the nitrile oxide **12f** [a]

Temperature/°C	$K_{[12f]/[8e]}$	Percentage **8e**
26	17.5	5.4
0	11.8	7.8
−10	10.4	8.8
−20	9.9	9.2
−30	9.6	9.4

[a] Determined in CD_2Cl_2 utilising δ_H 3.68, 4.42 (**12f**) and 3.83, 4.59 (**8e**).

Scheme 2 diagram showing transformations 1f–h → 7a–e, 2f–h → 8a–f, 1e → 9a, 9b, 2e → 10

7	(from)	E	Z	R²	R⁴	8	(from)
a	(1f)	Ac	Me	Me	Me		
		Ac	Me	Ph	Me	**a**	(2f)
b	(1h)	CY=CHY[a]	OMe	Me	Ph	**b**	(2h)
c	(1h)	N=NPh	OMe	Me	Ph	**c**	(2h)
d	(1g)	NO	Me	Me	Ph		
		NO	Me	Ph	Ph	**d**[b]	(2g)
e	(1h)	NO	OMe	Me	Ph	**e**[b]	(2h)
		Br	OMe	Me	Ph	**f**	(2h)

[a] Y = CO_2Me; (E)- and/or (Z)-isomer obtained (see text). [b] Exists predominantly as the respective valence-isomeric nitrile oxide **12** (Scheme 3, eqn. 5).
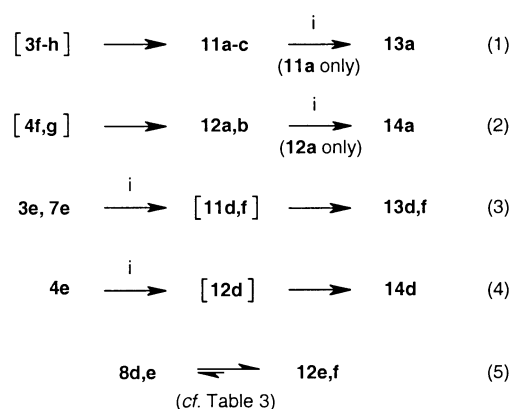
Scheme 2 *Reagents*: i, Ac_2O (for **7a** and **8a**), DMAD (for **7b** and **8b**), PhN_2Cl (for **7c** and **8c**), $NaNO_2$–AcOH (for **7d,e** and **8d,e**), Br_2 (for **8f**); ii, Ac_2O (for **9a**), PhN_2Cl (for **9b**).

11-14	R¹	R²	R⁴	X
a	H	Me	Ph	O
b	H	Ph	Ph	O
c	H	Me	Me	O
d	H	Me	Ph	NPh
e	Ac	Ph	Ph	O
f	CO_2Me	Me	Ph	O

$$[3f\text{-}h] \longrightarrow 11a\text{-}c \xrightarrow[\text{(11a only)}]{i} 13a \quad (1)$$

$$[4f,g] \longrightarrow 12a,b \xrightarrow[\text{(12a only)}]{i} 14a \quad (2)$$

$$3e, 7e \xrightarrow{i} [11d,f] \longrightarrow 13d,f \quad (3)$$

$$4e \xrightarrow{i} [12d] \longrightarrow 14d \quad (4)$$

$$8d,e \rightleftharpoons 12e,f \quad (5)$$

$$(cf.\ \text{Table 3})$$

Scheme 3 *Reagents and conditions*: i, DMAD, heat.

5-nitrosoimidazo[1,2-*d*]tetrazole.[12] Nitroso derivatives that are stable at room temperature such as **7d,e** ring-open on being heated and can be trapped with DMAD to give, like **11a** and **12a**, the respective isoxazoles **13** or **14** (*cf.* ref. 2). The azo compounds **3e** and **4e**, which are isolable in contrast to **3f–h** and **4f,g**, undergo pyrrole ring cleavage also at elevated temperature to afford, in the presence of DMAD, the pyrazoles **13d**[2] and **14d** [Scheme 3, eqns. (3) and (4)]. In agreement with the much easier ring opening of **8d,e** compared to **7d,e**, the azo derivative **4e** reacts more readily than does **3e**. Nevertheless, the acceptor-substituted congener **8c** proved entirely unreactive (as paralleled by **7c**[2]).

Michael-type addition of the 1*H*-pyrrolotetrazoles **1c** and **1h** onto DMAD, proceeding in a 1 : 1 molar ratio, gave the fumarates (*E*)-**3d** and (*E*)-**7b**, respectively. In both cases we obtained only one stereoisomer. Assignment was made on the basis of the $^3J_{C(5),H(vinyl)}$ coupling constants (9.4 and 10.1 Hz, respectively), in conjunction with the shift value of the β carbon atom of the vinyl group (δ_C 124.6 and 128.6; $^1J_{C,H}$ 166 Hz) which, in the case of a (*Z*)-isomer, would adsorb at higher field (δ_C < 120; see ref. 13 and Experimental section for the respective derivatives of **4** and **8**). Also from class **2** we obtained 1 : 1 adducts. The substrates, belonging to 'type C' of Ramsden's

non-classical heteropentalenes,[14] are 1,3-dipoles (Scheme 4). While the azimine function of the tetrazolic half-ring need not be considered,[15] the potential azomethine imine might give rise to a cyclazine such as **15** [reaction (a); *cf.* ref. 16]. This species, because of three adjacent azane-type nitrogen atoms, is expected to ring-open immediately giving the 6*H*-pyrrolo-[1,2-*b*]pyrazole **16**. However, we had no indications of the occurrence of such a process and observed only linear addition (as with **1c,h**) [reaction (b)]. But in contrast with the stable fumarates (*E*)-**3d** and (*E*)-**7b**, the 2*H*-analogues (*E*)-**4d** and (*E*)-**8b** tend to isomerise into the maleates, the former remarkably readily: thus, a solution of pure (*E*)-**4d** showed as soon as 5 minutes after dissolving the material in chloroform a 1 : 1 mixture of the (*E*)- and (*Z*)-forms, and 30 minutes later there was a mere 5% of the starting isomer detectable. We believe that the ease of this interconversion is a consequence of the enhanced electron density at C(5) of the 2*H*-pyrrolotetrazole series (Table 1), which facilitates polarisation of the olefinic double bond; an acceptor group at C(7), present with **8b**, inhibits this so as to slow down isomerisation. The predominance of the (*Z*)-adduct derived from **2** parallels observations made earlier in the pyrrolo[2,1-*b*]thiazole series (**I**; a = b = CH/CR, c = S).[5a]
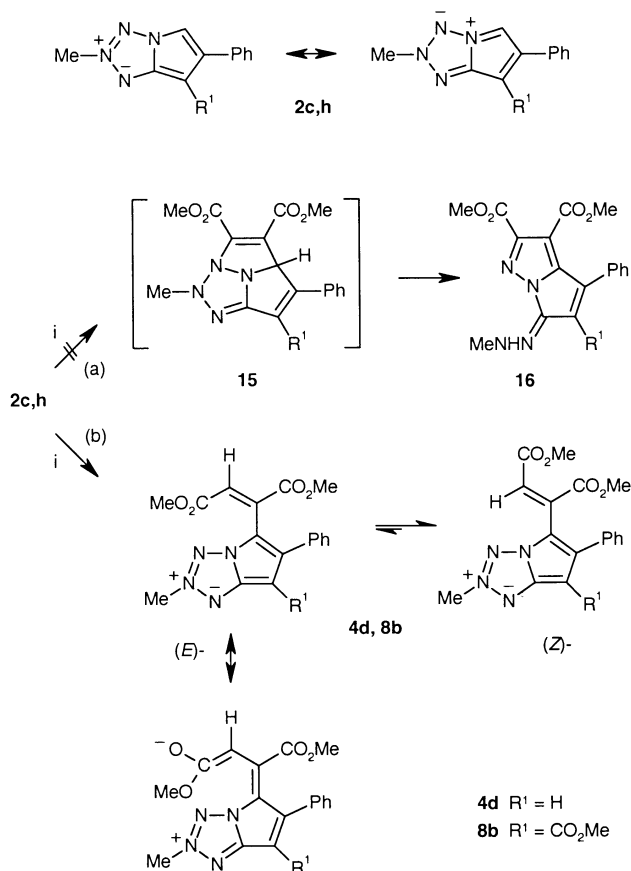
Scheme 4 *Reagents and conditions*: i, DMAD, rt.

Experimental

For instruments used and preparation of starting pyrrolo-tetrazoles **1** and **2**, see ref. 1. AM1 calculations were performed on an IBM 100 MHz Pentium PC using version 4.5 of the HyperChem program (Hypercube, Inc., 419 Philip Street, Waterloo N2L 3X2, Canada). The geometries of **1a** and **2a** were optimised (Polak-Ribiere optimiser, RMS gradient $\leq 10^{-1}$ kcal Å^{-1} mol^{-1}, convergence limit $\leq 10^{-5}$ kcal mol^{-1}).

1-/2-Methyl-6-phenyl-1H-/2H-pyrrolotetrazolium perchlorates 1c·HClO₄, 2c·HClO₄. General procedure

To a solution of the pyrrolotetrazole **1c** (0.60 g, 3 mmol) or **2c** (0.30 g, 1.5 mmol) in hot acetic acid (10 cm³; 80 °C) was added dropwise 10 M HClO₄. After cooling, the salt was filtered off and recrystallised from methanol–water (9 : 1).

1c·HClO₄: Yield 0.78 g (87%), mp 206–209 °C (Found: C, 44.2; H, 3.6; N, 18.7. [C₁₁H₁₁N₄]ClO₄ requires C, 44.2; H, 3.7; N, 18.8%); for δ_H, see Table 2.

2c·HClO₄: Yield 0.27 g (60%), mp 256 °C (Found: C, 44.1; H, 3.8; N, 18.6. [C₁₁H₁₁N₄]ClO₄ requires C, 44.2; H, 3.7; N, 18.8%); for δ_H, see Table 2.

Substituted 5-acetyl- and 7-acetyl-1H-/2H-pyrrolotetrazoles 3a,b, 4a,b, 7a, 8a, 9a, 10. General procedure

Acetic anhydride (5.0–8.0 g, *ca.* 50–80 mmol) was added to the appropriate pyrrolotetrazole **1** or **2** (2 mmol) and the mixture was kept as detailed below: **1b**: 20 °C, 24 h; **1c**: 20 °C, 7 d or 100–110 °C, 3.5 h; **1e**: 20 °C, 3 d; **1f**: 100–110 °C, 2 d [after addition of anhydrous sodium acetate (0.33 g, 4 mmol)]; **2b**: 120 °C, 2.5 h; **2c**: 20 °C, 24 h; **2e**: 20 °C, 24 h; **2f**: 120 °C, 8 h. For work-up, the cooled solution was diluted with water (10–20 cm³) to allow hydrolysis of the unconsumed reagent whereupon the mixture was neutralised with sodium carbonate and extracted with dichloromethane. Recrystallisation was effected

with chloroform–diethyl ether (**3a**, **7a**, **10**), chloroform–light petroleum (**3b**), dichloromethane–light petroleum (**4a,b**), dichloromethane–diethyl ether (**8a**) or diethyl ether–light petroleum (**9a**).

3a: Yield 0.24 g (67%), mp 121–122 °C (Found: C, 53.9; H, 5.7; N, 31.4%. C₈H₁₀N₄O requires C, 53.9; H, 5.7; N, 31.4%); ν_{max}(KBr)/cm⁻¹ 3120 and 1630; δ_H(CDCl₃) 2.55 (3 H, s), 2.64 (3 H, s), 4.08 (3 H, s) and 5.62 (1 H, s); δ_C(CDCl₃) 15.7 (q), 29.4 (q), 34.7 (q), 80.9 (d), 117.2 (s), 135.4 (s), 140.7 (s) and 185.2 (s).

3b: Yield 0.37 g (77%), mp 119–121 °C (Found: C, 64.9; H, 5.1; N, 23.4. C₁₃H₁₂N₄O requires C, 65.0; H, 5.0; N, 23.3%); ν_{max}(KBr)/cm⁻¹ 3125 and 1625; δ_H(CDCl₃) 2.28 (3 H, s), 4.11 (3 H, s), 5.77 (1 H, s), 7.38–7.43 (3 H, m) and 7.46–7.49 (2 H, m); δ_C(CDCl₃) 29.0 (q), 34.8 (q), 80.7 (d), 116.3 (s), 128.1 (2 × d), 128.2 (d), 129.6 (2 × d), 135.4 (s), 135.6 (s), 143.0 (s) and 185.0 (s).

4a: Yield 0.39 g (81%), mp 139–141 °C (Found: C, 64.65; H, 5.1; N, 23.4. C₁₃H₁₂N₄O requires C, 65.0; H, 5.0; N, 23.3%); ν_{max}(KBr)/cm⁻¹ 1631; δ_H(CDCl₃) 2.63 (3 H, s), 2.64 (3 H, s), 5.99 (1 H, s), 7.49–7.57 (3 H, m) and 8.15–8.17 (2 H, m); δ_C[(CD₃)₂SO] 15.9 (q), 29.1 (q), 86.9 (d), 119.9 (s), 120.4 (2 × d), 130.2 (2 × d), 130.7 (d), 136.9 (s), 141.4 (s), 147.8 (s) and 183.0 (s).

4b: Yield 0.30 g (62%), mp 96–97 °C (Found: C, 65.0; H, 5.1; N, 23.3. C₁₃H₁₂N₄O requires C, 65.0; H, 5.0; N, 23.3%); ν_{max}(KBr)/cm⁻¹ 1616; δ_H(CDCl₃) 2.09 (3 H, s), 4.53 (3 H, s), 6.07 (1 H, s) and 7.42–7.49 (5 H, m); δ_C(CDCl₃) 28.1 (q), 42.0 (q), 86.8 (d), 114.4 (s), 128.20 (2 × d), 128.24 (d), 129.7 (2 × d), 136.0 (s), 143.9 (s), 148.5 (s) and 184.2 (s).

7a: Yield 0.10 g (23%), mp 130–131 °C (lit.,[17] 130–131 °C); ν_{max}(KBr)/cm⁻¹ and δ_H(CDCl₃) consistent with ref. 17.

8a: Yield 0.28 g (50%), mp 259 °C (Found: C, 63.8; H, 5.0; N, 19.7. C₁₅H₁₄N₄O₂ requires C, 63.8; H, 5.0; N, 19.85%); ν_{max}(KBr)/cm⁻¹ 1657 and 1644; δ_H(CDCl₃) 2.71 (3 H, s), 2.73 (3 H, s), 2.99 (3 H, s), 7.59–7.67 (3 H, m) and 8.25–8.28 (2 H, m); δ_C(CDCl₃) 13.9 (q), 30.1 (q), 30.5 (q), 100.9 (s), 116.8 (s), 120.4 (2 × d), 129.9 (2 × d), 131.1 (d), 136.9 (s), 145.0 (s), 149.9 (s), 185.9 (s) and 191.2 (s).

9a: Yield 0.36 g (71%), mp 67–69 °C (Found: C, 66.0; H, 5.55; N, 22.3. C₁₄H₁₄N₄O requires C, 66.1; H, 5.55; N, 22.0%); ν_{max}(KBr)/cm⁻¹ 1635; δ_H(CDCl₃) 1.82 (3 H, s), 2.32 (3 H, s), 4.54 (3 H, s), 7.32–7.35 (2 H, m) and 7.39–7.48 (3 H, m); δ_C(CDCl₃) 8.9 (q), 28.9 (q), 37.5 (q), 97.1 (s), 111.3 (s), 127.9 (d), 128.4 (2 × d), 130.2 (s), 130.4 (2 × d), 134.7 (s), 135.4 (s) and 191.7 (s).

10: Yield 0.06 g [62%; from 0.08 g (0.38 mmol) **2e** and 1.00 g (*ca.* 10 mmol) acetic anhydride], mp 163–164 °C (Found: C, 66.2; H, 5.6; N, 22.0. C₁₄H₁₄N₄O requires C, 66.1; H, 5.55; N, 22.0%); ν_{max}(KBr)/cm⁻¹ 1640; δ_H(CDCl₃) 2.33 (3 H, s), 2.34 (3 H, s), 4.45 (3 H, s) and 7.34–7.44 (5 H, m); δ_C(CDCl₃) 9.3 (q), 29.1 (q), 41.8 (q), 96.7 (s), 109.6 (s), 127.4 (d), 127.8 (2 × d), 130.3 (2 × d), 134.3 (s), 134.5 (s), 148.0 (s) and 188.9 (s).

1-/2-Methyl-6-phenyl-1H-/2H-pyrrolotetrazole-5-carbaldehydes 3c, 4c. General procedure

Phosphoryl chloride (0.61 g, 4 mmol) was cautiously mixed with dimethylformamide (DMF; 0.44 g, 6 mmol) at 0 °C. 30 min later a solution of the pyrrolotetrazole **1c** or **2c** (0.40 g, 2 mmol) in DMF (2.00 g) was added and the mixture was stirred at 0 °C for another 15 min. Then aqueous sodium carbonate (10%; 20 cm³) and ethanol or methanol (5 cm³) were added; after heating under reflux for 1 h, the solution was extracted with dichloromethane to afford the product which was recrystallised from chloroform–diethyl ether (**3c**) or dichloromethane–light petroleum (**4c**).

3c: Yield 0.31 g (68%), mp 128–129 °C (Found: C, 63.8; H, 4.4; N, 24.85. C₁₂H₁₀N₄O requires C, 63.7; H, 4.5; N, 24.8%); ν_{max}(KBr)/cm⁻¹ 3130 and 1630; δ_H(CDCl₃) 4.17 (3 H, s), 5.92 (1 H, s), 7.42–7.48 (3 H, m), 7.51–7.54 (2 H, m) and 9.66 (1 H,

s); δ_C(CDCl$_3$) 34.9 (q), 79.9 (d), 116.0 (s), 128.81 (2 × d), 128.84 (d), 129.6 (2 × d), 133.2 (s), 137.3 (s), 146.4 (s) and 175.6 (d).

4c: Yield 0.26 g (57%), mp 144–146 °C (Found: C, 63.7; H, 4.4; N, 24.7. C$_{12}$H$_{10}$N$_4$O requires C, 63.7; H, 4.5; N, 24.8%); ν_{max}(KBr)/cm^{-1} 1634; δ_H(CDCl$_3$) 4.53 (3 H, s), 6.18 (1 H, s), 7.42–7.48 (3 H, m), 7.56–7.58 (2 H, m) and 9.60 (1 H, s); δ_C(CDCl$_3$) 42.1 (q), 85.6 (d), 113.8 (s), 128.7 (d), 128.8 (2 × d), 129.6 (2 × d), 133.5 (s), 146.2 (s), 150.0 (s) and 174.6 (d).

Substituted dimethyl (1*H*-pyrrolotetrazol-5-yl)fumarates (*E*)-3d, (*E*)-7b. General procedure

A solution of the 1*H*-pyrrolotetrazole **1c** or **1h** (1 mmol) and DMAD (0.57 g, 4 mmol) in methanol (20 cm³) was stirred at room temperature for 1 h (**1c**) or heated under reflux for 3 h (**1h**). After evaporation of the solvent and treatment of the residue with diethyl ether the product was filtered off and recrystallised from chloroform–diethyl ether [(*E*)-**3d**] or methanol–diethyl ether [(*E*)-**7b**].

[(*E*)-**3d**]: Yield 0.13 g (38%), mp 131–133 °C (Found: C, 59.95; H, 4.7; N, 16.3. C$_{17}$H$_{16}$N$_4$O$_4$ requires C, 60.0; H, 4.7; N, 16.5%); ν_{max}(KBr)/cm^{-1} 1730 and 1715; δ_H(CDCl$_3$) 3.29 (3 H, s), 3.68 (3 H, s), 4.05 (3 H, s), 5.88 (1 H, s), 6.80 (1 H, s), 7.27–7.31 (1 H, m) and 7.35–7.40 (4 H, m); δ_C(CDCl$_3$) 34.6 (q), 51.9 (q), 52.5 (q), 76.0 (d), 106.7 (s, $^3J_{C,H}$ 9.4, $^3J_{C,H}$ 5.9), 124.6 (d), 127.4 (d), 128.4 (2 × d), 128.6 (2 × d), 133.0 (s), 134.3 (s), 136.1 (s), 137.8 (s), 165.6 (s) and 167.1 (s).

[(*E*)-**7b**]: Yield 0.16 g (40%), mp 147–149 °C (Found: C, 57.45; H, 4.7; N, 14.0. C$_{19}$H$_{18}$N$_4$O$_6$ requires C, 57.3; H, 4.55; N, 14.1%); ν_{max}(KBr)/cm^{-1} 1735 and 1720; δ_H[(CD$_3$)$_2$SO] 3.28 (3 H, s), 3.57 (3 H, s), 3.66 (3 H, s), 4.38 (3 H, s), 6.80 (1 H, s), 7.22–7.24 (2 H, m) and 7.34–7.39 (3 H, m); δ_C[(CD$_3$)$_2$SO] 37.1 (q), 50.7 (q), 52.0 (q), 52.6 (q), 84.6 (s), 108.7 (s, $^3J_{C,H}$ 10.1), 127.5 (2 × d), 127.8 (d), 128.6 (d), 130.2 (2 × d), 131.0 (s), 131.9 (s), 132.9 (s), 135.6 (s), 162.1 (s), 164.5 (s) and 165.2 (s).

Reaction of the 2*H*-pyrrolotetrazoles 2c and 2h with DMAD. General procedure

To a solution of **2c** or **2h** (1 mmol) in methanol (20 cm³), prepared by gentle warming, was added at room temperature the reagent DMAD (0.57 g, 4 mmol). The mixture was stirred at 20 °C for 1 h (**2c**) or 8 h (**2h**) [or heated under reflux for 1 h (**2h**)] and then allowed to stand at 0–5 °C for 12 h. Isolation of products occurred as detailed below.

In the case of **2c**, 0.16 g orange to red *dimethyl (2-methyl-6-phenyl-2H-pyrrolo[1,2-d]tetrazol-5-yl)fumarate* (*E*)-**4d**,‡ mp 168–170 °C, was filtered off and a second crop (0.02 g) was obtained from the concentrated filtrate (total yield 53%). Crystallisation from dichloromethane–light petroleum gave a mixture of (*E*)-**4d**, mp as above, and yellow *dimethyl (2-methyl-6-phenyl-2H-pyrrolo[1,2-d]tetrazol-5-yl)maleate* (*Z*)-**4d**,‡ mp 135–139 °C, which was in turn separated by picking out the pertinent crystals. Recrystallisation of these materials was effected with chloroform–diethyl ether [(*E*)-**4d**; both rapid precipitation and filtration] or methanol [(*Z*)-**4d**].

In the case of **2h**, 0.05 g pale yellow *dimethyl (7-methoxycarbonyl-2-methyl-6-phenyl-2H-pyrrolo[1,2-d]tetrazol-5-yl)maleate* (*Z*)-**8b**,‡ mp 232–234 °C, was filtered off. The concentrated filtrate crystallised on standing at room temperature within 2 d to afford, after addition of diethyl ether and cooling at 0–5 °C for 12 h, 0.27 g deep yellow *dimethyl (7-methoxycarbonyl-2-methyl-6-phenyl-2H-pyrrolo[1,2-d]tetrazol-5-yl)fumarate* (*E*)-**8b**,‡ mp 140 °C, which was collected by filtration (total yield 80%). Recrystallisation was effected with dichloromethane–diethyl ether [(*E*)-**8b**] or methanol [(*Z*)-**8b**].

(*E*)-**4d**: Mp 171–172 °C (Found: C, 59.4; H, 4.8; N, 16.2. C$_{17}$H$_{16}$N$_4$O$_4$ requires C, 60.0; H, 4.7; N, 16.5%); ν_{max}(KBr)/cm^{-1}

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‡ The IUPAC name for the parent structure of **4d** and **8b** is 1*H*-pyrrolo[1,2-*d*]tetrazol-2-ium-1-ide.

1730 and 1715; δ_H(CDCl$_3$) 3.206 (3 H, s), 3.67 (3 H, s), 4.37 (3 H, s), 6.25 (1 H, br), 6.62 (1 H, s), 7.25–7.29 (1 H, m), 7.34–7.38 (2 H, m) and 7.41–7.43 (2 H, m); δ_C(CDCl$_3$) 41.6 (q), 51.7 (q), 52.4 (q), 82.5 (d), 104.2 (s), 121.0 (d), 127.3 (d), 128.5 (4 × d), 133.5 (s), 136.3 (s), 140.7 (s), 147.4 (s), 165.5 (s) and 167.5 (s).

(*Z*)-**4d**: Mp 138–139 °C (Found: C, 60.0; H, 4.7; N, 16.4. C$_{17}$H$_{16}$N$_4$O$_4$ requires C, 60.0; H, 4.7; N, 16.5%); ν_{max}(KBr)/cm^{-1} 1740 and 1710; δ_H(CDCl$_3$) 3.208 (3 H, s), 3.71 (3 H, s), 4.46 (3 H, s), 6.09 (1 H, s), 6.54 (1 H, s) and 7.36 (5 H, s); δ_C(CDCl$_3$) 41.9 (q), 51.4 (q), 51.9 (q), 87.3 (d), 106.1 (s, $^3J_{C,H}$ 6.3), 107.4 (d), 127.5 (2 × d), 127.9 (d), 130.0 (2 × d), 134.6 (s), 138.0 (s), 142.1 (s), 148.0 (s), 166.2 (s) and 166.8 (s).

(*E*)-**8b**: Mp 145–147 °C (Found: C, 57.2; H, 4.6; N, 14.0. C$_{19}$H$_{18}$N$_4$O$_6$ requires C, 57.3; H, 4.55; N, 14.1%); ν_{max}(KBr)/cm^{-1} 1735, 1720 and 1690; δ_H(CDCl$_3$) 3.31 (3 H, s), 3.66 (3 H, s), 3.83 (3 H, s), 4.48 (3 H, s), 6.79 (1 H, s) and 7.31–7.43 (5 H, m); δ_C(CDCl$_3$) 42.1 (q), 51.1 (q), 52.0 (q), 52.6 (q), 87.5 (s), 107.6 (s, $^3J_{C,H}$ 9.8), 126.8 (d), 127.6 (2 × d), 128.1 (d), 130.7 (2 × d), 133.1 (s), 133.2 (s), 140.8 (s), 148.5 (s), 163.1 (s), 164.9 (s) and 166.1 (s).

(*Z*)-**8b**: Mp 234–235 °C (Found: C, 56.9; H, 4.5; N, 13.8. C$_{19}$H$_{18}$N$_4$O$_6$ requires C, 57.3; H, 4.55; N, 14.1%); ν_{max}(KBr)/cm^{-1} 1750, 1715 and 1695; δ_H(CDCl$_3$) 3.18 (3 H, s), 3.72 (3 H, s), 3.73 (3 H, s), 4.57 (3 H, s), 6.65 (1 H, s), 7.32–7.36 (2 H, m) and 7.39–7.42 (3 H, m); δ_C(CDCl$_3$) 42.5 (q), 51.2 (q), 51.7 (q), 52.2 (q), 91.4 (s), 109.2 (s, $^3J_{C,H}$ 6.8), 111.8 (d), 127.2 (2 × d), 128.4 (d), 130.5 (2 × d), 131.8 (s), 137.4 (s), 142.5 (s), 148.9 (s), 162.3 (s), 165.3 (s) and 166.1 (s).

5-Benzoyl-1,6-dimethyl-1*H*-pyrrolo[1,2-*d*]tetrazole 3i

A solution of the 1*H*-pyrrolotetrazole **1b** (0.27 g, 2 mmol) and benzoic anhydride (0.90 g, 4 mmol) in diethyl ether (10 cm³) was allowed to stand at room temperature for 12 h. After evaporation of the solvent the residue was dissolved in the minimum amount of chloroform; addition of diethyl ether–light petroleum (1 : 1) caused precipitation of the product which was collected by filtration and recrystallised from chloroform. Yield 0.16 g (33%), mp 170–171 °C (Found: C, 64.8; H, 5.05; N, 23.5. C$_{13}$H$_{12}$N$_4$O requires C, 65.0; H, 5.0; N, 23.3%); ν_{max}(KBr)/cm^{-1} 3125 and 1610; δ_H(CDCl$_3$) 2.23 (3 H, s), 4.05 (3 H, s), 5.64 (1 H, s), 7.42–7.53 (3 H, m) and 7.63–7.66 (2 H, m); δ_C(CDCl$_3$) 15.8 (q), 34.6 (q), 81.3 (d), 116.7 (s), 128.20 (2 × d), 128.22 (2 × d), 131.0 (d), 136.3 (s), 140.3 (s), 141.4 (s) and 183.6 (s).

1-Methyl-*N*,6-diphenyl-1*H*-pyrrolo[1,2-*d*]tetrazole-5-carboxamide 3j

A solution of the 1*H*-pyrrolotetrazole **1c** (0.40 g, 2 mmol) and phenyl isocyanate (0.36 g, 3 mmol) in anhydrous dichloromethane (5 cm³) was stirred at room temperature for 2 d. The mixture was concentrated and the residue briefly heated under reflux with ethanol (5 cm³) whereupon crystals of the product separated which were thoroughly washed with ethanol. Yield 0.24 g (38%), mp 156–158 °C (Found: C, 68.1; H, 4.7; N, 22.0. C$_{18}$H$_{15}$N$_5$O requires C, 68.1; H, 4.8; N, 22.1%); ν_{max}(KBr)/cm^{-1} 3385 and 1660; δ_H(90 MHz; CDCl$_3$) 4.04 (3 H, s), 5.74 (1 H, s), 6.97–7.72 (10 H, m) and 8.33 (1 H, br).

Substituted 5,7-dibromo- and 5-bromo-1*H*-/2*H*-pyrrolotetrazoles 5, 6, 8f. General procedure

Bromine [0.64 g, 4 mmol (for **5**); 0.74 g, 4.6 mmol (for **6**, **8f**)], dissolved in chloroform (5 cm³), was added with stirring and ice cooling to a solution of the pyrrolotetrazole **1c**, **2c** or **2h** (2 mmol) in the same solvent (5 cm³). After 30 min the mixture was shaken with aqueous sodium carbonate (5%; 10 cm³) until the solid disappeared. The product was isolated by concentration of the organic layer and recrystallised from chloroform–light petroleum (**5**) or dichloromethane–light petroleum (**6**, **8f**).

5: Yield 0.33 g (46%), mp 112–114 °C (Found: C, 37.2; H, 2.2; N, 15.7. $C_{11}H_8Br_2N_4$ requires C, 37.1; H, 2.3; N, 15.7%); $\delta_H(CDCl_3)$ 4.16 (3 H, s), 7.38–7.42 (1 H, m) and 7.45–7.54 (4 H, m); $\delta_C[(CD_3)_2SO]$ 35.0 (q), 59.6 (s), 78.7 (s), 128.1 (d), 128.5 (2 × d), 129.8 (2 × d), 130.9 (s), 131.1 (s) and 131.5 (s).

6: Yield 0.48 g (67%), mp 143–144 °C (Found: C, 36.9; H, 2.3; N, 15.6. $C_{11}H_8Br_2N_4$ requires C, 37.1; H, 2.3; N, 15.7%); $\delta_H(CDCl_3)$ 4.40 (3 H, s), 7.38–7.42 (1 H, m), 7.45–7.49 (2 H, m) and 7.56–7.59 (2 H, m); $\delta_C(CDCl_3)$ 42.0 (q), 64.3 (s), 75.3 (s), 128.1 (d), 128.2 (2 × d), 130.2 (2 × d), 132.2 (s), 134.0 (s) and 144.0 (s).

8f: Yield 0.60 g (90%), mp 225 °C (Found: C, 46.5; H, 3.4; N, 16.5. $C_{13}H_{11}BrN_4O_2$ requires C, 46.6; H, 3.3; N, 16.7%); $v_{max}(KBr)/cm^{-1}$ 1687; $\delta_H(CDCl_3)$ 3.80 (3 H, s), 4.50 (3 H, s) and 7.40–7.51 (5 H, m); $\delta_C(CDCl_3)$ 42.2 (q), 51.1 (q), 81.3 (s), 87.5 (s), 127.7 (2 × d), 128.2 (d), 130.5 (2 × d), 132.2 (s), 138.0 (s), 147.5 (s) and 162.6 (s).

Substituted 5-(phenylazo)- and 7-(phenylazo)-1H-/2H-pyrrolotetrazoles 3e, 4e, 7c, 8c, 9b. General procedure

To the respective pyrrolotetrazole **1** or **2** (2 mmol), dissolved in acetic acid (10.0 g), was added at 0 °C a freshly prepared solution of benzenediazonium chloride (2.5–3 mmol; from equimolar amounts of aniline and sodium nitrite in 5–6 M HCl). The mixture was stirred at room temperature for 15 min (in the case of **1h** and **2h** for 1 h), then diluted with water (50 cm³) and neutralised with sodium carbonate. The product was separated by extraction with dichloromethane and recrystallised from chloroform–diethyl ether (**3e**, **7c**, **9b**) or dichloromethane–diethyl ether (**4e**, **8c**), in the latter two cases after chromatography on silica gel [chloroform–ethyl acetate (*ca.* 2 : 1) as eluent].

3e: Yield 0.49 g (81%), mp 169–171 °C (lit.,[2] 168–170 °C) (Found: C, 67.6; H, 4.6; N, 27.9. $C_{17}H_{14}N_6$ requires C, 67.5; H, 4.7; N, 27.8%); for δ_H and δ_C, see ref. 2.

4e: Yield 0.47 g (78%), mp 142–144 °C (Found: C, 67.6; H, 4.6; N, 27.8. $C_{17}H_{14}N_6$ requires C, 67.5; H, 4.7; N, 27.8%); $\delta_H(CDCl_3)$ 4.37 (3 H, s), 6.43 (1 H, s), 7.21–7.28 (1 H, m), 7.36–7.48 (5 H, m), 7.83–7.85 (2 H, m) and 8.00–8.02 (2 H, m); $\delta_C(CDCl_3)$ 41.8 (q), 85.2 (d), 121.6 (2 × d), 125.7 (s), 127.8 (d), 128.3 (d), 128.4 (2 × d), 128.9 (2 × d), 129.7 (2 × d), 134.0 (s), 140.5 (s), 148.7 (s) and 154.4 (s).

7c: Yield 0.46 g (64%), mp 240–242 °C (lit.,[2] 240–242 °C) (Found: C, 63.4; H, 4.4; N, 23.3. $C_{19}H_{16}N_6O_2$ requires C, 63.3; H, 4.5; N, 23.3%); $v_{max}(KBr)/cm^{-1}$ 1710; $\delta_H[(CD_3)_2SO]$ 3.71 (3 H, s), 4.42 (3 H, s), 7.37–7.41 (1 H, m), 7.47–7.49 (5 H, m) and 7.60–7.64 (4 H, m).

8c: Yield 0.50 g (69%), mp 238–240 °C (Found: C, 63.4; H, 4.4; N, 22.9. $C_{19}H_{16}N_6O_2$ requires C, 63.3; H, 4.5; N, 23.3%); $v_{max}(KBr)/cm^{-1}$ 1709; $\delta_H(CDCl_3)$ 3.87 (3 H, s), 4.58 (3 H, s), 7.29–7.42 (1 H, m), 7.46–7.52 (5 H, m) and 7.73–7.76 (4 H, m); $\delta_C(CDCl_3)$ 42.4 (q), 51.4 (q), 90.2 (s), 122.0 (2 × d), 127.3 (2 × d), 128.2 (s), 128.7 (d), 129.0 (2 × d), 129.3 (d), 131.4 (s), 131.9 (2 × d), 142.6 (s), 149.3 (s), 153.7 (s) and 162.7 (s).

9b: Yield 0.39 g (62%), mp 148–150 °C (Found: C, 68.1; H, 5.15; N, 26.3. $C_{18}H_{16}N_6$ requires C, 68.3; H, 5.1; N, 26.6%); $\delta_H(CDCl_3)$ 2.59 (3 H, s), 4.51 (3 H, s), 7.22–7.26 (1 H, m), 7.34–7.39 (3 H, m), 7.44–7.48 (2 H, m) and 7.59–7.62 (4 H, m); $\delta_C(CDCl_3)$ 9.6 (q), 38.2 (q), 110.6 (s), 114.4 (s), 121.1 (2 × d), 125.1 (s), 127.1 (d), 127.9 (d), 128.0 (2 × d), 128.9 (2 × d), 129.7 (s), 131.0 (2 × d), 133.1 (s) and 153.4 (s).

Substituted 5-nitroso-1H-pyrrolotetrazoles 7d,e and substituted 3-(1H-/2H-tetrazol-5-yl)acrylonitrile oxides 11a–c, 12a,b,e,f. General procedure

To a solution of the respective pyrrolotetrazole **1** or **2** (2 mmol) in acetic acid (10.0 g) was added at 0 °C sodium nitrite (0.28 g, 4 mmol) in a small amount of water. The mixture was stirred

at room temperature for 15–30 min and then neutralised with 8 M NH_3. The products **7d,e** and **11a–c** were filtered off and washed with water, while **12a,b,e,f** were extracted with dichloromethane. Recrystallisation was effected with chloroform (**7e**), chloroform–diethyl ether (**7d**), dichloromethane–diethyl ether (**12a,f**), methanol (**11c**) or methanol–diethyl ether (**11a,b**, **12b,e**).—In ref. 2, preparation of **11c** failed (*cf.* note 4).

7d: Yield 0.38 g (71%), mp 144–147 °C (lit.,[2] 141–143 °C) (Found: C, 57.8; H, 4.0; N, 25.9. $C_{13}H_{11}N_5O_2$ requires C, 58.0; H, 4.1; N, 26.0%); $v_{max}(KBr)/cm^{-1}$ 1650; $\delta_H(CDCl_3)$ 2.11 (3 H, s), 4.60 (3 H, s), 7.54–7.61 (3 H, m) and 7.74–7.76 (2 H, m); $\delta_C(CDCl_3)$ 29.6 (q), 38.3 (q), 103.7 (s), 128.5 (2 × d), 130.1 (d), 130.6 (s), 131.0 (2 × d), 138.2 (s), 147.3 (s), 149.9 (s) and 193.0 (s).

7e: Yield 0.45 g (79%), mp 138–140 °C (lit.,[2] 138–140 °C) (Found: C, 54.9; H, 3.95; N, 24.5. $C_{13}H_{11}N_5O_3$ requires C, 54.7; H, 3.9; N, 24.55%); for v_{max}/cm^{-1}, δ_H and δ_C, see ref. 2.

11a: Yield 0.23 g (51%), mp 138–139 °C (lit.,[2] 138–139 °C) (Found: C, 58.0; H, 3.7; N, 31.0. $C_{11}H_9N_5O$ requires C, 58.15; H, 4.0; N, 30.8%); for v_{max}/cm^{-1}, δ_H, δ_C and λ_{max}/nm, see ref. 2.—¹⁵N-**11a** (having C¹⁵NO group; *cf.* ref. 2): $\delta_C[(CD_3)_2SO]$ 33.9 (q), 34.7 (s, $^1J_{N,C}$ 81.0, $^3J_{C,H}$ 17.5), 118.3 (d, $^3J_{N,C}$ 1.7), 120.4 (s, $^2J_{N,C}$ 2.1), 126.8 (2 × d), 129.2 (2 × d), 130.7 (d), 133.8 (s, $^3J_{N,C}$ 0.8) and 150.7 (s).

11b: Yield 0.39 g (67%), mp 144–146 °C (lit.,[2] 144–146 °C) (Found: C, 66.3; H, 3.8; N, 24.2. $C_{16}H_{11}N_5O$ requires C, 66.4; H, 3.8; N, 24.2%); $v_{max}(KBr)/cm^{-1}$ 2305; $\delta_H[(CD_3)_2SO]$ 7.47 (1 H, s), 7.52–7.53 (3 H, m) and 7.70–7.77 (7 H, m); $\delta_C[(CD_3)_2SO]$ 118.1 (d), 122.0 (s), 125.4 (2 × d), 126.8 (2 × d), 129.3 (2 × d), 130.1 (2 × d), 130.8 (d), 130.9 (d), 133.0 (s), 133.7 (s) and 150.3 (s) [C of CNO group not observed (*cf.* ref. 18)].

11c: Yield 0.11 g (33%), mp 114–115 °C (Found: C, 43.8; H, 4.3; N, 43.0. $C_6H_7N_5O$ requires C, 43.6; H, 4.3; N, 42.4%); $v_{max}(KBr)/cm^{-1}$ 2290; $\delta_H[(CD_3)_2SO]$ 2.29 (3 H, d, *J* 1.6), 4.08 (3 H, s) and 7.34 (1 H, q, *J* 1.6); $\delta_C[(CD_3)_2SO]$ 22.7 (q), 33.6 (q), 118.6 (s), 120.2 (d) and 150.3 (s) [C of CNO group not observed (*cf.* ref. 18)].

12a: Yield 0.42 g (92%), mp 97–99 °C (Found: C, 58.0; H, 3.8; N, 30.9. $C_{11}H_9N_5O$ requires C, 58.15; H, 4.0; N, 30.8%); $v_{max}(KBr)/cm^{-1}$ 2305; $\delta_H(CDCl_3)$ 4.45 (3 H, s), 7.45–7.50 (3 H, m), 7.57 (1 H, s) and 7.65–7.68 (2 H, m); $\delta_C(CDCl_3)$ 39.9 (q), 119.3 (s), 123.0 (d), 126.3 (2 × d), 129.2 (2 × d), 130.2 (d), 134.4 (s) and 161.9 (s) [C of CNO group not observed (*cf.* ref. 18)]; $\lambda_{max}(TFA)/nm$ 400 (log $\varepsilon/dm^3 mol^{-1} cm^{-1}$ 3.55) and 263 (4.14).

12b: Yield 0.45 g (78%), mp 132–133 °C (Found: C, 66.4; H, 3.85; N, 24.2. $C_{16}H_{11}N_5O$ requires C, 66.4; H, 3.8; N, 24.2%); $v_{max}(KBr)/cm^{-1}$ 2297; $\delta_H(CDCl_3)$ 7.45–7.54 (4 H, m), 7.57–7.61 (2 H, m), 7.68 (1 H, s), 7.69–7.72 (2 H, m) and 8.25–8.27 (2 H, m); $\delta_C(CDCl_3)$ 119.90 (2 × d), 119.91 (s), 122.8 (d), 126.4 (2 × d), 129.2 (2 × d), 129.8 (2 × d), 130.1 (d), 130.3 (d), 134.2 (s), 136.5 (s) and 161.8 (s) [C of CNO group not observed (*cf.* ref. 18)].

12e: Yield 0.32 g (48%), mp 110–111 °C (Found: C, 65.25; H, 4.0; N, 20.8. $C_{18}H_{13}N_5O_2$ requires C, 65.25; H, 4.0; N, 21.1%); $v_{max}(KBr)/cm^{-1}$ 2284 and 1701; $\delta_H(CDCl_3)$ 2.26 (3 H, s), 7.45–7.51 (5 H, m), 7.53–7.61 (3 H, m) and 8.21–8.23 (2 H, m) [**8d**: 2.50 (integral < 5% of s at 2.26)]; $\delta_C(CDCl_3)$ 31.4 (q), 119.2 (s), 120.1 (2 × d), 128.6 (2 × d), 129.4 (2 × d), 129.9 (2 × d), 130.4 (d), 130.7 (d), 133.7 (s), 136.4 (s), 138.3 (s), 160.9 (s) and 199.6 (s) [C of CNO group not observed (*cf.* ref. 18)].

12f: Yield 0.31 g (54%), mp 112–113 °C (Found: C, 54.5; H, 3.8; N, 24.3. $C_{13}H_{11}N_5O_3$ requires C, 54.7; H, 3.9; N, 24.55%); $v_{max}(KBr)/cm^{-1}$ 2291, 2254 and 1732; $\delta_H(CDCl_3)$ 3.69 (3 H, s), 4.44 (3 H, s) and 7.44–7.49 (5 H, m) [**8e**: 3.88, 4.59 (integrals *ca.* 5% of s at 3.69 and 4.44, respectively)]; $\delta_C(CDCl_3)$ 40.0 (q), 53.1 (q), 121.2 (s), 127.8 (2 × d), 129.1 (2 × d), 130.3 (s), 130.4 (d), 134.4 (s), 160.7 (s) and 165.2 (s) [C of CNO group not observed (*cf.* ref. 18)].

Substituted dimethyl 3-[2-(1*H*-/2*H*-tetrazol-5-yl)vinyl]isoxazole-4,5-dicarboxylates 13a,f, 14a. General procedure

To a suspension of the nitrile oxide **11a** (0.11 g, 0.5 mmol) or **12a** (0.45 g, 2 mmol) in methanol (10 and 40 cm³, respectively) or of the 1*H*-pyrrolotetrazole **7e** (0.14 g, 0.5 mmol) in toluene (10 cm³) was added dimethyl acetylenedicarboxylate (DMAD; **11a**, **7e**: 0.14 g, 1 mmol; **12a**: 0.57 g, 4 mmol). The mixture was heated under reflux for 0.5 h (**11a**, **12a**) or 2 h (**7e**). Evaporation of the solvent and addition of diethyl ether caused precipitation of the product which was collected by filtration and recrystallised from methanol (**13a**), chloroform–diethyl ether (**13f**) or dichloromethane–light petroleum [**14a**; after preceding purification on silica gel using chloroform–diethyl ether–ethyl acetate (6 : 1 : 2) as eluent].

13a: Yield 0.17 g (92%), mp 161–162 °C (lit.,[2] 161–162 °C) (Found: C, 55.2; H, 4.0; N, 18.95. $C_{17}H_{15}N_5O_5$ requires C, 55.3; H, 4.1; N, 19.0%); for ν_{max}/cm^{-1}, δ_H and δ_C, see ref. 2.

13f: Yield 0.10 g (47%), mp 129–131 °C (lit.,[2] 129–131 °C) (Found: C, 53.4; H, 4.1; N, 16.4. $C_{19}H_{17}N_5O_7$ requires C, 53.4; H, 4.0; N, 16.4%); ν_{max}(KBr)/cm^{-1} 1746 and 1728; δ_H(CDCl$_3$) 3.62 (3 H, s), 3.66 (3 H, s), 3.94 (3 H, s), 4.02 (3 H, s), 7.34–7.36 (2 H, m) and 7.40–7.48 (3 H, m); δ_C(CDCl$_3$) 34.2 (q), 52.7 (q), 53.0 (q), 53.6 (q), 116.0 (s), 120.7 (s), 128.5 (2 × d), 128.8 (2 × d), 130.6 (d), 134.8 (s), 145.8 (s), 151.1 (s), 155.9 (s), 159.1 (s), 160.8 (s), 160.9 (s) and 164.0 (s).

14a: Yield 0.29 g (39%), mp 78–79 °C (Found: C, 55.2; H, 4.2; N, 18.5. $C_{17}H_{15}N_5O_5$ requires C, 55.3; H, 4.1; N, 19.0%); ν_{max}(KBr)/cm^{-1} 1753 and 1717; δ_H(CDCl$_3$) 3.59 (3 H, s), 4.00 (3 H, s), 4.19 (3 H, s) and 7.35–7.45 (6 H, m); δ_C(CDCl$_3$) 39.4 (q), 52.4 (q), 53.5 (q), 116.2 (s), 118.0 (d), 126.7 (2 × d), 128.9 (2 × d), 129.4 (d), 134.4 (s), 137.3 (s), 156.8 (s), 159.9 (s), 160.90 (s), 160.94 (s) and 162.1 (s).

Substituted dimethyl 3-[2-(1*H*-/2*H*-tetrazol-5-yl)vinyl]pyrazole-4,5-dicarboxylates 13d, 14d. General procedure

A stirred mixture of the pyrrolotetrazole **3e** or **4e** (0.30 g, 1 mmol) and DMAD (0.57 g, 4 mmol) in toluene (20 cm³) was heated under reflux for 24 h (**3e**) or kept at 80 °C for 2.5 h (**4e**) whereupon the solvent was evaporated. In the case of **13d**, the residue was chromatographed on silica gel [chloroform–ethyl acetate (4 : 1) as eluent] and the product crystallised from chloroform–diethyl ether. **14d** was isolated by dissolving the residue in a small amount of dichloromethane, followed by addition of diethyl ether, purification of the precipitate on silica gel [chloroform–ethyl acetate (5 : 3) as eluent] and recrystallisation from dichloromethane–diethyl ether.

13d: Yield 0.34 g (76%), mp 174–176 °C (lit.,[2] 174–176 °C) (Found: C, 61.9; H, 4.8; N, 18.7. $C_{23}H_{20}N_6O_4$ requires C, 62.15; H, 4.5; N, 18.9%); for ν_{max}/cm^{-1}, δ_H and δ_C, see ref. 2 (solvent quoted with δ_H to be corrected into CDCl$_3$).

14d: Yield 0.33 g (74%), mp 98–101 °C (Found: C, 62.1; H, 4.6; N, 18.8. $C_{23}H_{20}N_6O_4$ requires C, 62.15; H, 4.5; N, 18.9%); ν_{max}(KBr)/cm^{-1} 1742 and 1720; δ_H(CDCl$_3$) 3.55 (3 H, s), 3.89 (3 H, s), 4.19 (3 H, s), 7.33–7.38 (4 H, m), 7.39–7.47 (3 H, m) and 7.50–7.55 (4 H, m); δ_C(CDCl$_3$) 39.2 (q), 51.6 (q), 53.4 (q), 114.9 (s), 116.6 (d), 124.1 (2 × d), 126.9 (2 × d), 128.5 (2 × d), 128.7 (d), 129.0 (d), 129.3 (2 × d), 137.8 (s), 139.0 (s), 139.10 (s), 139.12 (s), 150.5 (s), 161.3 (s), 162.0 (s) and 163.0 (s).

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