Azapropellanes: New Fused Tetra-azatriazolo[n.3.3.0^{1,x}]-dodecenes and tridecenes. Substituted 3,3a,4,5,6,6a-Hexahydropyrrolo[2,3-d]-1,2,3-triazoles from a General Tandem Cycloaddition–Rearrangement Reaction of 1,2,3-Triazolium Imides with Substituted Alkenes: Kinetics and Mechanism: Azolium 1,3-Dipoles. Part 3.†

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Reactions of substituted 1,2,3-triazolium-1-imide 1,3-dipoles with a range of substituted alkene and alkyne dipolarophiles gave rise to derivatives of the new ring systems hexahydropyrrolo[2,3-d]-1,2,3-triazoles and the azapropellanes tetra-aza-tricyclo[5.3.3.0^{1,7}]tridecenes and -tricyclo[4.3.3.0^{1,6}]-dodecenes. The reactions, which are regio- and stereo-specific, are shown to be tandem 1,3-dipolar (*endo*) cycloadditions and sigmatropic rearrangements. X-Ray crystal structures of 6*exo*-ethoxycarbonyl-2,3a,4,6a-tetraphenyl-3,3a,4,5,6,6a-hexahydropyrrolo[2,3-d]-1,2,3-triazol-2-ium-3-ide (**9a**) and 12*exo*-cyano-8,10-diphenyl-7,8,9,10-tetra-azatricyclo[4.3.3.0^{1,6}]dodec-7-en-8-ium-9-ide (**4a**; m = 2) are reported.

Substituted (*Z*)-bis(areneazo)ethylenes (**1A**) exist in equilibrium with a cyclic 1,2,3-triazolium-1-imide form (**2**).[1] This latter form is a reactive 1,3-dipole which dominates the reactivity of these systems.[2–5] Cycloaddition reactions of these 1,3-dipoles with alkene dipolarophiles gave derivatives of a new pyrrolo[2,3-*d*]-1,2,3-triazole ring system[6] in a general reaction which is established herein[6] as involving a tandem 1,3-dipolar cycloaddition and sigmatropic rearrangement. When 1,2-bis(areneazo)cycloalkenes (**1B**) were used in these reactions interesting new tricyclic azapropellanes were obtained from the same reaction sequence.

Results and Discussion

(i) *Cycloaddition Products: New Ring Systems.*—When compounds (**1B**; m = 2,3) were treated with acrylonitrile or ethyl acrylate in acetone the products (**4**; m = 2,3) and (**5**; m = 2,3) were obtained in high yield (Table 1). These products arose from the triazolium 1,3-dipole form (**3**) and when this azolium dipole could not be formed because of structural strain preventing cyclisation in (**1B**) [*i.e.*, for m = 1 or 0][1] no reaction occurred and no trace of products such as (**4**) or (**5**) was detected. The products (**4**) and (**5**) are new azapropellanes, the first examples of tetra-azatricyclo-[4.3.3.0^{1,6}]dodecenes (m = 2) and -[5.3.3.0^{1,7}]tridecenes (m = 3). They are obviously the end products of a multi-step reaction. Key signals in the carbon NMR spectra which readily indicate their formation are those of the quaternary bridgehead carbons at δ_C 80–110. Figures 1 and 2 show the X-ray crystal structures of compounds (**4a**; m = 2) and (**9a**). Their formation is regiospecific and the substituent Z is in the *exo*-position. The products (**6**) and (**7**) were formed when dimethyl acetylenedicarboxylate (DMAD) and *N*-phenylmaleimide were used as dipolarophile, respectively (Scheme 1). The basic structural unit of compounds (**4**)–(**7**) is a new, reduced, fused aziminoazapentalene[7] ring system, a substituted 3,3a,4,5,6,6a-hexahydropyrrolo[2,3-*d*]-1,2,3-triazole.

All of the derivatives show the characteristic bridgehead carbon signals (Scheme 1). When the substrate was a 1,2-bis(arylazo)stilbene (**1A**) the products (**8**)–(**12**) were formed *via* the dipole form (**2**). These products contain the basic pyrrolo[2,3-*d*]-1,2,3-triazole structure but without the continuous tricyclic link between the bridgeheads. Some of these latter products were described previously[5] but with the wrong structure since the complexity of the tandem reaction was not then understood (*cf.* ref. 6).

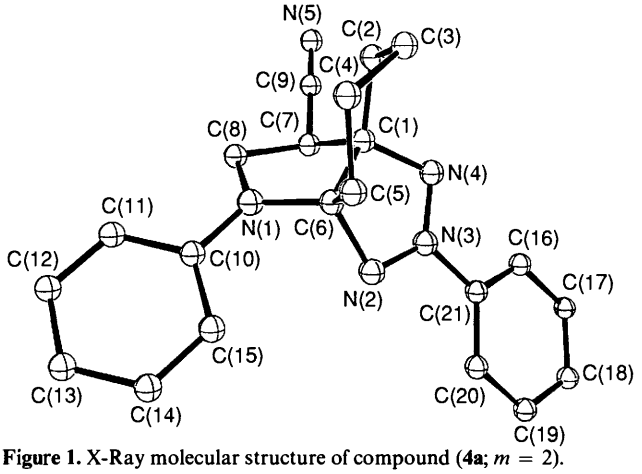


Figure 1. X-Ray molecular structure of compound (**4a**; m = 2).

(ii) *Stereospecificity.*—Dimethyl maleate and dimethyl fumarate were used as probes of the stereospecificity of the reaction. The dipoles (**2a**) (Scheme 2) and (**3c**) (Scheme 3) were heated with these dipolarophiles in acetone and the products were worked up carefully. Repeated runs gave isolated yields of the products (**13**)–(**16**) (Schemes 2 and 3) (Table 1) in the range 81–96% and the remaining residues were recovered and analysed by high-field NMR spectroscopy. The reactions were stereospecific (>99%) and no traces of mixtures were found.

† Part 2 is ref. 2.

Table 1. New fused-ring products.

No.	Dipole (4π)	Dipolarophile[a] (2π)	Product Compound	M.p. (°C)	Yield (%)	Microanalysis Found% (Required %) C	H	N
1	(**3a**; *m* = 2)	AN	(**4a**; *m* = 2)	175[d,e]	90	73.6(73.5)	6.1(6.1)	20.4(20.4)
2	(**3a**; *m* = 2)	PMI	(**7a**; *m* = 2)	226[d]	78	72.3(72.5)	5.6(5.4)	15.0(15.1)
3	(**3b**; *m* = 2)	AN	(**4b**; *m* = 2)	171[f]	84	50.2(50.3)	4.0(3.8)	14.1(14.0)
4	(**3c**; *m* = 2)	AN	(**4c**; *m* = 2)	239[f]	86	58.3(58.2)	4.6(4.4)	22.4(22.6)
5	(**3c**; *m* = 2)	EA	(**5c**; *m* = 2)	208[d]	84	57.7(57.6)	5.1(5.0)	17.2(17.5)
6	(**3c**; *m* = 2)	PMI	(**7c**; *m* = 2)	259[d]	83	61.0(60.7)	3.9(4.2)	17.6(17.7)
7	(**3b**; *m* = 2)	DMAD	(**6b**; *m* = 2)	180[d]	73	48.4(48.8)	3.8(3.8)	9.3(9.5)
8	(**3c**; *m* = 2)	DMAD	(**6c**; *m* = 2)	207[d]	86	55.4(55.2)	4.2(4.3)	15.8(16.1)
9	(**3c**; *m* = 3)	AN	(**4c**; *m* = 3)	250[g]	75	59.5(59.1)	5.0(4.7)	21.9(21.9)
10	(**3c**; *m* = 3)	EA	(**5c**; *m* = 3)	218[d]	68	58.1(58.3)	5.5(5.3)	17.0(17.0)
11	(**3c**; *m* = 3)	PMI	(**8c**; *m* = 3)	307[h]	34	61.8(61.4)	4.4(4.4)	17.2(17.3)
12	(**3a**; *m* = 3)	DMAD	(**6a**; *m* = 3)	178[i]	85	56.0(56.0)	4.7(4.5)	15.5(15.7)
13	(**2a**)	AN	(**8a**)	269[d]	90	78.6(78.9)	5.5(5.2)	16.0(15.9)
14	(**2a**)	DMAD	(**12a**)	187[d]	85	72.6(72.5)	4.9(4.9)	10.3(10.6)
15	(**2a**)	EA	(**9a**)	210[d]	87	76.3(76.2)	5.6(5.7)	11.6(11.5)
16	(**2a**)	MA	(**10a**)	224[d]	80	74.0(74.1)	4.3(4.5)	11.7(11.5)
17	(**2a**)	PMI	(**11a**)	228[j]	88	77.1(77.0)	4.9(4.8)	12.3(12.5)
18	(**2b**)	AN	(**8b**)	234[d]	84	58.3(58.1)	3.8(3.5)	11.8(11.7)
19	(**3c**)	EA	(**9c**)	229[d]	81	64.1(64.3)	4.5(4.5)	14.2(14.5)
20	(**2a**)	*Z*-DMM[b]	(**13**)	200[d]	81	72.0(72.1)	5.5(5.3)	10.2(10.5)
21	(**2a**)	*E*-DMF[c]	(**14**)	205[d]	96	72.2(72.1)	5.5(5.3)	10.4(10.5)
22	(**3c**; *m* = 2)	*Z*-DMM	(**15**)	210[d]	81	55.1(55.0)	4.7(4.6)	15.8(16.0)
23	(**3c**; *m* = 2)	*E*-DMF	(**16**)	215[d]	91	54.9(55.0)	4.7(4.6)	15.7(16.0)

[a] See Scheme 1. [b] Dimethyl maleate. [c] Dimethyl fumarate. [d] Recrystallised from ethanol. [e] From acetone. [f] From benzene–acetone (1:1, v/v). [g] From ethyl acetate. [h] From benzene. [i] From aq. ethanol. [j] From 1:1 (v/v) benzene–light petroleum (b.p. 60–80 °C).

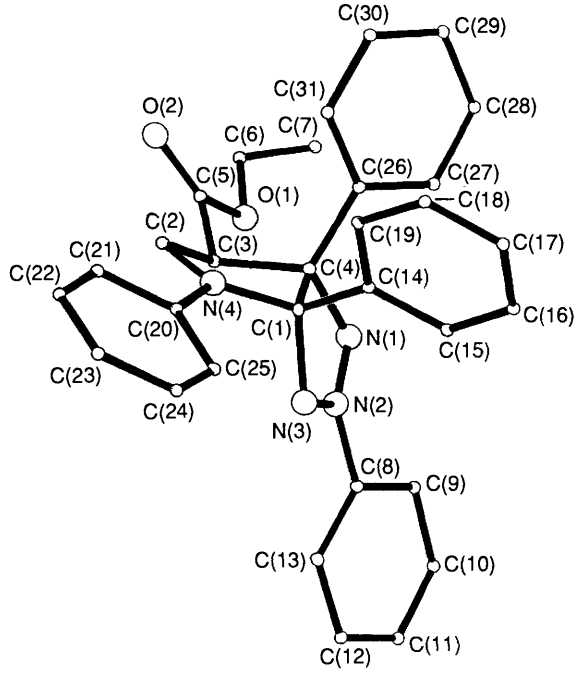
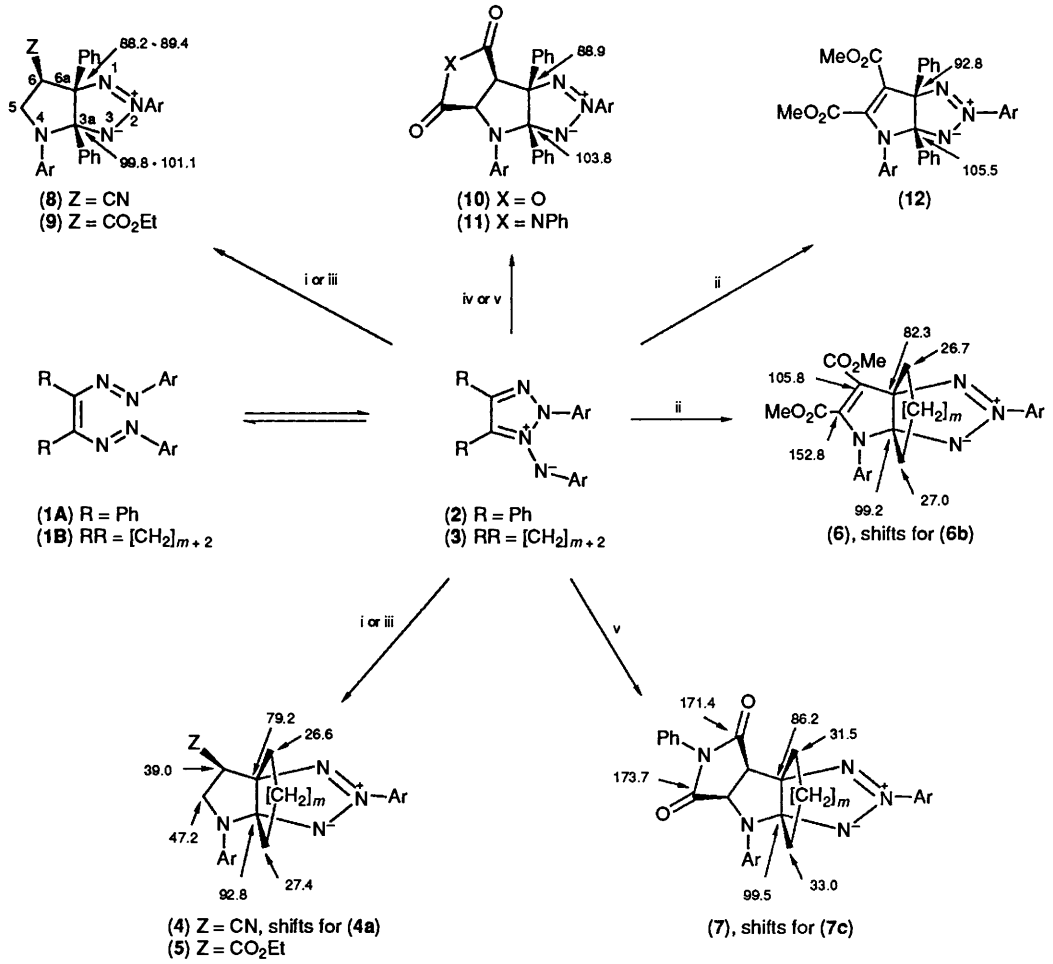


Figure 2. X-Ray molecular structure of compound (**9a**).

These would have been easy to identify because of the availability of clear-cut NMR signals. The product pairs (**13**),(**14**) and (**15**),(**16**) were readily identified as *cis*- and *trans*-isomers from the dihedral coupling constant $J(H_A–H_B)$ (Schemes 2 and 3). Further, the molecules (**13**) and (**15**) provided models for the *endo*-H_A and -H_B in these systems and therefore allowed a full identification of compounds (**14**) and (**16**) from the other possible *trans*-isomeric structures with H_A *exo* and H_B *endo*.

The reaction can be looked upon as a tandem, concerted 1,3-dipolar cycloaddition and 1,4-N→C sigmatropic rearrangement (Scheme 4). However, it could also be a multistep Michael reaction involving initial nucleophilic addition of the exocyclic $-N^-$–terminal of the dipole (which is nucleophilic[2]) to the alkene giving a new N–C single bond followed by subsequent ring closure and cleavage of the N–N bond to give a second intermediate. Perusal of such a mechanism shows that it *necessitates* a loss of stereochemistry due to rotations on the single bonds in a number of intermediates which, because of the substituents, should be sufficiently long-lived for a bond rotation. The stereospecificity[8] of the reaction therefore favours a tandem, concerted 1,3-dipolar cycloaddition–sigmatropic rearrangement reaction (Scheme 4). The *exo*-arrangement of substituents in the products (**4**)–(**11**) requires an initial *endo*-cycloaddition. Dreiding models show that a subsequent N→C sigmatropic rearrangement will result in a final *exo*-orientation for the substituents.

(iii) *Kinetics and Mechanism.*—The kinetics of the reaction for the dipole (**2a**) with acrylonitrile and (*E*)-cinnamaldehyde were measured by following the disappearance of the dipole at a suitable UV wavelength. The synthetic reaction with(*E*)-cinnamaldehyde (reported in the following paper) followed the same pattern but occurred on the C=O bond in a rare case. If any of these reactions was likely to be a nucleophilic addition this case with a carbonyl group was considered to be the most likely. The rates were measured under pseudo-first-order conditions with a large excess of alkene and second-order rate constants were also determined (Table 2). The reactions were second order overall and first order in each reagent. Arrhenius measurements gave high negative entropies for both reactions (Table 2), consistent with a cycloaddition transition state. More



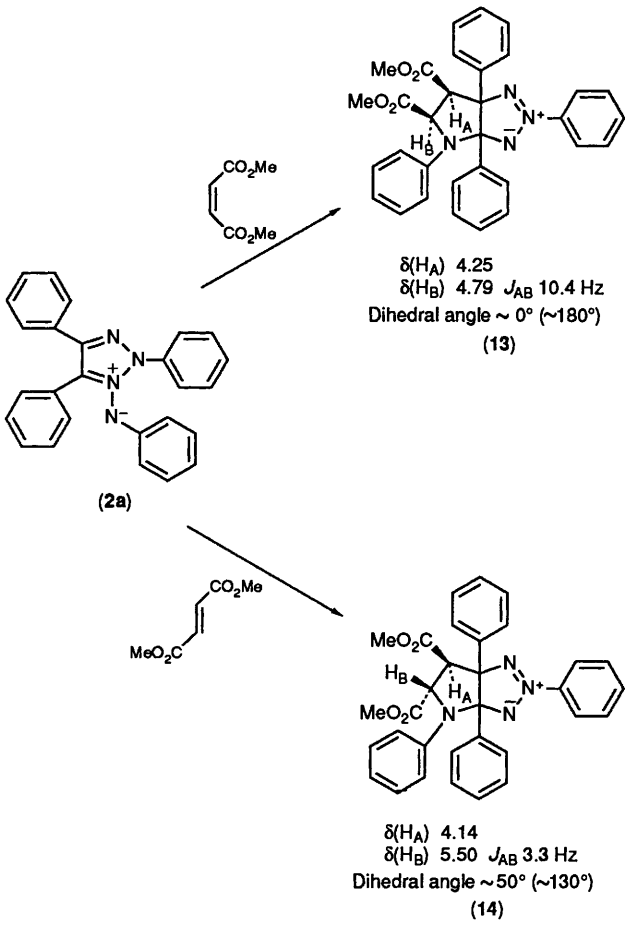
Scheme 1. *Reagents:* i, acrylonitrile (AN); ii, DMAD; iii, EA; iv, maleic anhydride (MA); v, *N*-phenylmaleimide PMI. Ar: (**a**) Ph; (**b**) *p*-C_6H_4Br; (**c**) *p*-$C_6H_4NO_2$; (**d**) *p*-C_6H_4Me. ^{13}C NMR shifts ($CDCl_3$) are shown.

significantly the reactions were quite insensitive to solvent polarity and showed a slight decrease in rate for increasing solvent polarity from benzene to ethyl acetate and aliphatic ketones (Table 3). This insensitivity to solvent was similar for the reactions with acrylonitrile and (*E*)-cinnamaldehyde as dipolarophiles. Hence both reactions are likely to have similar rate-determining steps which we suggest are non-synchronous,[9] pericyclic, 6π-cycloadditions. Somewhat increased rates were observed when chloroform was used as solvent. Increased rates in chlorinated solvents have also been observed with some other cycloadditions, for example that between anthracene and tetracyanoethylene.[10] These kinetic results, combined with the stereospecificity of the reaction, strongly support the tandem 1,3-dipolar cycloaddition–rearrangement mechanism in Scheme 4.

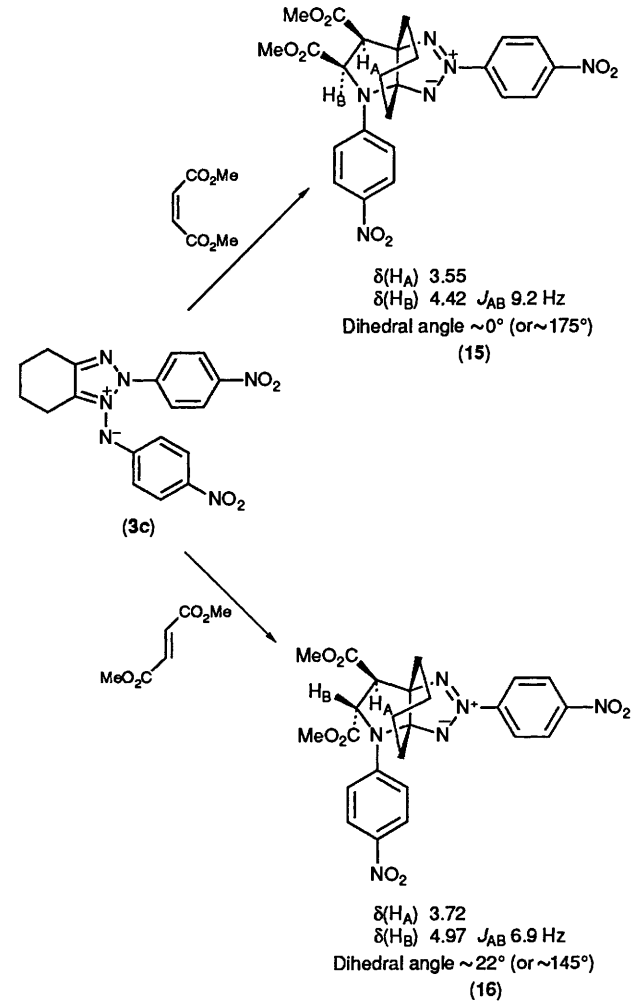
Some preliminary substituent effects were measured for *para*-substituents (Me, Br, NO_2) in the *N*-Ar ring of the dipole (**2**) with acrylonitrile as dipolarophile (Table 3). The data were limited due to difficulties with *p*-MeO derivatives which could not be measured. The four points involved (using σ_p^- for NO_2) would give a crude Hammett ρ-value of -1.4 (r 0.982). Of significance is the reduction in rate by electron-withdrawing groups which is expected for normal electron-demand dipole-HOMO-controlled reactions.[11] The dipole (**2**) contains an electron-rich azomethine imide structure and would be expected to give dipole-HOMO-controlled reactions.[12] For such a transition state the *endo*-orientation of substituents containing π-bonds could readily arise due to favourable secondary orbital interactions or due to a favourable opposed alignment of dipoles. Hence we suggest a rate-determining *endo*-transition state as is shown in Figure 3, followed by a rapid sigmatropic rearrangment in the tandem reaction.

Experimental

M.p.s were measured on an Electrothermal apparatus and are uncorrected. IR spectra were measured with a Perkin-Elmer 983G spectrophotometer. NMR spectra were measured on JEOL JNM-GK-270 and MH-100 instruments with tetramethylsilane as internal reference and deuteriochloroform or hexadeuteriodimethyl sulphoxide as solvent. UV–visible absorption spectra were measured with a Shimadzu UV-260 Spectrophotometer. The substrates (**2**) and (**3**) were prepared by oxidation of the bishydrazones of the corresponding 1,2-diketones. The bishydrazones were prepared as previously described.[1,2,13] Those from cycloalkane-1,2-diones were oxidised at ambient temperature with (i) nickel peroxide in dry benzene and/or (ii) lead dioxide in dichloromethane. Insoluble salts were removed, the solutions were evaporated, and the residual products (**3**) were recrystallised. Details have been reported [1,2] for all of the substrates (**3**). The bis-arylhydrazones of benzil were oxidised by either of these procedures and also by lead tetra-acetate in acetic acid to give the 1,2-bis(arylazo)-stilbenes (**1A**)/(**2**), some of which are already known.[3,4]



Scheme 2.



Scheme 3.

I. *Azapropellanes.*—The following are typical examples.

(*a*) (No. 10, Table 1). A mixture of 1,2-bis-(*p*-nitrophenylazo)cycloheptene (**1Bc**)/(**3c**) (*m* = 3) (260 mg, 0.7 mmol) and excess of ethyl acrylate (EA) (5 cm^3, 46 mmol) was stirred and heated under reflux for 1.5 h; there was a colour change from red to yellow. Removal of excess of EA under reduced pressure, and recrystallisation of the residue from ethanol, gave 13 exo-*ethoxycarbonyl*-11-*bis*(p-*nitrophenyl*)-8,9,10,11-*tetra-azatri-cyclo*[5.3.3.$0^{1,7}$]*tridec*-8-*en*-9-*ium*-10-*ide* (**5c**; *m* = 3) (68%), m.p. 218 °C (from EtOH); ν_{max}(KBr) 1 720 cm^{-1} (C=O); δ_H($CDCl_3$) 0.93–2.92 (13 H, m, Me and $[CH_2]_5$), 3.45–3.70 (3 H, pyrrolidino CH_2CH), 4.31 (q, CO_2CH_2Me), 7.16 (2 H, d, J_{AB} 9.4 Hz) and 8.14 (2 H, d) (AA'BB' of 11-$C_6H_4NO_2$-*p*), and 8.35 (2 H, d) and 8.42 (2 H, d, J_{AB} 9.4 Hz) (AA'BB' of 9-$C_6H_4NO_2$-*p*); δ_C($CDCl_3$) 14.33, 24.42, 24.45, 30.19, 31.71, 46.91, 54.56, 61.51 (86.32 and 98.10, bridgeheads), 114.95, 124.00, 124.34, 125.48, 138.89, 144.00, 149.39, 149.74, and 171.06.

(*b*) (No. 1, Table 1). Acrylonitrile (1.0 cm^3) was added to a solution of 1,2-bis(phenylazo)cyclohexene (**1Ba**)/(**3a**) (*m* = 2) (0.5 g) in dry acetone (10 cm^3) and the solution was stirred under reflux for 1 h; the solution changed colour from brown to yellow. Cooling of the solution in ice gave crystals of 12 exo-*cyano*-8,10-*diphenyl*-7,8,9,10-*tetra-azatricyclo*[4.3.3.$0^{1,6}$]*dodec*-7-*en*-8-*ium*-9-*ide* (**4a**; *m* = 2) (90%), m.p. 175 °C (from acetone); ν_{max}(KBr) 2 244 cm^{-1} (C≡N); δ_H($CDCl_3$) 1.39–2.20 (8 H, m, $[CH_2]_4$), 3.35–3.55 (3 H, m, CH_2CH of tetrahydropyrrole), 6.88–7.45 (8 H, m, 8- and 10-phenyl), and 8.11 (2 H, m, H_{ortho} of 8-Ph); δ_C($CDCl_3$) 17.98, 18.38, 26.62, 27.39, 38.94, 47.75 (78.87 and 92.7, bridgeheads), 117.10, 118.02, 119.90, 122.57, 128.90, 128.96, 131.63, 140.57, and 144.25.

(*c*) (No. 7, Table 1). A solution of 1,2-bis-(*p*-bromophenylazo)cyclohexene (**1Bb**)/(**3b**) (*m* = 2) (0.5 g, (1.1 mmol) in benzene–acetone (2:1) v/v) (15 cm^3) was treated with excess of DMAD (2.0 cm^3, 16 mmol) and stirred under reflux for 5 min; the mixture changed colour from brown to yellow. The solvent was evaporated off under reduced pressure and recrystallisation of the residue from diethyl ether gave 8,10-*bis*(p-*bromophenyl*)-11,12-*bis*(*methoxycarbonyl*)-7,8,9,10-*tetra-azatricyclo*-[4.3.3.$0^{1,6}$]*dodec*-7,11-*dien*-8-*ium*-9-*ide* (**6b**; *m* = 2) (73%), m.p. 180 °C (from EtOH); ν_{max}(KBr) 1 695 and 1 741 cm^{-1} (C=O); δ_H($CDCl_3$) 1.2–2.6 (8 H, m, $[CH_2]_4$), 3.74 (3 H, s) and 3.75 (3 H, s, 2 × MeO), 7.26 (2 H, d) and 7.46 (2 H, d, J_{AB} 8.9 Hz) (AA'BB' of 10-C_6H_4Br-*p*), and 7.60 (2 H, d) and 8.06 (2 H, d, J_{AB} 8.9 Hz) (AA'BB' of 8-C_6H_4Br-*p*); δ_C($CDCl_3$) 16.76, 16.84, 26.73, 27.02, 31.34, 53.09 (82.30 and 99.20 bridgeheads, see Scheme 1), 105.77, 120.62, 124.42, 125.94, 127.17, 131.95, 132.33, 136.76, 139.50, 152.78, 163.31, and 164.54.

(*d*) (No. 22, Table 1). A solution of 1,2-bis(*p*-nitrophenylazo)cyclohexene (**1Bc**)/(**3c**) (*m* = 2) (380 mg) in dry acetone (2.0 cm^3) was treated with (*Z*)-dimethyl maleate (1.0 cm^3) and the mixture was stirred under reflux for 2.5 h. The solvent was allowed to evaporate off and the residual oil was stirred at 80 °C for 1 h, cooled, and crystallised from ethanol to give 11 exo, 12 exo-*bis*(*methoxycarbonyl*)-8,10-*bis*(p-*nitrophenyl*)-7,8,9,10-*tetra-azatricyclo*[4.3.3.$0^{1,6}$]*dodec*-7-*en*-8-*ium*-9-*ide* (**15**) (81%),

Table 2. Arrhenius data and thermodynamics of activation.

T(K)	$10\,k_2$ (dm^3 mol^{-1} s^{-1})	ΔE^{act} (kJ mol^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (JK mol^{-1})	$\Delta G^{\ddagger}$ (kJ mol^{-1})
Part I: Substrates (**2a**) and acrylonitrile; solvent acetone; λ 450 nm					
(i) Second order					
298	1.28	63.5[a]	70.0	−59.4	78.1
303	1.72	63.5	60.95	−58.6	78.7
308	3.28	63.5	60.9	−56.7	78.4
313	4.18	63.5	60.9	−58.1	79.1
(ii) First order $10^4\,k_1$ (s^{-1})					
298	2.93	57.15[b]	54.7	−129.1	93.15
303	3.92	57.15	54.6	−130.0	94.0
308	4.93	57.15	54.6	−131.3	95.0
313	9.53	57.15	54.55	−128.9	94.9
Part II: Substrates (**2a**) and (*E*)-cinnamaldehyde; solvent ethyl methyl ketone; λ 450 nm					
(i) Second order $10^3\,k_2$ (dm^3 mol^{-1} s^{-1})					
298	1.12	64.2[c]	61.7	−94.3	89.8
303	2.21	64.2	61.7	−92.3	89.7
308	2.63	64.2	61.7	−94.4	90.7
319	4.32	64.2	61.6	−93.8	91.0
(ii) First order $10^4\,k_1$ (s^{-1})					
298	4.16	46.9[d]	45.4	−157.4	92.3
303	5.78	46.9	45.3	−157.45	93.0
308	7.50	46.9	45.3	−157.9	94.0
313	11.10	46.9	45.3	−157.3	93.5

[a] r 0.982. [b] r 0.969. [c] r 0.975. [d] r 0.997.

Table 3. Kinetic data: solvent effects (298 K) and substituent effects (313 K).

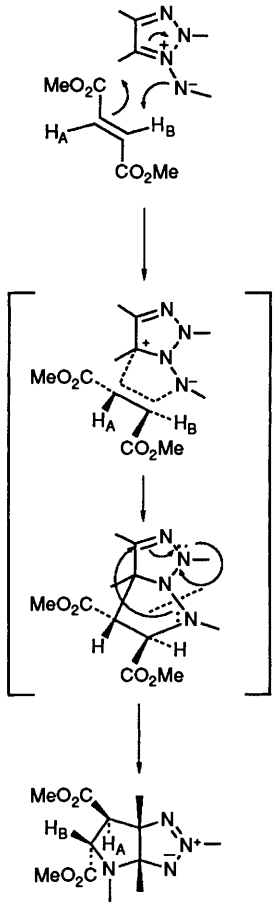
Dipole	Solvent	ε[d]	E_T	T(K)	Dipolarophile: (*E*)-Cinnamaldehyde[a] $10^4\,k$ (s^{-1})	Dipolarophile: Acrylonitrile $10^4\,k$ (s^{-1})
(**2a**)[a]	C_6H_6	2.2	34.5	298	6.60	2.44
(**2a**)	EtOAc	6.0	38.1	298	1.51	1.51
(**2a**)	MeCOEt	18.5	41.3	298	4.16	
(**2a**)	MeCOMe	20.7	42.2	298		2.93
(**2a**)	$CHCl_3$	4.8	39.1	298	25.0	4.13
(**2a**)	C_6H_6	2.2	34.5	313		6.84
(**2b**)[b]	C_6H_6	2.2	34.5	313		2.17
(**2c**)[c]	C_6H_6	2.2	34.5	313		0.049
(**2d**)[a]	C_6H_6	2.2	34.5	313		3.35

[a] 450 nm. [b] 410 nm. [c] 500 nm. [d] Dielectric constant.

m.p. 210 °C (from EtOH); ν_{max}(mull) 1 747 and 1 735 cm^{-1} (C=O); δ_H($CDCl_3$) 1.2–2.3 (8 H, m, $[CH_2]_4$), 3.56 and 4.42 (2 d, 1 H, each, J 9.2 Hz, pyrrolidino CHCHN *cis*), 3.84 (3 H, s, MeO), 3.87 (3 H, s, MeO), 7.13 and 8.13 (4 H, 2 d, AA'BB', J_{AB} 9.2 Hz, 10-$C_6H_4NO_2$-*p*), and 8.31–8.41 (4 H, overlapping dd, 8-$C_6H_4NO_2$-*p*); δ_C($CDCl_3$) 16.9, 17.4, 24.6, 27.9, 52.9, 57.7, 59.4 (81.1 and 95.3, bridgeheads), 114.4, 124.1, 124.4, 125.6, 139.5, 144.25, 148.8, 149.6, 168.8, and 172.1. Careful work-up of filtrates show further small quantities of compound (**15**) not included in the quoted yield. No isomers were detected.

II. *Substituted Pyrrolo*[2,3-d]-1,2,3-*triazoles.*—(*a*) (No.18, Table 1). A solution of 1,2-bis(*p*-bromophenylazo)stilbene (**1Ab**)/(**2b**) (546 mg) in dry acetone (10 cm^3) was treated with acrylonitrile (1.0 cm^3) and the mixture was stirred under reflux for 1 h and then evaporated under reduced pressure. Recrystallisation of the residue from ethanol gave 2,4-*bis*(p-*bromophenyl*)-6 exo-*cyano*-3a,6a-*diphenyl*-3,3a,4,5,6,6a-*hexahydropyrrolo*[2,3-d]-1,2,3-*triazol*-2-*ium*-3-*ide* (**8b**) (84%), m.p. 234 °C (from EtOH); ν_{max}(mull) 2 248 cm^{-1} (C≡N); δ_H($CDCl_3$) 3.90–4.30 (3 H, m, CH_2CHCN), 6.75–7.25 (12 H, m, ArH), 7.65 (4 H, m, ArH), and 8.18 (2 H, d, H_{ortho} of 2-C_6H_4Br-*p*); δ_C($CDCl_3$) 41.5, 51.5 (88.4) and 99.9, bridgeheads), 111.8, 118.25, 118.3, 124.4, 126.8, 127.5, 127.7, 127.8, 128.2, 128.3, 131.55, 132.4, 136.1, 139.0, and 143.0.

(*b*) (No. 19, Table 1). Ethyl acrylate (1.0 cm^3) was added to a solution of 1,2-bis(*p*-nitrophenylazo)stilbene (**1Ac**)/(**2c**) (478 mg) in dry ethylmethyl ketone and the mixture was heated under reflux for 2 h, then evaporated under reduced pressure, and the orange oily residue was crystallised from ethanol to give orange crystals of 6 exo-*ethoxycarbonyl*-2,4-*bis*(p-*nitrophenyl*)-3a,6a-*diphenyl*-3,3a,4,5,6,6a-*hexahydropyrrolo*[2,3-d]-1,2,3-*triazol*-2-*ium*-3-*ide* (**9c**) (81%), m.p. 229 °C (from EtOH); ν_{max}(mull) 1 727 cm^{-1} (C=O); δ_H($CDCl_3$) 0.79 (3 H, s, Me), 3.7–



Scheme 4.

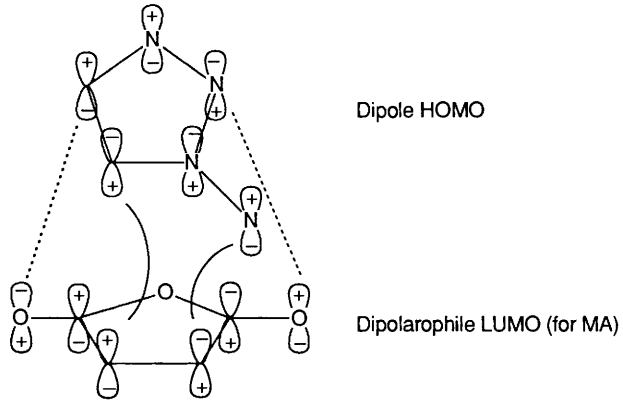


Figure 3. Favoured *endo*-transition state. Primary orbital interactions, heavy line; secondary orbital interactions, dashed line.

4.45 (5 H, m, $CH_2CHCO_2CH_2Me$), 6.9–7.6 (16 H, m, ArH), 8.09 (2 H, d, 4-$C_6H_4NO_2$-*p*), and 8.4 and 8.67 (4 H, dd, AA'BB', 2-$C_6H_4NO_2$-*p*); δ_C ($CDCl_3$) 13.8, 50.5, 58.2, 61.0 (89.6 and 102.0, bridgeheads), 115.1, 124.2, 124.6, 125.3, 126.8, 127.3, 127.5, 128.2, 128.2, 129.2, 129.4, 135.8, 140.3, 148.3, 152.5, and 174.5.

(*c*) (No. 21, Table 1). A mixture of 1,2-bis(phenylazo)stilbene (**1Aa**)/(**2a**) (777 mg), (*E*)-dimethyl fumarate (288 mg), and dry acetone (4.0 cm^3) was stirred under reflux for 2 h. The solvent was allowed to evaporate off and the remaining oil was stirred at 110 °C for 8 h, cooled, and crystallised from ethanol to give 5 endo, 6 exo-*bis*(*methoxycarbonyl*)-2,3a,4,6a-*tetraphenyl*-3,3a,-4,5,6,6a-*hexahydropyrrolo*[2,3-d]-1,2,3-*triazol*-2-*ium*-3-*ide* (**14**) (96%), m.p. 205 °C (from EtOH); ν_{max}(mull) 1 734 cm^{-1} (C=O);

Table 4. Crystal data for compound (**4a**; m = 2).

Formula	$C_{21}H_{21}N_5$
M (daltons)	343.43
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	9.328(2)
b (Å)	10.925(3)
c (Å)	11.462(3)
α (°)	64.84(3)
β (°)	86.57(3)
γ (°)	115.37(3)
V (Å^3)	912.60
Z	2
D_c (g cm^{-3})	1.25
μ (cm^{-1})	0.43
F(000)	364
Radiation	Mo-K_α
Graphite monochromator	λ 0.710 69 Å
Diffractometer	Hilger Y290
Orienting reflections;	
Range	12; 13 < θ < 20°
Temperature (°C)	22
Scan method	ω–2θ
Data collection range	2 < 2θ < 44°
No. unique data	2 099
Total $I > 5\sigma(I)$	1 519
No. of parameters fitted	235
R_a	4.08%
R_w[b]	6.67%
Largest shift/esd, final cycle	<0.001
Largest positive peak (e Å^{-3})	0.06
Largest negative peak (e Å^{-3})	−0.10

[a] $R = [\Sigma||F_o| - |F_c||]/\Sigma|F_o|$. [b] $R_w = \{[\Sigma w(F_o - F_c)^2]/[\Sigma_w(|F_o|)^2]\}^{\frac{1}{2}}$; $w = 1/[(\sigma F_o)^2 - 0.000\,82 \cdot F_o^2]$. The transformation (1,0,0/1,1,0/−1,−1,1) gives the Niggli cell a 9.328, b 10.911, c 11.452, α 61.61°, β 69.76°, γ 64.79°.

δ_H($CDCl_3$) 3.37 (3 H, s, CO_2Me), 3.39 (3 H, s, CO_2Me), 4.14 (1 H, d, J_{AB} 3.3 Hz, pyrrolidino CH_ACH_BN, *trans*), 5.50 (1 H, d, pyrrolidino CH_ACH_BN, *trans*), 6.87–7.2 (14 H, m, ArH), 7.5–7.58 (4 H, m, ArH), 8.3 (2 H, m, H_{ortho} of 2-Ph), δ_C($CDCl_3$) 52.2, 52.6, 59.7, 63.9 (88.6 and 101.4, bridgeheads), 117.3, 119.0, 123.2, 127.16, 127.3, 127.7, 127.74, 128.5, 128.7, 129.0, 131.7, 136.6, 136.64, 143.5, 171.25, and 172.4. Careful analysis of the ethanol filtrate showed that no other isomers were present. Full ^1H and ^{13}C NMR assignments of many of the compounds in Table 1 are provided as Supplementary Publication. SUP 56795 (4 pp.).* Assignments were confirmed by decoupling experiments.

III. *Kinetics.*—Rates were measured by following the disappearance of the dipole (bis-arylazoalkene) at a chosen wavelength (Tables 2 and 3) using a Pye-Unicam SP1800 double-beam spectrophotometer with water-circulating thermostatted cell compartments. Temperatures were accurate to ±0.5 °C. The dipolarophiles were present in 2 000 molar excess for the pseudo-first-order measurements and in the range 1 200–200 molar excess for measurements of the second-order rate constants. In a typical run a UV cell containing a fresh stock solution (2.5×10^{-4}M); 3.0 cm^3) of dipole (**2**) was pre-equilibrated with the dipolarophile and the falling absorbance, (A_t), was recorded. A plot of $\ln(A_t - A_\infty)$ *versus* t gave a straight line with slope k_1, the first-order rate constant. For varying (excess) concentrations of the dipolarophile a plot of log k_1 *versus* the dipolarophile concentration gave a straight line with slope k_2, the second-order rate constant.

* For details of the supplementary publications scheme, see section 4.0 of the Instructions for Authors, in the January issue.

Table 5. Crystal data for compound (**9a**).

Formula	$C_{31}H_{27}N_4O_2$
M (daltons)	487.58
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	10.507(3)
b (Å)	13.529(4)
c (Å)	11.297(3)
α (°)	124.5(3)
β (°)	92.1(3)
γ (°)	79.28(3)
V (Å^3)	1 295.64
Z	2
D_c (g cm^{-3})	1.25
μ (cm^{-1})	0.45
$F(000)$	514
Radiation	Mo-K_α
Graphite monochromator	λ 0.710 69 Å
Diffractometer	Hilger Y290
Orienting reflections;	
Range	12; 13 < θ < 20°
Temperature (°C)	22
Scan method	ω–2θ
Data collection range	< 2θ < 48°
No. unique data	2 704
Total $I > 3\sigma(I)$	2 166
No. of parameters fitted	334
R_a	7.46%
R_w [b]	9.62%
Largest shift/esd, final cycle	<0.01
Largest positive peak (e Å^{-3})	0.20
Largest negative peak (e Å^{-3})	−0.11

[a] $R = [\Sigma||F_o| - |F_c||]/\Sigma|F_o|$. [b] $R_w = \{[\Sigma w(F_o - F_c)^2]/[\Sigma_w(|F_o|)^2]\}^{\frac{1}{2}}$; $w = 1/[(\sigma F_o)^2 - 0.0010 \cdot F_o^2]$. The transformation $(-1) \times (1,0,0/0,0,1/0,1,1,)$ gives the Niggli cell a 10.507, b 11.297, c 11.727, α 108.05°, β 100.33°, γ 92.10°.

Table 6. Fractional atomic co-ordinates for compound (**4a**; $m = 2$).

Atom	x	y	z
N(1)	0.643 6(3)	0.493 5(3)	0.147 9(2)
N(2)	0.378 7(3)	0.247 0(3)	0.270 3(2)
N(3)	0.354 8(3)	0.121 1(3)	0.268 6(2)
N(4)	0.477 4(3)	0.099 4(3)	0.241 3(3)
N(5)	0.870 2(5)	0.337 0(4)	−0.103 3(4)
C(1)	0.624 0(4)	0.252 6(3)	0.196 5(3)
C(2)	0.773 5(4)	0.239 3(4)	0.234 1(3)
C(3)	0.768 4(5)	0.200 4(4)	0.378 8(4)
C(4)	0.748 4(5)	0.318 9(4)	0.404 4(4)
C(5)	0.582 2(4)	0.306 8(4)	0.390 9(3)
C(6)	0.560 7(4)	0.331 5(3)	0.252 7(3)
C(7)	0.664 4(4)	0.358 7(4)	0.041 8(3)
C(8)	0.735 3(4)	0.522 4(4)	0.022 8(3)
C(9)	0.778 4(5)	0.346 3(4)	−0.041 0(4)
C(10)	0.621 3(4)	0.609 3(3)	0.155 9(3)
C(11)	0.738 9(5)	0.766 8(4)	0.068 2(4)
C(12)	0.716 2(6)	0.881 6(4)	0.074 1(4)
C(13)	0.581 2(6)	0.843 9(5)	0.165 2(5)
C(14)	0.465 5(6)	0.688 3(5)	0.252 8(4)
C(15)	0.483 7(4)	0.572 0(4)	0.246 9(3)
C(16)	0.055 2(4)	0.014 6(4)	0.344 7(4)
C(17)	−0.105 0(5)	−0.102 5(5)	0.376 8(4)
C(18)	−0.134 1(5)	−0.227 5(5)	0.360 9(4)
C(19)	−0.004 2(5)	−0.238 3(4)	0.313 5(4)
C(20)	0.157 7(4)	−0.123 7(4)	0.281 0(3)
C(21)	0.186 3(4)	0.000 7(3)	0.299 1(3)

Table 7. Fractional atomic co-ordinates for (**9a**).

Atom	x	y	z
O(1)	0.524 0(5)	0.159 9(3)	0.179 6(5)
O(2)	0.503 8(5)	0.358 5(4)	0.284 5(5)
N(1)	0.376 6(4)	0.100 6(3)	0.356 3(4)
N(2)	0.255 7(4)	0.108 6(3)	0.389 7(4)
N(3)	0.182 9(4)	0.208 1(3)	0.495 5(4)
N(4)	0.226 4(4)	0.410 4(3)	0.580 8(4)
C(1)	0.270 3(5)	0.295 5(4)	0.566 5(5)
C(2)	0.284 0(5)	0.418 1(4)	0.468 8(5)
C(3)	0.354 9(5)	0.285 6(4)	0.358 0(5)
C(4)	0.393 1(5)	0.228 8(4)	0.447 8(5)
C(5)	0.469 2(6)	0.274 2(5)	0.273 2(5)
C(6)	0.636 4(11)	0.135 3(7)	0.091 8(11)
C(7)	0.730 2(11)	0.049 8(13)	0.071 1(15)
C(8)	0.202 1(5)	−0.002 0(4)	0.302 0(5)
C(9)	0.286 7(6)	−0.112 6(5)	0.222 9(6)
C(10)	0.236 9(9)	−0.217 9(5)	0.140 0(7)
C(11)	0.106 5(10)	−0.211 5(6)	0.135 6(8)
C(12)	0.022 0(8)	−0.099 8(8)	0.215 1(9)
C(13)	0.069 9(7)	0.009 6(6)	0.299 1(8)
C(14)	0.306 1(5)	0.311 3(4)	0.708 0(4)
C(15)	0.332 8(5)	0.420 3(4)	0.826 9(5)
C(16)	0.366 1(6)	0.429 9(5)	0.951 7(5)
C(17)	0.377 5(6)	0.329 6(5)	0.957 8(6)
C(18)	0.362 6(6)	0.220 1(5)	0.841 1(6)
C(19)	0.315 7(6)	0.212 6(4)	0.717 2(6)
C(20)	0.115 1(5)	0.496 0(4)	0.668 9(5)
C(21)	0.035 6(5)	0.474 2(5)	0.743 5(5)
C(22)	−0.068 8(6)	0.562 6(5)	0.833 2(6)
C(23)	−0.096 7(6)	0.674 7(6)	0.849 9(6)
C(24)	−0.019 8(7)	0.695 6(5)	0.775 5(7)
C(25)	0.085 1(6)	0.609 3(4)	0.685 5(6)
C(26)	0.527 0(5)	0.237 3(4)	0.499 2(5)
C(27)	0.567 1(5)	0.350 2(4)	0.578 9(5)
C(28)	0.692 9(6)	0.355 9(6)	0.614 2(6)
C(29)	0.782 4(6)	0.253 0(6)	0.576 9(7)
C(30)	0.744 6(6)	0.141 9(6)	0.501 6(7)
C(31)	0.618 5(5)	0.132 5(5)	0.460 7(6)

IV. *X-Ray Crystal Data.*—The structures of compounds (**9a**) and (**4a**; $m = 2$) were solved by direct methods and refined by full-matrix least-squares using SHELX76.[14] Data were corrected for Lorentz and polarisation effects but not for absorption. Hydrogen atoms were included in calculated positions with fixed thermal parameters (0.06). All non-hydrogen atoms were refined anisotropically. The atomic scattering factors for non-hydrogen and hydrogen atoms and the anomalous dispersion correction factors for non-hydrogen atoms were taken from the literature.[15–17] All calculations were performed on a VAX 8700 computer. The ORTEP program was used to obtain the drawings.[18] Crystal data for compounds (**4a**; $m = 2$) and (**9a**) are given in Tables 4 and 5, and Tables 6 and 7 contain the fractional atomic co-ordinates for these two compounds.*

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* *Supplementary data* (see section 5.6.3 of the Instructions for Authors, in the January issue). Tables of H-atom co-ordinates and thermal parameters, and bond length and angles, have been deposited at the Cambridge Crystallographic Data Centre.

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