Tricyclic phenanthrene systems: substituted phenanthro[9,10-*e*]-1,2,3-triazines and fused phenanthro-azolo-1,2,3-triazoles from cycloaddition–rearrangement sequences of 9,10-bisarylazophenanthrenes with 2π-dipolarophiles. Azolium 1,3-dipoles

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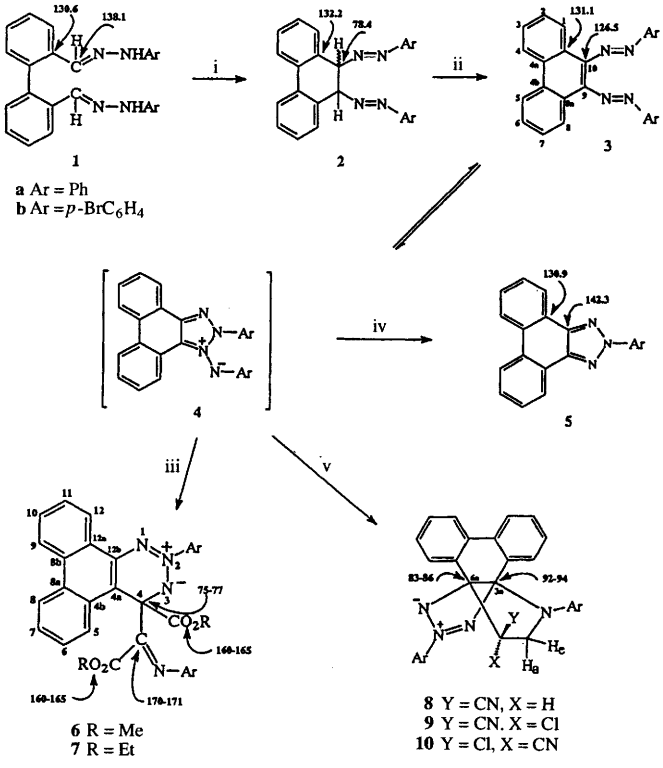
A range of new fused ring systems based on phenanthrene were obtained from cycloaddition–rearrangement reactions of 9,10-bisarylazophenanthrenes with alkyne and alkene dipolarophiles. These new rings include substituted phenanthro[9,10-*e*]-1,2,3-triazines, the tricyclic systems, substituted 3a,6a-(biphen-2,2′-yl)hexahydropyrrolo[2,3-*d*]-1,2,3-triazoles and substituted 3a,6a-(biphen-2,2′-yl)-hexahydroimidazo[4,5-*d*]-1,2,3-triazoles. X-Ray crystal structures are reported on 2-(*p*-bromophenyl)-4-methoxycarbonyl-4-(*p*-bromophenyliminomethoxalyl)-3,4-dihydrophenanthro[9,10-*e*]-1,2,3-triazin-2-ium-3-ide 6b, and 2,4-diphenyl-3a,6a-(biphen-2,2′-yl)-5,6-*endo*-dicarboxy-*N*-phenylimido)-1,3a,4,5,6,6a-hexahydropyrrolo[2,3-*d*]-1,2,3-triazol-2-ium-1-ide 11a.

Intramolecular cyclisations of 2,2′-disubstituted biphenyls are a main route to phenanthrene systems.[1–3] Despite wide studies of such cyclisations 9,10-bisarylazophenanthrene derivatives **3** have not been reported from previous studies[2,3] of the oxidations of arylhydrazines of biphenyl-2,2′-dicarbaldehyde. Neither are such compounds readily available from a route *via* 9,10-phenanthraquinone since this reacts with aryl hydrazines to give only monohydrazone derivatives which tautomerise to the unreactive conjugated 9-hydroxy-10-arylazo-form.[3] We sought[4] 9,10-bisarylazophenanthrenes **3** because we expected the bisarylazo units to cyclise to the new phenanthreno-1,2,3-triazolium-1-imide system **4** which when viewed as a 1,3-dipole should open up a wide new synthetic scope in the phenanthrene series. Herein we report the first[4] 9,10-bisarylazophenanthrenes **3**. These have allowed the synthesis of a range of new tricyclic systems fused at the 9,10-bond of phenanthrene by using variations on the cycloaddition–rearrangement sequences which we have developed for the 1,2,3-triazolium-1-imide 1,3-dipole system.[5,6] Among the benzenoid hydrocarbons only a few 1,2,3-triaza derivatives are known and these are confined to the 1,2,3-triazanaphthalene and 1,2,3-triazanthracene series.[7] The present work has opened a route to the first derivatives of the 1,2,3-triazatriphenylene system.

Results and discussion

The 9,10-bisarylazophenanthrenes **3** were obtained in two steps from the 2,2′-biphenylbisaldehyde bisarylhydrazones **1** after exploring a variety of oxidation methods. A one-pot direct oxidation of **1** to **3** did not prove feasible for us. Thus, treatment of **1** with PbO_2 in toluene at ambient temperatures gave high yields of the 9,10-dihydro-9,10-bisarylazophenanthrenes **2** (Table 1). The stereochemistry of these was not pursued (precedent with hydroxy derivatives would suggest it should be *cis*). Careful dehydrogenation of **2** with lead tetraacetate in dichloromethane containing triethylamine gave high yields of **3** (Table 1). The structures of compounds **2** and **3** were confirmed by ^1H and ^{13}C NMR spectra which showed all of the expected signals and also the planes of symmetry in these molecules (Scheme 1). A low concentration of the cyclic form **4**, however, dominates the reactivity of **3**. Simple treatment with phosphorus trichloride gives deamination to the phenanthreno[9,10-*d*]-1,2,3-triazoles **5** in high yield. There has been wide interest in the fusion of azole rings at the 9,10-bond of phenanthrene[8–10] and recently a range of phenanthro[9,10-*d*]-1,2,3-triazole derivatives has been reported.[10] Heating of compound **3a** and **3b** with dialkyl acetylenedicarboxylates in toluene for 1–4 h gave high yields of the new 1,2,3-triazatriphenylene derivatives **6** and **7** (Scheme 1, Table 1). This experimentally simple, one-pot reaction involves a complicated cycloaddition–ring expansion process which appears to be dominated by the need to preserve the phenanthrene structure. In the absence of the 4a–4b bond of the phenanthrene system (*i.e.*, with a 4,5-diphenyl-1,2,3-triazole substrate) the reaction

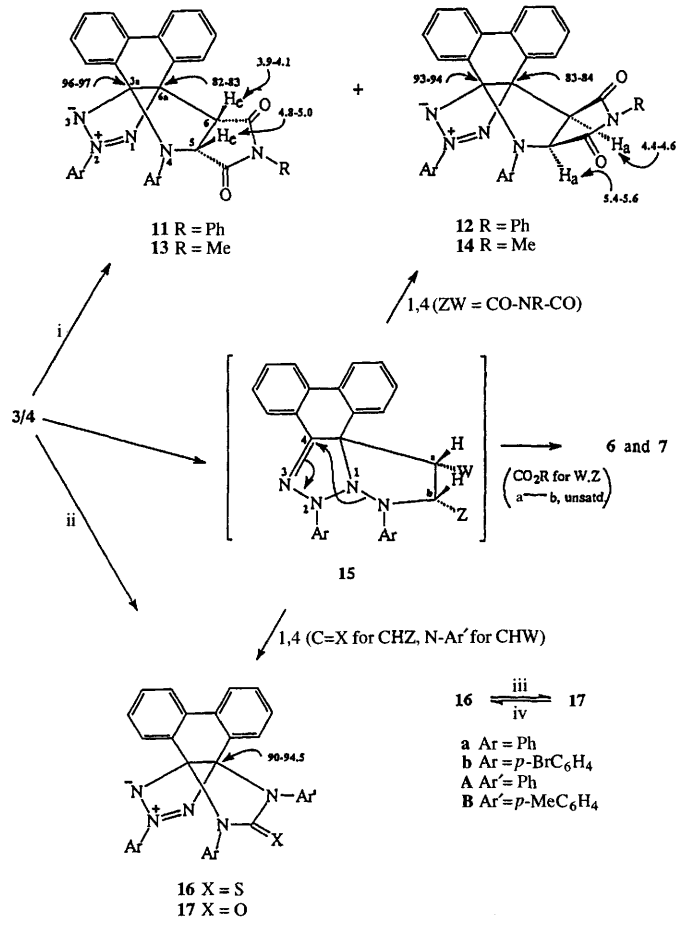


Scheme 1 *Reagents:* i, PbO_2, toluene; ii, $Pb(OAc)_4$, CH_2Cl_2, Et_3N, 0 °C; iii, $RO_2C{-}C{\equiv}C{-}CO_2R$; iv, PCl_3; v, $CH_2{=}CXY$; some key ^{13}C NMR shifts ($CDCl_3$) shown for the **a** series

Table 1 Products

Entry no.	Compd.	Mp (T/°C)	Yield (%)	Microanalysis found % (required %) C	H	N
1	**1a**	150–151[a]	82	79.8 (80.0)	5.9 (5.7)	14.2 (14.3)
2	**1b**	184–185[a]	88	56.9 (57.0)	3.7 (3.65)	10.4 (10.2)
3	**2a**	135–137[b]	89	80.4 (80.4)	5.3 (5.15)	14.2 (14.2)
4	**2b**	127–128[b]	88	57.4 (57.1)	3.2 (3.3)	10.0 (10.25)
5	**3a**	144–145[a]	89	80.6 (80.8)	4.6 (4.7)	14.4 (14.5)
6	**3b**	201–202[a]	78	57.3 (57.35)	2.9 (2.9)	10.1 (10.3)
7	**5a**	197–199[b]	93	81.6 (81.4)	4.35 (4.4)	14.1 (14.2)
8	**5b**	238–240[b]	87	64.0 (64.2)	3.2 (3.2)	11.1 (11.2)
9	**6a**	166–168[c]	94	72.4 (72.7)	4.6 (4.5)	10.6 (10.6)
10	**6b**	154–156[c]	80	55.9 (56.0)	3.0 (3.2)	8.1 (8.2)
11	**7a**	132–133[a]	60.5[f]	73.5 (73.4)	4.8 (5.0)	9.9 (10.1)
12	**7b**	139–141[a]	50[f]	57.1 (57.1)	3.8 (3.6)	7.9 (7.8)
13	**8a**	148–150[d]	60[f]	79.2 (79.3)	5.0 (4.8)	15.7 (15.9)
14	**8b**	197–199[b]	48[f]	58.2 (58.3)	3.0 (3.2)	11.6 (11.7)
15	**9a**	170–172[e]	32.5[g]	73.6 (73.5)	4.3 (4.2)	14.7 (14.8)
	10a	160–161[e]	32[g]	73.3 (73.5)	4.2 (4.2)	14.9 (14.8)
16	**11a**	236–237[a]	37[g]	77.6 (77.3)	4.7 (4.45)	12.6 (12.5)
	12a	261–262[a]	38[g]	77.5 (77.3)	4.3 (4.45)	12.7 (12.5)
17	**11b**	231–232[e]	36[g]	60.1 (60.25)	3.0 (3.2)	9.7 (9.8)
	12b	248–249[e]	38[g]	60.0 (60.25)	3.2 (3.2)	9.7 (9.8)
18	**13a**	268–270[e]	38[g]	74.9 (74.85)	4.6 (4.6)	13.9 (14.1)
	14a	252–254[e]	33[g]	74.6 (74.85)	4.7 (4.6)	13.9 (14.1)
19	**16aA**	227–228[e]	65[g]	76.0 (76.0)	4.4 (4.4)	13.3 (13.4)
20	**16aB**	219–221[e]	55[g]	76.1 (76.3)	4.8 (4.7)	12.9 (13.1)
21	**16bA**	232–233[e]	65[g]	57.9 (58.3)	3.3 (3.1)	10.1 (10.3)
22	**16bB**	251–253[e]	58[g]	58.9 (58.9)	3.6 (3.3)	10.1 (10.1)
23	**17aA**	257–259[e]	93	78.6 (78.4)	4.5 (4.6)	14.1 (13.9)
24	**17bA**	267–268[e]	87	59.6 (59.7)	3.1 (3.2)	10.4 (10.6)

[a] From light petroleum (bp 40–60 °C)–toluene. [b] From ethanol. [c] From methanol. [d] From hexane. [e] From MeCN. [f] Recovered substrate **3** made up the product balance. [g] Compound **5** (20–25%) was also obtained in these reactions.



Scheme 2 *Reagents:* i, N-substituted maleimide; ii, Ar'–N=C=S; iii, $Hg(OAc)_2$; iv, Lawesson's Reagent (some key ^1H and ^{13}C NMR shift ranges ($CDCl_3$) shown)

proceeds quite differently.[5,11] Similar reactions, involving prolonged heating of **3** with the alkene dipolarophiles, acrylonitrile, 1-chloro-1-cyanoethene and some *N*-substituted maleimides, gave the series of new tricyclic phenanthrene derivatives **8**–**14** (Schemes 1 and 2, Table 1). The reaction with acrylonitrile was regio- and stereo-selective, giving the products **8** only along with low yields of the triazoles **5** (Table 1). With the other alkenes approximately equal mixtures of the *endo–exo* pairs **9**,**10**, **11**,**12** and **13**,**14** were obtained (Table 1). These isomeric pairs were not interconvertible under the reaction conditions. Treatment of the substrates **3** with some *p*-substituted phenylisothiocyanates gave the products **16** from a cycloaddition on the N=C bond. No reaction could be induced between the compounds **3** and substituted phenylisocyanates but the expected products **17** from such reactions were obtained by treating the thiones **16** with mercuric acetate following a literature[12,13] procedure. The products **17** were also converted back to **16** with Lawesson's reagent.[14] The formation of the novel products **8**–**16** involves an initial cycloaddition giving an intermediate of general type **15**. This undergoes an *in situ* 1,4-sigmatropic rearrangement to the products.[5,6] Substituents which are *exo*-(to the 5,5 ring system) in the products will be *endo*- in this initial intermediate and *vice versa*.[5,6] Normally, the preferred initial cycloaddition follows the *endo* mode giving *exo*-isomers as products, but the presence of the phenanthrene moiety has negated the favourable *endo*-transition state resulting in almost equal mixtures of both isomeric products, except for compounds **8**. For the reaction with alkyne dipolarophiles the initial adduct, corresponding to **15**, contains a double bond at the 4,5-site (a–b) of the fused pyrazolidine ring. This double bond allows for a ring expansion and sigmatropic rearrangement to the products **6** and **7**. This rearrangement and ring-expansion could occur either directly in the initial adduct **15** or after the 1,4-rearrangement in structures such as **12** and **14** (with unsaturation at a–b) and the immediate precursor to the triazatriphenylene derivatives **6** and **7** is not known at present. The initial adduct **15** as well as undergoing

rearrangement may also aromatise to the phenanthrenotriazoles **5** and low yields of these often accompanied the main product (Table 1, entries, 19–22).

Products

The structures of the products were established from microanalyses, IR, ^1H and ^{13}C NMR spectra which showed all of the expected signals. Some key NMR shifts are shown in the Schemes. The bridgehead quaternary carbons at the saturated 9-, 10-positions of the fused phenanthreno moiety showed up in the region 80–100 ppm. In the structures **8–10** the equatorial proton H_e was the most deshielded when *cis* to the CN substituent because of the deshielding influence of the triple bond and this allowed a distinction of the *exo*, *endo* pairs **9** and **10**. (The terms *exo* and *endo* refer to the fused 5,5-bicycle of the tricyclic systems.) For the series **11–14** the isomeric pairs could be distinguished by a special shielding of the equatorial protons H_e (in the *endo*-isomers **11** and **13**) by the phenanthrene unit which they are facing. The structures and NMR assignments were bolstered by X-ray crystal structure determinations on compounds **6b** and **11a** (Figs. 1 and 2). These confirmed the structures and stereochemistry. For compounds **16** and **17** the structures were also supported by the ready interconversions of these thiono- and oxo-derivatives. The ^{13}C signal of the thiono group in **16** was at 182–183 ppm while in compounds **17** this was replaced by the amido C=O signal at 156–157 ppm.

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. NMR assignments were supported by decoupled and off-resonance decoupled spectra. Microanalyses were measured on a Perkin-Elmer model 240 CHN analyser.

I. 9,10-Bis(arylazo)phenanthrenes 3

Phenylhydrazine (0.94 cm^3, 9.52 mmol) was added to biphenyl-2,2′-dicarbaldehyde (1 g, 4.76 mmol) in light petroleum (bp 40–60 °C)-toluene (7:3 v/v) and the mixture stirred at ambient temperature for 1 h, during which the bishydrazone **1a** separated, mp 150–151 °C) (lit.,[3] mp 150–151 °C) (83%) (Found: C, 79.8; H, 5.9; N, 14.2. Calcd. for $C_{26}H_{22}N_4$ C, 80.0; H, 5.7; N, 14.3%). A solution of **1a** (1.5 g, 3.84 mmol) in toluene (40 cm^3) was treated with lead dioxide (1.01 g, 4.22 mmol) and the mixture stirred at ambient temperatures for three days, filtered to remove salts, evaporated under reduced pressure and the residue crystallised with ethanol to give 9,10-bisphenylazo-9.10-dihydrophenanthrene **2a**, mp 135–137 °C (EtOH) (89%); $\delta_H(CDCl_3)$ 5.44 (2 H, s, 9- and 10-H), 7.19–7.47 (m, 12 H, N–Ph: $H_{meta,para}$, phenanthrene: 1-, 2-, 3-, 6-, 7-, 8-H), 7.55–7.59 (m, 4 H, N–Ph: H_{ortho}, phenanthrene: 4-H, 5-H). $\delta_C(CDCl_3)$ 78.4 (9-CH); 152.1, 122.6, 128.9 and 130.8 (N–Ph: C-1′, C-2′, C-3′ and C-4′ resp.), 129.4, 129.0, 128.3, 123.9, 134.0 and 132.2 (phenanthrene: C-1, C-2, C-3, C-4, C-4a and C-10a resp.). A solution of **2a** (2.66 g, 6.86 mmol) in dry CH_2Cl_2 at 0 °C was treated with Et_3N (3.82 cm^{-3}, 27.44 mmol) and lead tetraacetate (3.65 g, 8.23 mmol), stirred at 0 °C for 8 h followed by 15 h at ambient temperatures, filtered to remove salts, evaporated under reduced pressure and the residue crystallised from MeOH to give 9,10-bis(phenylazo)phenanthrene **3a**, mp 144–145 °C (89%); $\delta_H(CDCl_3)$ 7.47–7.49 (m, 6 H, N–Ph: H_{meta} and H_{para}) 7.61–7.75 (4 H, m, phenanthrene: H-2 and H-3), 7.88–7.91 (m, 4 H, N–Ph: H_{ortho}), 8.49 (2 H, d, phenanthrene: H-4 and H-5), 8.74 (2 H, d, phenanthrene: H-1 and H-8); $\delta_C(CDCl_3)$ 152.9, 123.2, 129.2 and 131.45 (N–Ph: C-1′, C-2′, C-3′ and C-4′ resp.), 126.75, 126.0, 127.8, 123.0, 136.4, 126.5 and 131 (phenanthrene: C-1, C-2, C-3, C-4, C-4a, C-9 and C-10a resp.). Compounds **2b** and **3b** were prepared similarly.

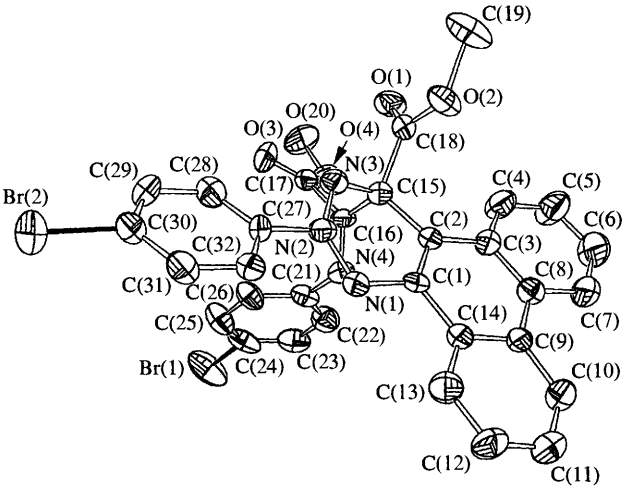


Fig. 1 X-Ray crystal structure of compound **6b**

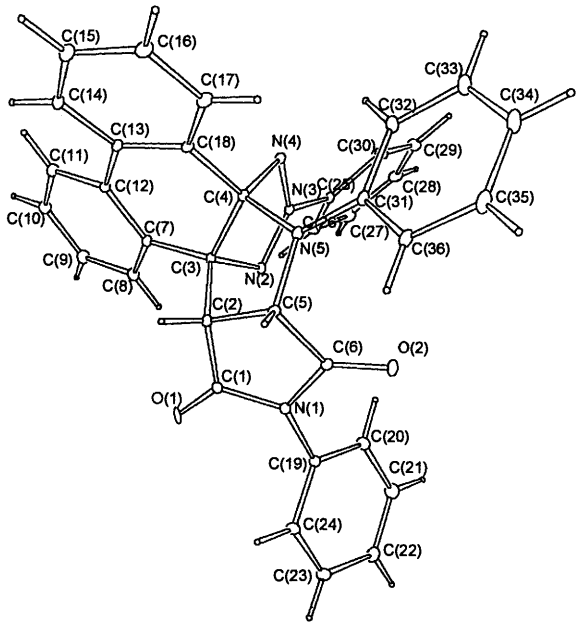


Fig. 2 X-Ray crystal structure of compound **11a**

II. Phenanthro[9,10-*d*]-1,2,3-triazoles 5

A solution of **3a** (0.35 g, 0.91 mmol) in PCl_3 (10 cm^3) was stirred under reflux for 1 h, evaporated under reduced pressure and the residue crystallised from ethanol to give 2-phenylphenanthro[9,10-*d*]-1,2,3-triazole **5a**, mp 197–199 °C (93%); δ_H-($CDCl_3$) 7.43 (t, 1 H, N–Ph, H_{para}), 7.54–7.59 (m, 6 H, N–Ph: H_{meta}, H-5, H-6, H-9 and H-10), 8.45–8.56 (m, 4 H, H-4, H-7, H-8, H-11); 8.33–8.36 (m, 2 H, N–Ph: H_{ortho}); $\delta_C(CDCl_3$; 60 °C) 140.5, 119.8, 123.8 and 128.1 (N–Ph: C-1′, C-2′, C-3′ and C-4′ resp.), 142.3 (triazole C-3a), 130.9 (C-3b), 129.5, 128.0, 127.7, 124.0 and 128.6 (C-4, C-5, C-6, C-7 and C-7a resp.). Compound **5b** was prepared similarly.

III. Cycloadditions with alkynes: phenanthro[9,10-*e*]-1,2,3-triazines 6

Typical examples. (*a*) A solution of **3a** (0.4 g, 1.04 mmol) in toluene (10 cm^3) was treated with dimethyl acetylenedicarboxylate (0.38 cm^3, 3.11 mmol), stirred at 80 °C for 1 h, evaporated under reduced pressure and the residue crystallised from MeOH to give 4-methoxycarbonyl-4-phenyliminomethoxalyl-2-phenyl-3,4-dihydrophenanthro[9,10-*e*]-1,2,3-triazin-2-ium-3-ide **6a**,

Table 2 Crystal data and structure refinement

Compound	**6b**	**11a**
Empirical formula	$C_{32}H_{22}Br_2N_4O_4$	$C_{36}H_{25}N_5O_2$
Formula weight	686.36	559.61
Temperature	293(2)	293(2) K
Wavelength	0.710 69	0.710 69 Å
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions	a = 11.485(2)	a = 9.3120(8) Å
	b = 16.373(4)	b = 10.0806(8) Å
	c = 17.697(5)	c = 15.5920(10) Å
	α = 112.82(2)	α = 102.09(2)°
	β = 101.54(2)	β = 95.10(2)°
	γ = 98.26(2)	γ = 100.95(2)°
Volume	2913.7(12)	1392.4(2) Å^3
Z	2	2
Density (calculated)	1.565	1.335 Mg m^{-3}
Absorption coefficient	2.827	0.085 mm^{-1}
F(000)	1376	584
Crystal size	0.34 × 0.30 × 0.22	0.35 × 0.32 × 0.40 mm
Theta range for data collection	2.03 to 25.91	2.12 to 29.97°
Index ranges	$0 <= h <= 12$; $-16 <= k <= 16$; $-17 <= l <= 17$	$0 <= h <= 11$; $-14 <= k <= 13$; $-21 <= l <= 21$
Reflections collected	10 635	8442
Independent reflections	10 045 [R(int) = 0.0269]	7660 [R(int) = 0.0250]
Reflections observed ($>2\sigma$)	3932	5333
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	10 045/0/761	7660/0/389
Goodness-of-fit on F^2	0.839	1.073
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0550 wR_2 = 0.1356	R_1 = 0.0536 wR_2 = 0.1604
R indices (all data)	R_1 = 0.0841 wR_2 = 0.1607	R_1 = 0.0744 wR_2 = 0.1729
Largest diff. peak and hole	0.68 and −0.67	0.39 and −0.24 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 = $[\Sigma_w(|F_o^2| - |F_c^2|)^2/(N_{obs} - N_{parameters})]^{\frac{1}{2}}$

mp 166–168 °C (MeOH), (94%); ν_{max}/cm^{-1}(Nujol mull), 1737 (ester C=O); δ_H($CDCl_3$), 3.49 (s, 3 H, C-4-CO_2Me), 3.70 [s, 3 H, C=N(CO_2Me)], 6.59 (d, 2 H, –C=N–Ph: H_{ortho}), 6.97–7.19 (m, 4 H, aromatic), 7.54–7.67 (m, 8 H, aromatic), 7.99–8.78 (m, 4 H, 2-N–Ph; H_{ortho}, C=N–Ph: H_{meta}); δ_C($CDCl_3$) 52.0 and 53.5 (MeO); 76.3 (C-4), 103.5 (C-4a), 149.1, 118.7 and 126.7 (C=N–Ph: C-1′, C-2′, and C-4′ resp.), 136.2, 123.5, 128.8 and 131.5 (2-N–Ph: C-1′, C-2′, C-3′ and C-4′ resp.), 146.95 (C-12b), 160.4 and 164.2 (ester C=O, 170.9 C=N), 122.5, 123.35, 123.9, 125.1, 125.7, 126.5, 127.0, 128.0, 128.4, 128.6, 131.6, 131.2 and 131.8 (remaining aromatic) (one signal overlapped at 125–130 ppm).

(*b*) Compounds **6** and **7** (Table 1) were obtained similarly. For example, orange **7b**, mp 139–141 °C (light petroleum) (bp 40–60 °C), (50%) (recovered **3b**, 46%); ν_{max}/cm^{-1}(Nujol mull), 1741 (ester C=O); δ_H($CDCl_3$) 0.88 (t, 3 H, 4-$CO_2CH_2CH_3$) and 4.01 (q, 2 H, 4-$CO_2CH_2CH_3$), 1.09 [t, 3 H, C=N(CO_2-CH_2CH_3)] and 4.25 [q, 2 H, C=N($CO_2CH_2CH_3$)], 6.51 [d, 2 H, C=N-C_6H_4Br-*p*: H_{ortho}), 7.28 (m, 4 H, aromatic), 7.36–7.68 (overlapping m, 8 H, aromatic), 8.06–8.76 [overlapping AA′BB′ ds, 4 H, 2-N–C_6H_4Br-*p*: H_{ortho}, C=N–C_6H_4Br-*p*: H_{meta}); δ_C($CDCl_3$) 13.6, 13.9, 61.5 and 62.7 (2 × EtO), 74.95 (C-4), 103.6 (C-4a), 148.1, 120.4 and 118.1 (C=N–C_6H_4Br-*p*: C-1′, C-2′ and C-4′ resp.), 136.1, 124.9, 131.5 and 125.9 (2-N–C_6H_4Br-*p*: C-1′, C-2′, C-3′ and C-4′ resp.), 147.75 (C-12b), 161.3 and 163.0 (ester C=O), 169.9, (C=N), 122.5, 123.2, 123.5, 126.2, 126.6, 126.8, 127.2, 127.7, 128.0, 131.0 and 132.1 remaining aromatic (one signal overlapped at 126–128 ppm).

IV. Cycloadditions with alkenes and maleimides

Typical examples. (*a*) A solution of **3a** (0.5 g, 1.3 mmol) and acrylonitrile (1.0 cm^3, *15.2* mmol) in dry toluene (10 cm^3) was stirred at 55 °C for 48 h, evaporated under reduced pressure and the residue in CH_2Cl_2 (3 cm^3) placed on a silica gel column (70–200 mesh ASTM) packed in light petroleum (bp 40–60 °C) and eluted with gradient mixtures of light petroleum (bp 40–60 °C)–dichloromethane (1.0–0.1 v/v), yielding compound **5a** (5%), followed by 2,4-diphenyl-3a,6a-(biphenyl-2,2′-yl)-6-exo-cyano-1,3a,4,5,6,6a-hexahydropyrrolo[2,3-*d*]-1,2,3-triazol-2-ium-1-ide **8a**, mp 148–150 °C (hexane) (60%); ν_{max}/cm^{-1}(Nujol mull) 2242 (CN); δ_H($CDCl_3$) 3.63 (m, 1 H, H_{ax}-5), 3.74 (m, 1 H, H-6), 4.14 (m, 1 H, H_{eq}-5), 6.98–7.96 (m, 18 H, aromatic), δ_C($CDCl_3$) 40.9 (C-6); 52.55 (C-5); 83.2 (C-6a); 92.5 (C-3a); 118.0 (CN), 145.1, 121.8, 123.5 and 128.2 (4-N–Ph: C-1′, C-2′, C-3′ and C-4′ resp.), 140.0, 122.8, 128.9 and 131.8 (2-N–Ph: C-1′, C-2′, C-3′ and C-4′ resp.), 122.1, 124.2, 128.8, 129.2, 129.4, 129.5, 130.9, 131.1, 131.3 and 131.7 remaining aromatic (two signals overlapped at 127–131 ppm). Starting material **3a** (32%) was subsequently recovered from the column.

(*b*) A solution of compound **3a** (0.45 g, 1.17 mmol) and *N*-phenylmaleimide (1.2 g, 7.02 mmol) in dry toluene (15 cm^3) was stirred at 80 °C for 24 h, evaporated under reduced pressure and the residue in CH_2Cl_2 (2 cm^3) placed on a silica gel column (70–200 mesh ASTM) and eluted with gradient mixtures of light petroleum (bp 40–60 °C)–dichloromethane (1:0–0:1 v/v), yielding the triazole **5a** (22.8%) followed by 2,4-diphenyl-3a-6a-(biphen-2,2′-yl)-5,6-*endo*-dicarboxy-*N*-phenylimido)-1,3a,4,5,6,6a-hexahydropyrrolo[2,3-*d*]-1,2,3-triazol-2-ium-1-ide-**11a**, mp 236–237 °C (acetonitrile) (38%); ν_{max}/cm^{-1}(Nujol mull) 1719 (C=O); δ_H($CDCl_3$), 4.07 (d, 1 H, H-6, *J* 8.1), 4.93 (d, 1 H, H-5), 7.05–7.12 (m, 5 H, Ar), 7.24–7.48 (m, 12 H, Ar), 7.59 (2 H, d, Ar), 7.89 (d, 2 H, Ar), 8.12 (d, 2 H, 2-N–Ph: H_{ortho}); δ_C($CDCl_3$) 55.8 (C-6), 62.2 (C-5), 81.9 (C-6a), 96.4 (C-3a), 140.3 (2-N–Ph: C-1′), 144.2 (4-N–Ph: C-1′), 172.0 and 173.9 (C=O), 122.7, 123.0, 123.2, 123.9, 125.8, 126.4, 127.9, 128.5, 128.7, 128.9, 129.2, 129.5, 130.5, 130.7, 131.2, 131.8 and 132.6 (remaining aromatic) (aromatic signals overlapped at 126–132 ppm); X-ray crystal structure, Fig. 2. This was followed from

the column by the corresponding exo-isomer **12a**, mp 261–262 °C (acetonitrile) (37%); ν_{max}/cm^{-1}(Nujol mull) 1719 (C=O); $\delta_H(CDCl_3)$, 4.58 (d, 1 H, *J* 7.8, H-6), 5.38 (d, 1 H, 5-H), 6.38–6.42 (m, 2 H, Ar), 6.88–7.46 (m, 13 H, Ar), 7.74–7.88 (m, 7 H, Ar), 8.15 (d, 2 H, 2-N–Ph: H_{ortho}); $\delta_C(CDCl_3)$, 50.6 (C-6), 60.6 (C-5), 84.0 (C-6a), 93.4 (C-3a), 144.2, 117.3 and 119.6 (4-N–Ph: C-1′, C-2′ and C-4′ resp.), 140.0 (2-N–Ph: C-1′), 171.2 and 172.6 (C=O), 123.1, 123.2, 124.5, 126.3, 128.6, 128.7, 128.9, 129.5, 130.0, 130.9, 131.1, 132.1 and 132.7 remaining aromatic (aromatic signals overlapped at 128–132 ppm).

V. Cycloadditions with arylisothiocyanates

Typical examples. (*a*) A solution of **3a** (0.4 g, 1.04 mmol) in dry toluene (20 cm^3) was treated with phenyl isothiocyanate (0.37 cm^3, 3.12 mmol), stirred at 90 °C for 40 h, evaporated under reduced pressure and the residue in dichloromethane (3 cm^3) placed on a silica gel flash column (280–400 mesh ASTM) and eluted with gradient mixtures of light petroleum (bp 40–60 °C)–CH_2Cl_2 (1:0–1:1.5 v/v) to give **5a** (22%) followed by 2,4,6-triphenyl-3a-6a-(biphen-2,2′-yl)-5-thioxo-1,3a,4,5,6,6a-hexahydroimidazo[4,5-*d*]-1,2,3-triazol-2-ium-1-ide **16aA**, mp 227–228 °C (acetonitrile) (65%); $\delta_H(CDCl_3)$, 6.82 (2 H, d, Ar), 6.99 (2 H, t, 4- and 6-Ph: H_{para}), 7.22–7.96 (18 H, m, Ar), 8.29 (2 H, d, 2-N–Ph: H_{ortho}); $\delta_C(CDCl_3)$, 94.0 (C-3a and C-6a), 140.0, 123.5, 128.9 and 128.4 (2-N–Ph: C-1′, C-2′, C-3′: C-4′ resp.), 137.6, 122.8, 129.8 and 127.7 (4- and 6-NPh: C-1′, C-2′, C-3′ and C-4′ resp.), 182.8 (5-C=S), 129.2, 129.6, 130.9, 131.5 and 132.3 remaining aromatic (signals overlapped at 129–132 ppm).

(*b*) A solution of **16aA** (0.3 g, 0.58 mmol) in dry acetonitrile (20 cm^3) was treated with mercury(II) acetate (0.92 g, 2.9 mmol), stirred for 12 h under reflux, cooled, filtered through Celite and the filtrate evaporated under reduced pressure to give 2,4,6-triphenyl-3a,6a-(biphen-2,2′-yl)-5-oxo-1,3a,4,5,6,6a-hexahydroimidazo[4,5-*d*]-1,2,3-triazol-2-ium-1-ide **17aA**, mp 257–259 °C (acetonitrile) (93%); $\delta_H(CDCl_3)$, 6.96–7.56 (17 H, m, Ar), 7.93 (4 H, d, 4- and 6-NPh: H_{ortho}), 8.29 (2 H, d, 2-N–Ph: H_{ortho}); $\delta_C(CDCl_3)$, 90.0 (C-3a and C-6a), 140.2, 122.7, 128.9 and 129.1 (2-NPh: C-1′, C-2′, C-3′, C-4′ resp.), 136.2, 123.5, 125.3 and 127.8, (4- and 6-N–Ph: C-1′, C-2′, C-3′ and C-4′ resp.), 157.0 (5-C=O), 127.0, 129.4, 129.6, 130.0, 130.4, 130.7 and 132.2 (remaining aromatic) (one signal overlapped).

A solution of **17aA** (0.30 g, 0.58 mmol) in acetonitrile was stirred with Lawesson's reagent (0.23 g, 2.3 mmol) under reflux for 36 h, evaporated and the residue crystallised with ethanol to give compound **16aA** (67%).

X-Ray crystal structure determination of compounds 6b and 11a

The structures were 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. All calculations were performed on a Silicon Graphics R4000 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 quotation and the reference number 207/10.

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