Competitive reactivity of the aryl isothiocyanate dipolarophile at N=C *versus* C=S with nucleophilic 1,3-dipoles: a combined experimental and theoretical study. The reactions of substituted 1,2,3-triazolium-1-aminide 1,3-dipoles with aryl isothiocyanates: new tricyclic thiazolo[4,5-*d*][1,2,3]triazoles

Richard N. Butler,*[a] Denise C. Grogan,[a] Peter D. McDonald[a] and Luke A. Burke*[b]

[a] *Chemistry Department, University College Galway, Ireland*
[b] *Chemistry Department, Rutgers University, Camden, New Jersey 08102, USA*

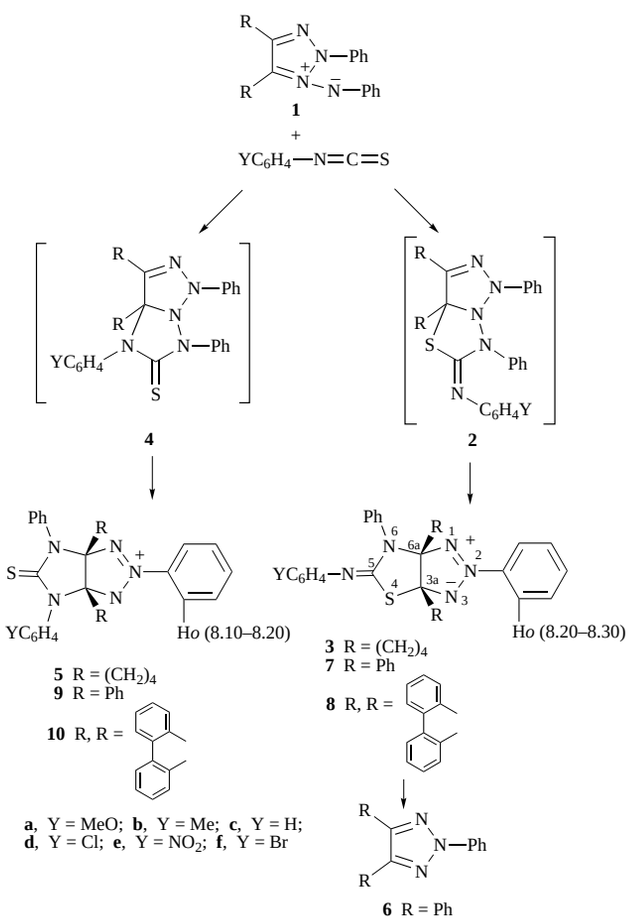
Substituted 1,2,3-triazolium-1-aminide 1,3-dipoles react with aryl isothiocyanates at both the N=C and C=S sites to give mixtures of substituted imidazolo[4,5-*d*][1,2,3]triazoles and new thiazolo[4,5-*d*][1,2,3]-triazoles including tricyclic derivatives with the C-3a and C-6a bridgeheads linked *via* $(CH_2)_4$ and phenanthro groups. The product distribution is controlled by the *para*-substituent of the aryl isothiocyanate. Theoretical calculations, 3-21G* and 6-31G*, suggest that linear triple bonded canonical forms of the aryl isothiocyanate system play a key role in the ambident reactivity of these systems.

Because of their high reactivity, thiones have been classified as super dipolarophiles among the hetero-double bond 2π-systems in reactions with a range of 1,3-dipoles.[1–4] A favourable charge-transfer orientation complex as well as a strong HOMO–LUMO interaction has been suggested as the principal reason for the high thione reactivity towards nitrone 1,3-dipoles.[4] When the C=S moiety is part of the isothiocyanate cumulene system cycloaddition reactions are often observed on both the N=C and C=S bonds in a competitive manner and the C=S site is not the exclusive reactive centre. Thus diphenyl nitrile imide reacted with phenyl isothiocyanate to give a mixture of 58% of the C=S adduct and 24% of the N=C adduct,[5] while *C*-trifluoromethyl-*N*-phenyl nitrile imide gave only 14% of the C=S adduct with methyl isothiocyanate.[6] Nitrone 1,3-dipoles may also react with substituted isothiocyanates at the N=C or C=S sites.[7–9] Some cyclic nitrones have been reported to react with benzoyl isothiocyanate exclusively at C=S but with phenyl and methyl isothiocyanates at N=C.[7,10] Herein we describe the reactions of the dipoles **1** with aryl isothiocyanates where competitive reactivity at both the N=C and C=S sites has been observed. Substituents on the aryl isothiocyanate had a large influence on the competition between the alternative reaction sites and the factors influencing the relative behaviour of the cumulene C=S and N=C bonds for a given 1,3-dipole are assessed through experimental product distributions and calculated bond distances and atomic charges.

Results and discussion

Products

When the substituted dipoles **1** were treated with a series of *p*-substituted phenyl isothiocyanates, mixtures of the corresponding imidazolo[4,5-*d*][1,2,3]triazoles **5**, **9** and **10**, and the new substituted thiazolo[4,5-*d*][1,2,3]triazoles **3**, **7** and **8**, were obtained (Scheme 1, Table 1). These products, which are not interconvertible, arose from the cycloaddition–rearrangement sequence *via* the intermediates **2** and **4**, which we have established[11,12] as a general reaction pathway for the dipoles **1** with many dipolarophiles. Throughout the series of reactions, electron-withdrawing groups at the *para*-position of the phenyl



Scheme 1

isothiocyanates oriented the reaction strongly towards the C=S site, and a good correlation of the log **3**:**5** ratio with the Hammett σ_p value of this substituent was observed for the series with the dipole **1** [R,R = $(CH_2)_4$] (r^2 = 0.9813, slope 0.7102, intercept 0.239 63). The log of this **3**:**5** ratio also correlated

Table 1 Product distribution from reaction of **1** with *p*-substituted aryl isothiocyanates

			Products					
Entry	Y (σ_p)	Ratio[a] **3**:**5**	Comp.	Mp (*T*/°C)	Yield (%)	Comp.	Mp (*T*/°C)	Yield (%)
1	MeO (−0.27)	1:1	**3a**	132–134	42.5	**5a**	186–188	42.5
2	Me (−0.17)	1.3:1	**3b**	140–142	49	**5b**	209–211	37
3	H (0)	1.9:1	**3c**	140–142	58	**5c**	211–212	30
4	Cl (0.23)	2.8:1	**3d**	144–146	63.5	**5d**	213–215	22.5
5	NO_2 (0.78)	5.8:1	**3e**	126–128	75	**5e**	241–243	13
6	MeO	1:1.2[b]	**9a**	109–111	40.5	**7a**	231–232	48.5
7	H	1.1:1[b]	**9c**	126–128	52	**7c**	265–266	46.3
8	NO_2	3:1[b]	**9e**	98–100	60.5	**7e**	247–248	20.2
9	MeO	—	—[c,d]	—	—	**8a**	216–218	60
10	Me	—	—[c,d]	—	—	**8b**	219–221	55
11	H	—	—[c,d]	—	—	**8c**	227–228	65
12	Br	—	**10f**	210–211	22	**8f**	238–239	46
13	NO_2	—	**10e**	209–211	44	—[c]	—	—

[a] In acetone at 20 °C. [b] **9**:**7** product ratio. [c] Not detected. In each of these reactions 2-phenyl-2*H*-phenanthro[9,10-*d*]triazole was isolated in 18–25% yield. [d] Reactions at 90 °C in toluene.

with the resonance enhanced σ_p values with lower correlation coefficient ($r^2 = 0.9540$, slope 0.3848, intercept 0.298 28). The products **7** were unstable and broke down to the corresponding 4,5-diphenyl-2-aryl-1,2,3-triazole **6** and a mixture of isothiocyanates on being heated or under prolonged stirring. In a previous study[13] with the dipoles **1** (R = Ph) this decomposition occurred unknowingly under the conditions employed which involved heating and this prevented the detection of the new ring system **7**. The new tricyclic systems **3** and **8** were more stable but with the phenanthro series heat was necessary for the reaction and the products **8** also tended to decompose to 2-phenyl-2*H*-phenanthro[9,10-*d*]triazole which was always encountered (Table 1, entries 9–13). Hence the reaction with the dipole **1** [R,R = $(CH_2)_4$], which gave clean high-yield mixtures of the stable products **3** and **5**, was the most suitable for assessing the reactivity of the separate unsaturated bonds of the aryl isothiocyanate system with the triazolium-1-aminide 1,3-dipole (Table 1, entries 1–5). The product ratios (Table 1, entries 1–5) were obtained by direct analysis of the product mixture using 270 MHz proton NMR spectroscopy prior to separation. For any **3**–**5** pair the *ortho*-H atoms, H_o, of the azimine moiety in **5** were about 0.1 ppm more deshielded and readily distinguished from those in **3**. These assignments and ratios were fully confirmed within experimental error (±1%) by direct isolation of both products. The ratio quoted for the products from *p*-nitrophenyl isothiocyanate is obtained by direct separation and isolation of the products **3e** and **5e** since there was an overlap of the H_o proton signals with those of the H atoms *ortho* to the NO_2 substituent. The results for the product series **3** and **5** were the same for reactions carried out at ambient temperatures in either of the solvents acetone, ethyl acetate, acetonitrile or toluene and product decomposition was not a problem.

Structure of the products

The structures of the products were established from microanalyses, IR, proton, carbon-13 and nitrogen-15 NMR spectra which showed all of the expected signals. The products **9** have been previously reported[13] and fully characterised. The compounds **5** and **10** showed the expected similar spectral features. In these compounds the key quaternary N–C–N bridgehead carbons appear at 93–106 ppm in the carbon-13 NMR spectra and the thioamido carbon appears at 182–186 ppm. In the new fused ring systems **3** the N–C–N bridgehead appeared in the range 94–96 ppm while the S–C–N bridgehead appeared at 87–89.5 ppm. The *ortho* H-atoms of the exocyclic imino aryl group (YC_6H_4) of the series **3** lie under the N=C in an *endo* direction towards the bent fused bicyclic 5,5-structure and it shows exceptional shielding at 6.8–7.0 ppm in the proton NMR spectrum. In compounds **5** these *ortho* H-atoms of the YC_6H_4 group appear in the normal aromatic envelope. In the N-15 NMR spectra of the series **5** the imidazole N-atoms N-4 and N-6 appeared at −234 to −235 ppm (from $MeNO_2$) while in compound **3e** the thiazole N-6 appeared at −256 ppm and the other signal was replaced by the exocyclic imino C=N at −146 ppm. All of the compounds showed the azimine nitrogens, N-1 and N-3 at −63 to −76 ppm and 2-N-Ph at −84 to −94 ppm.

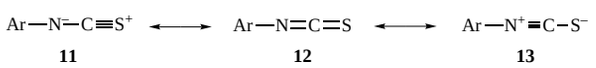
Theoretical method

All calculations were carried out using the gamess (US) program.[14] The aryl isothiocyanate structures were optimised with the 3-21G* basis set using gradient methods. As there is some question as to the experimental structure of phenyl and other isothiocyanates[15–17] optimisations were also performed on HNCO, HNCS, MeNCO, MeNCS, PhNCO and PhNCS at the 3-21G* and 6-31G* levels. The results for the detailed dimensions and energy values for this series will be published separately. The main features relevant to the current synthetic work are as follows. The NCX bond angle is slightly less than linear, −175°, as has been found theoretically for many other cumulenes.[18] The Z–N=C bond angle varies from 125° to 180° according to species and theoretical method. In all cases the 3-21G* basis set gives linear or near linear angles. With the 6-31G* set, the Z–N=C angles in HNCO, MeNCO and PhNCO are 125°, 143° and 142°, while the barriers to their linear counterparts are 7, 1 and 1 kcal mol^{-1}, respectively. Only HNCS of the thio molecules gave a bent Z–N=C angle of 142° with a barrier of 0.4 kcal mol^{-1}. At least at the Hartree–Fock level, methyl and phenyl isothiocyanates are nearly linear, while the isocyanates are angular but with small barriers to the linear structure. Preliminary studies using large basis sets and high level correlation techniques for the H and Me molecules show similar trends, with electron correlation slightly increasing with barriers.

Since explaining the effects of substituents on the synthetic product distributions is the primary object of this study, fifteen aryl isothiocyanate structures were optimised at the 3-21G* level. These were: H, *p*-Cl, *m*-Cl, *p*-Me, *m*-Me, *p*-CN, *m*-CN, *p*-NH_2, *m*-NH_2, *p*-NO_2, *m*-NO_2, *p*-OH, *m*-OH, *p*-COMe, *p*-OMe. From the optimised structures, bond distances and the Mulliken charges were obtained. Of particular use are the total atomic and π orbital charges on the N and S atoms. The π orbital charges were obtained by summing the charges of the two $2p_z$ orbitals on N and the two $3p_z$ and appropriate $3d_z$ orbitals on S, *z* being the direction involved in the conjugated π system in the aryl and NCS moieties. π Orbital charges typically vary from zero, one and two corresponding to an empty p orbital, a one electron atomic orbital contributing to a π molecular orbital, and a lone pair in resonance structures, **13**, **12** and **11** for the N atom and **11**, **12** and **13** for the S atom, respectively. The calculated values of bond lengths, charges and HOMO–LUMO energies are given in Table 2.

Table 2 Bond distances (Å), Hammett and enhanced σ values, total Mulliken and π orbital charges on the N and S atoms, and highest occupied (HOMO) and lowest unoccupied molecular orbital (LUMO) energies (au)

Y	Bond distance CN/Å	Bond distance CS/Å	Hammett σ	Enhanced σ +/−	(S) Total Mulliken charge	(S) π orbital charge	(N) Total Mulliken charge	(N) π orbital charge	Energy HOMO/ au	Energy LUMO/ au
H	1.158 870 0	1.597 230 0	0.00	—	16.058 578	1.761 23	7.041 981	1.428 28	−0.3195	0.0875
p-Cl	1.159 958 1	1.594 224 9	0.22	0.11	16.043 879	1.752 78	7.051 541	1.433 39	−0.3251	0.0737
m-Cl	1.160 112 2	1.593 593 3	0.37	—	16.041 144	1.750 81	7.051 096	1.435 19	−0.3290	0.0744
p-CH_3	1.158 489 2	1.598 460 2	−0.16	−0.31	16.064 229	1.765 90	7.042 317	1.424 94	−0.3128	0.0914
m-CH_3	1.158 703 0	1.597 814 9	−0.07	—	16.061 390	1.762 45	7.043 042	1.427 71	−0.3167	0.0887
p-CN	1.161 240 5	1.590 702 8	0.70	0.99	16.026 963	1.739 15	7.060 261	1.440 35	−0.3357	0.0465
m-CN	1.160 784 8	1.591 832 0	0.61	—	16.032 265	1.746 47	7.058 731	1.437 85	−0.3358	0.0595
p-NH_2	1.157 404 5	1.602 750	−0.57	−1.30	16.082 926	1.782 87	7.036 921	1.412 09	−0.2848	0.1108
m-NH_2	1.158 365 1	1.598 225 9	−0.09	—	16.061 686	1.761 76	7.041 473	1.429 41	−0.3013	0.0947
p-NO_2	1.162 213 0	1.588 005 0	0.78	1.28	16.013 646	1.728 51	7.065 560	1.445 66	−0.3463	0.0148
m-NO_2	1.161 316 7	1.590 276 4	0.71	—	16.024 375	1.742 26	7.061 898	1.440 21	−0.3406	0.0228
p-OH	1.158 465 4	1.598 831 6	−0.38	−0.92	16.065 065	1.769 72	7.042 710	1.422 24	−0.3087	0.0965
m-OH	1.159 298 5	1.595 727 4	0.13	—	16.051 578	1.755 58	7.047 843	1.432 75	−0.3203	0.0836
p-$COCH_3$	1.160 192 7	1.593 431 1	0.47	0.84	16.040 775	1.747 25	7.053 363	1.435 74	−0.3278	0.0522
p-OCH_3	1.158 069 0	1.599 889 5	−0.27	−0.78	16.070 189	1.772 87	7.041 576	1.419 95	−0.3026	0.1007



11 **12** **13**

Scheme 2

Ambident behaviour of aryl isothiocyanates

Aryl isothiocyanates exhibit an exceptional linear structure between Ar and −N=C=S parts, or at least a low barrier of linearity, compared with isocyanates and most triatomic cumulenes −X=Y=Z. This suggests strong resonance contributions from the forms **11** and **13** each of which contains a triple bond. The contribution of **13** should be enhanced by electron donating groups and that of **11** by electron withdrawing substituents.

Due to the well known relationship between bond order and bond length rather good linearity can be expected from a plot of total charge to CS or CN bond length. These plots are available as supplementary material (**Sup 57307**; 6 Pages) deposited with the British Library. Details are available from the editorial office. The values greater than 16 or 7 show greater negative charge (electron density) on the S and N atoms respectively, thus favouring more lone pairs (single bond character) on structure **13** with electron donating groups and on **11** for withdrawing groups.

When plotting π atomic charge on S to C=S bond length (linear, $r^2 = 0.9770$, slope 0.285 63, intercept 1.093 84) one can see where the average value of 1.7 electrons for S corresponds to a bonding description between C=S‖ (1 e−) and C–S ||| (2 e−). As the π charge on S increases with donating groups, structure **13** is favoured; while the average charge of 1.4 on N increases with withdrawing groups, favouring structure **11** (plot of Mulliken π orbital charge on the N atom to C=N bond length, A, linear, $r^2 = 0.9092$, slope 0.149 91, intercept 0.945 03).

Triple bonds are more reactive than double bonds in 1,3-dipolar cycloadditions. Hence we envisage that form **13** enters the cycloaddition to favour **4** and ultimately the products **5** while products **3** arise from cycloaddition where form **11** is favoured. Plots of Hammett σ and enhanced σ constants against CS and CN bond lengths give rather good correlations considering that one is plotting reactivity indices with minute changes in bond length measured in the thousandths of angstroms (plot of Hammett σ values to C=S bond length, r^2, 0.9668, slope, −0.009 423 9, intercept 1.596 93; plot of Hammett σ values to C=N length, r^2, 0.9502, slope 0.003 160 8, intercept 1.159 10). For the product ratios there seems to be a better correlation with the ordinary σ values than with the enhanced ones but the synthetic yields are subject to ±1% errors. However the total charge contributed from the σ and perpendicular π systems as well as the conjugated π system (where the extra resonance effect of a *para* substituent manifested in enhanced Hammett values) may need to be accounted for in these linear cumulene systems.

Experimental

Mps were measured on an Electrothermal apparatus. IR spectra were measured with a Perkin-Elmer 983G spectrophotometer. NMR spectra were measured on JEOL JNM-GX270 and GXFT400 instruments with tetramethylsilane as internal reference and deuteriochloroform or hexadeuteriodimethyl sulfoxide as solvent. NMR assignments were supported by decoupled, off-resonance decoupled and DEPT spectra. *J* Values are given in Hz. Microanalyses were measured on a Perkin-Elmer model 240 CHN analyser. The 1,3-dipole substrates **1** [19,20] were prepared as previously described. The following are typical examples.

Reaction of *N*,2-diphenyl-4,5,6,7-tetrahydro-2*H*-benzo[1,2,3]-triazol-1-ium-1-aminide with phenyl isothiocyanate (Entry 3, Table 1)

A solution of **1** [R,R = $(CH_2)_4$] (0.5 g, 1.72 mmol) in dry acetone was treated with phenyl isothiocyanate (0.22 ml, 1.8 mmol), stirred at room temperature for 2 h, evaporated under reduced pressure and the residue, in dichloromethane (3 ml), placed on a silica gel column (230–400 mesh, ASTM) and eluted with a gradient mixture of petrol (bp 40–60 °C)–diethyl ether. The first product from the column was 2,6-*diphenyl*-5-*phenylimino*-3a,5,6,6a-*tetrahydro*-3a,6a-*butano*-3H-*thiazolo*[4,5-d][1,2,3]*triazol*-2-*ium*-3-*ide* **3c** (0.42 g, 58%); mp 140–142 °C (EtOH) (Found: C, 70.2; H, 5.2; N, 16.4. $C_{25}H_{23}N_5S$ requires C, 70.5; H, 5.4; N, 16.5%); $\delta_H(CDCl_3)$ 1.13, 1.89, 2.15, 2.75 (8H, 4 × m, cyclohexyl, 4 CH_2), 6.80–6.83 (2H, d, H_o of 5-imino Ph, *J* 8.1), 6.88–7.6 (11H, m, aromatic protons), 8.06–8.09 (2H, d, H_o of 2-N-Ph, *J* 7.3); $\delta_C(CDCl_3)$ 88.1, 95.4 (C-3a, C-6a resp.), 18.05, 21.3, 30.1, 34.35 $(CH_2)_4$, 140.8, 122.5, 128.9, 129.3 (C-1′, C-2′, C-3′ and C-4′ resp. of 2-N-Ph), 139.2, 121.8, 127.6, 129.1 (C-1′, C-2′, C-3′ and C-4′ resp. of 6-N-Ph), 151.8, 123.3, 128.6, 131.8 (C-1′, C-2′, C-3′ and C-4′ resp. of 5-imino Ph), 157.9 (C=N).

The second product eluted off the column was 2,4,6-triphenyl-5-thioxo-3,3a,4,5,6,6a-hexahydro-3a,6a-butanoimidazolo[4,5-*d*][1,2,3]triazol-2-ium-3-ide **5c** (0.22 g, 30%); mp 211–212 °C (EtOH) (lit.,[13] mp 211–212 °C) (Found: C, 70.1; H, 5.8; N, 16.7. Calc. for $C_{25}H_{23}N_5S$: C, 70.5; H, 5.4; N, 16.5%); $\delta_H(CDCl_3)$ 1.48–1.69 (4H, m, cyclohexyl protons), 1.89–2.13 (4H, m, cyclohexyl protons), 7.23–7.62 (13H, m, aromatics), 8.21–8.24 (2H, d, H_o of 2-N-Ph, *J* 7.7); $\delta_C(CDCl_3)$ 93.3 (C-3a, C-6a), 17.3, 27.9 $(CH_2)_4$, 137.4, 129.6, 128.9, 132.3 (C-1′, C-2′, C-3′ and C-4′ resp. of 2-N-Ph), 140.1, 128.3, 129.2, 122.7 (C-1′, C-2′, C-3′ and C-4′ resp. of 4- and 6-N-Ph), 181.1

(C=S); $\delta_{^{15}N}(CDCl_3)$ −60.7 (N-1, N-3), −89.7 (N-2), −234.2 (N-4, N-6).

Reaction of *N*,2,4,5-tetraphenyl-2*H*-[1,2,3]triazol-1-ium-1-aminide with phenyl isothiocyanate (Entry 7, Table 1)

A solution of **1** (R = Ph) (0.5 g, 1.29 mmol) in dry acetone (10 ml) was treated with phenyl isothiocyanate (0.17 ml, 1.4 mmol), stirred at room temperature for 4 h, evaporated under reduced pressure and the residue, in dichloromethane (3 ml), placed on a silica gel column (230–400 mesh ASTM) and eluted with a petrol (bp 40–60 °C)–diethyl ether gradient mixture. The first product from the column was 2,3a,6,6a-*tetraphenyl*-5-*phenylimino*-3a,5,6,6a-*tetrahydro*-3H-*thiazolo*[4,5-d][1,2,3]-*triazol*-2-*ium*-3-*ide* **7c** (0.35 g, 52%); mp 126–128 °C (EtOH) (Found: C, 75.8; H, 4.7; N, 12.9. $C_{33}H_{25}N_5S$ requires C, 75.7; H, 4.8; N, 13.4%); $\delta_H(CDCl_3)$ 8.18–8.21 (2H, d, H_o of 2-N-Ph, *J* 7.3), 6.93–7.69 (23H, m, aromatic protons); $\delta_C(CDCl_3)$ 94.7 and 103.1 (C-3a and C-6a), 152.2, 146.4, 140.6, 140.3, 132.8, 130.0, 129.7, 129.1, 128.9, 128.6, 128.4, 128.2, 128.1, 126.7, 126.1, 124.7, 124.0, 123.3, 122.4 and 119.2 (aromatics), 157.7 (N=C).

The second product off the column was 2,3a,4,6,6a-pentaphenyl-5-thioxo-3,3a,4,5,6,6a-hexahydroimidazolo[4,5-*d*]-[1,2,3]triazol-2-ium-3-ide **9c** (0.31 g, 46%); mp 265–266 °C (EtOH) (lit.,[13] mp 265–266 °C) (Found: C, 75.8; H, 4.9; N, 13.05. Calcd. for $C_{33}H_{25}N_5S$: C, 75.7; H, 4.8; N, 13.4%); $\delta_H(CDCl_3)$ 8.48–8.51 (2H, d, H_o of 2-N-Ph, *J* 7.3), 6.97–7.68 (23H, m, aromatics); $\delta_C(CDCl_3)$ 101.1 (C-3a and C-6a), 139.9, 138.5, 135.2, 132.8, 129.5, 129.2, 128.5, 127.8, 127.7, 127.6, 127.5 and 122.9 (aromatics), 185.0 (C=S).

Reaction of 9,10-bis(phenylazo)phenanthrene with *p*-bromophenyl isothiocyanate (Entry 12, Table 1)

A solution of 9,10-bis(phenylazo)phenanthrene (0.4 g, 1.04 mmol) in dry toluene (20 ml) was treated with *p*-bromophenyl isothiocyanate (0.67 g, 3.12 mmol), stirred at 90 °C for 40 h, evaporated under reduced pressure and the residue, in dichloromethane (3 ml), placed on a silica gel column (230–400 mesh ASTM) and eluted with a gradient mixture of petrol (bp 40–60 °C)–dichloromethane (1:0–1:1.5 *v*/*v*). The first product from the column was 2-phenyl-2*H*-phenanthreno[9,10-*d*]-triazole (16%). The next product eluted off the column was 6-(p-*bromophenyl*)-2,4-*diphenyl*-*5*-*thioxo*-3,3a,4,5,6,6a-*hexahydro*-3a,6a-(*biphenyl*-2,2′-*diyl*)*imidazolo*[4,5-d][1,2,3]*triazol*-2-*ium*-3-*ide* **10f** (0.28 g, 46%), mp 238–239 °C (MeCN) (Found: C, 66.4; H, 3.8; N, 11.5. $C_{33}H_{22}N_5SBr$ requires C, 66.0; H, 3.7; N, 11.7%); $\delta_H(CDCl_3)$ 7.15 and 7.92 (4H, 2 × d, H_m and H_o, resp. of 6-N-C_6H_4Br, AA′BB′, J_{AB} 8.6), 6.80–7.53 (16H, m, aromatics), 8.24 (2H, d, H_o of 2-N-Ph); $\delta_C(CDCl_3)$ 93.8 (C-3a), 94.1 (C-6a), 139.8, 122.7, 128.9 and 128.2 (C-1′, C-2′, C-3′ and C-4′ of 2-N-Ph), 137.5, 123.5, 129.1 and 129.4 (C-1′, C-2′, C-3′ and C-4′ of 4-N-Ph), 136.6, 123.6, 129.6 and 123.0 (C-1′, C-2′, C-3′ and C-Br of 6-N-C_6H_4Br), 182.6 (C=S), remaining aromatics; 127.7, 129.7, 129.9, 131.4, 132.2, 132.4 and 133.2. One signal overlapped in the 129–132 ppm region.

This was followed from the column by 5-(p-*bromophenyl*-*imino*)-2,6-*diphenyl*-3a,5,6,6a-*tetrahydro*-3H-3a,6a-(*biphenyl*-2,2′-*diyl*)*thiazolo*[4,5-d][1,2,3]*triazol*-2-*ium*-3-*ide* **8f** (0.14 g, 22%), mp 210–212 °C (MeCN) (Found: C, 66.1; H, 3.6; N, 11.5. $C_{33}H_{22}N_5SBr$ requires C, 66.0; H, 3.7; N, 11.7%); $\delta_H(CDCl_3)$ 6.78 and 7.93 (4H, 2 × d, H_m and H_o resp. of 5-imino-N-C_6H_4Br, AA′BB′, J_{AB} 8.2), 7.02–7.52 (16H, m, aromatics), 8.10 (2H, d, H_o of 2-N-Ph); $\delta_C(CDCl_3)$ 91.4 (C-3a and C-6a), 140.4, 122.9, 129.1 and 127.6 (C-1′, C-2′, C-3′ and C-4′ of 2-N-Ph), 137.6, 123.6, 128.5 and 129.9 (C-1′, C-2′, C-3′ and C-4′ of 4-N-Ph), 137.1, 123.7, 127.9 and 112.9 (C-1′, C-2′, C-3′ and C-Br of 5-imino-N-C_6H_4Br), 149.5 (C=N), remaining aromatics; 124.4, 129.5, 129.7, 130.4, 131.4, 131.7, 132.2 and 133.0.

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