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PAPER

Some cyclization reactions of 1,3-diphenylbenzo[e][1,2,4]triazin-7(1H)-one: preparation and computational analysis of non symmetrical zwitterionic biscyanines[†]

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Regioselective nucleophilic addition of bisnucleophiles 1,2-benzenediamine, 2-amino-benzenethiol, and *N*-phenyl-1,2-benzenediamine to 1,3-diphenylbenzo[*e*][1,2,4]triazin-7(1*H*)-one (1) at C6 followed by intramolecular cyclocondensation at the C7 carbonyl afforded highly coloured tetracenes 1,3-diphenyl-1,6-dihydro-[1,2,4]triazino[5,6-*b*]phenazin-4-ium 4-methylbenzenesulfonate (12), 1,3-diphenyl-1*H*-[1,2,4]triazino[6,5-*b*]phenothiazine (14) and 1,3,11-triphenyl-1,6-dihydro-[1,2,4]-triazino[5,6-*b*]phenazin-11-ium 4-methylbenzenesulfonate (15), respectively. Neutralization of the latter with alkali gave the free base 1,3,11-triphenyl-1*H*-[1,2,4]triazino[5,6-*b*]phenazin-11-ium-6-ide (16). Furthermore, the benzotriazinone 1 reacts with dimethyl malonate to give 6-(methoxycarbonyl)-7-oxo-1,3-diphenyl-1,2,4-benzotriazine (22) was formed in 15% yield. The free base 16 and 17 display negative solvatochromism, which supports charge separated ground states similar to those of zwitterionic biscyanines, and DFT calculations at the UB3LYP/6-31G(d) level afford ΔE_{sT} values of -13.6 and -18.7 kcal mol⁻¹, respectively that strongly favour the singlet ground state. All ring systems described are new and fully characterized.

1. Introduction

1,3-Diphenylbenzo[*e*][1,2,4]triazin-7(1*H*)-one (1) is a potentially useful heterocyclic scaffold that is highly coloured (λ_{max} 544 nm), and supports a quinonimine moiety. It was originally prepared in low yield (1–5%) by Neugebauer *et al.*,¹ preventing an in depth study of its potentially rich chemistry. However, by treating amidrazone **2** with KMnO₄,² or benzotriazinyl radical **3** with MnO₂,³ the benzotriazinone **1** can be prepared in high yields of 82 and 84%, respectively (Scheme 1).



Some chemistry of the benzotriazinone **1** has recently been reported:^{4,5} benzotriazinone **1** undergoes nucleophilic addition regioselectively at C6, and electrophilic substitution regio-selectively



at the C8 position,⁴ however, direct condensations on the car-

bonyl at C7 using primary amines or active methylenes failed.

Nevertheless, the ylidenemalononitrile 4 could be prepared in

low yield using either tetracyanoethene (TCNE) or tetracya-

noethylene oxide (TCNEO).⁴ Furthermore, oxidative and non-

oxidative silver-mediated palladium catalysed cyclizations at C8

afford the triazafluoranthenone 5⁵ that is structurally similar to

the canthinone alkaloids^{6,7} (Scheme 2).

Tentatively, the failure to perform condensation chemistry at the C7 carbonyl was attributed to the strong contribution of a zwitterionic resonance form (Scheme 3).⁴

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[†] Electronic supplementary information (ESI) available: ¹H and ¹³C NMR spectra for all new compounds and computational parameters for compounds **16–18**. See DOI: 10.1039/c1ob06622f



Scheme 3

In this paper we report a regioselective nucleophilic addition of bisnucleophiles at C6 and their subsequent intramolecular cyclocondensation at C7 to afford new fused heterocycles, two of which support zwitterionic motifs. Furthermore, we demonstrate a successful cycloaddition reaction across the C5–C6 double bond.

2. Results and discussion

Reactions with primary anilines

Intermolecular condensations of anilines or active methylenes with benzotriazinone **1** failed to give the desired C7 condensation products.⁴ Interestingly we had previously encountered similar difficulties in performing intermolecular condensation reactions with 3,5-dichloro-4H-1,2,6-thiadiazin-4-one **6**⁸ but found that reacting the thiadiazinone with bisnucleophiles like 1,2-benzenediamine (*ortho*-phenylenediamine) afforded the monochloro-monoaminothiadiazinone **7** which readily underwent intramolecular cyclocondensation to give the deep purple coloured quinazoline **8** (Scheme 4).⁹ In light of benzotriazinone's regioselective nucleophilic addition at C6⁴ a similar strategy could also lead to intramolecular condensations at the benzotriazinone's C7 carbonyl.



Ethanol solutions of benzotriazinone **1** were treated with a range of bisnucleophiles (1,2-benzenediamine, *N*-phenylbenzene-1,2-diamine and 2-aminobenzenethiol) and *N*-ethyl-*N*-isopropylpropan-2-amine (Hünig's base) (1.1 equiv.) and heated to reflux. In the first three cases the expected C6 substituted benzotriazinones **9–11** were obtained as highly coloured compounds.The reaction of 1,2-benzenediamine gave the orange coloured 6-(2-amino-phenylamino)-1,3-diphenylbenzo[*e*][1,2,4]triazin-7(1*H*)-one (**9**) (λ_{max} 431 nm) in 75% yield (Table 1, entry 1),

Table 1Reaction of benzotriazinone 1 with bisnucleophiles (2 equiv.)and i-Pr2NEt (1.1 equiv.) in EtOH at ca. 78 °C

NHR ¹	+	$\overset{Ph}{\swarrow}_{N}\overset{Ph}{\swarrow}_{Ph} \longrightarrow \overset{O}{\swarrow}_{N}\overset{Ph}{\swarrow}_{N}\overset{Ph}{\swarrow}_{N}$		Ph N N N Ph
		1		9-11
Entry	\mathbb{R}^1	Х	Time (h)	Yield (%)
1	Н	NH	25	9 (75)
2	Ph	NH	48	10 (51)
3	Η	SH	22	11 (99)

while the red coloured 1,3-diphenyl-6-[2-(phenylamino)phenylamino]-benzo[e][1,2,4]triazin-7(1H)-one (10) (λ_{max} 430 nm) was isolated from the reaction mixture of benzotriazinone 1 and *N*-phenylbenzene-1,2-diamine in a more moderate yield (51%) (Table 1, entry 2). The reaction of benzotriazinone 1 with 2-aminobenzenethiol gave the brown coloured 6-(2aminothiophenyl)-1,3-diphenylbenzo[e][1,2,4]triazin-7(1H)-one (11) (λ_{max} 520 nm) in 99% yield (Table 1, entry 3).

Subsequent treatment of substituted benzotriazinones 9–11 with TsOH·H₂O (1 equiv.) in EtOH heated at reflux for 10 or 20 min gave the expected cyclization products either as the tosylates or, when treated with aqueous alkali, as the free bases. In the absence of an alkali work up the reaction of benzotriazinone 9 with TsOH·H₂O gave 1,3-diphenyl-1,6-dihydro-[1,2,4]triazino[5,6-*b*]phenazin-4-ium 4-methylbenzenesulfonate (12) that readily precipitated from the reaction mixture on cooling and was isolated by filtration as deep blue needles (λ_{max} 560 nm) in 78% yield. Alkali (10% NaOH) treatment of this reaction mixture gave the free base 1,3-diphenyl-1,6-dihydro-[1,2,4]triazino[5,6-*b*]phenazine (13), giving correct elemental analysis, however, ¹H and ¹³C NMR spectroscopy in either CDCl₃, DMSO-*d*₆ or TFA-*d*₁, failed to give good spectra owing to poor solubility.

Similar treatment of 6-(2-aminothiophenyl)-1,3-diphenylbenzo[*e*][1,2,4]triazin-7(1*H*)-one (**11**) with TsOH·H₂O (1 equiv.), followed by a basic work-up (10% NaOH) gave 1,3-diphenyl-1*H*-[1,2,4]triazino[6,5-*b*]phenothiazine (**14**) as green needles (λ_{max} 674 nm) in 82% yield (Scheme 5).



On other hand, the reaction of 1,3-diphenyl-6-[2-(phenylamino)phenylamino]benzo[*e*]-[1,2,4]triazin-7(1*H*)-one (**10**) with TsOH·H₂O (1 equiv.) in EtOH heated at *ca.* 78 °C for 10 min gave 1,3,11-triphenyl-1,6-dihydro-[1,2,4]triazino[5,6-*b*]phenazin-11-ium 4-methylbenzenesulfonate (**15**) as blue needles (λ_{max} 620 nm) in 99% yield. Elemental analysis and ¹H NMR spectroscopy indicated that this compound co-crystallized with EtOH in a ratio of compound : EtOH (2 : 1). By treating the reaction mixture with a 10% solution of KOH, the free base 1,3,11-triphenyl-1*H*-[1,2,4]triazino[5,6-*b*]phenazin-11-ium-6-ide (**16**) could be isolated as blue needles (λ_{max} 635 nm) in 87% yield (Scheme 6). Interestingly, this compound showed negative solvatochromism¹⁰ (Fig. 1) typical of zwitterionic biscyanines.¹¹⁻¹⁸

A number of zwitterionic biscyanines have been reported in the recent literature and all have been symmetrical,¹¹⁻¹⁸ as such this compound is a rare example of a non symmetrical biscyanine. DFT studies [UB3LYP/6-31G(d)] indicated the molecule strongly preferred the singlet over the possible triplet ground state (ΔE_{ST} -13.6 kcal mol⁻¹). The HOMO and LUMO are similar to those reported for other zwitterionic biscyanines (Fig. 2) and a plot of electrostatic surface potentials (ESP) supports the molecule being charge separated as a biscyanine (Fig. 3).







Fig. 1 Correlation between solvent polarity $E_{\rm T}(30)^{19}$ and the maximum π - π^* absorption of 1,3,11-triphenyl-1*H*-[1,2,4]triazino[5,6-*b*]-phenazin-11-ium-6-ide (16) (n = 8; $r^2 = 0.94$; slope = -1.59).



Fig. 2 HOMO (-4.35 eV) and LUMO (-2.25 eV) orbitals of 1,3,11-triphenyl-1*H*-[1,2,4]triazino[5,6-*b*]phenazin-11-ium-6-ide (**16**) [DFT UB3LYP/6-31G(d)].

Furthermore, bond length analysis of the DFT [UB3LYP/6-31G(d)] computed ground state structure showed that the two proposed cyanine fragments were separated by relatively long C– C bonds (C5a–C11a, 146.6 and C4a–C12a, 145.9 pm) typical of zwitterionic biscyanines (Fig. 4).^{11–18} Nucleus independent chemical shift (NICS) values of the individual rings that comprise the [1,2,4]triazino[5,6-*b*]phenazine **16** supported the central benzene (ring *C*) being markedly less aromatic than the peripheral arene [NICS (1) (ring *A*) –8.3 vs. NICS (1) (ring *C*) –3.5] (Table 2).

However, since negative NICS (1) values are indicative of aromaticity we also calculated the harmonic oscillator model of



Fig. 3 The electrostatic potential (ESP) mapped on the electron density surface of 1,3,11-triphenyl-1H-[1,2,4]triazino[5,6-b]phenazin-11-ium-6-ide (16) [DFT UB3LYP/6-31G(d)].

Table 2 NICS (0) and NICS (1) values for rings A, B, C and D calculated at the B3LYP/6-31G* level for the singlet ground state of the [1,2,4]triazino[5,6-b]phenazine **16**



Fig. 4 Compound numbering and selected bond lengths (pm).

aromaticity (HOMA)²⁰ value for ring *C* (HOMA = 0.47) that is based only on geometric parameters and indicated a low level π -orbital overlap within ring *C* as expected for a zwitterion biscyanine. HOMA is defined as a normalized sum of squared deviations of bond lengths from the optimal value assumed for a fully aromatic system and a fully aromatic system has a HOMA = 1 and a non-aromatic HOMA = 0.

The UV-vis spectrum of monoprotonated 1,3,11-triphenyl-1,6-dihydro-[1,2,4]triazino[5,6-b]phenazin-11-ium 4-methylbenzenesulfonate (15) (H⁺/EtOH, λ_{max} 613 nm) showed a blue shift of the low energy π - π * transitions (~10 nm) when compared to the free base 1,3,11-triphenyl-1H-[1,2,4]triazino[5,6-b]phenazin-11-ium-6-ide (16) (EtOH, λ_{max} 624 nm) (Fig. 5). Similar blue shifts have been observed on mono and bis protonation of zwitterionic quinoxalino[2,3-b]phenazines^{11,12} and we found that careful addition of (37%) HCl to an EtOH solution of the free base 16 gave the monoprotonated species, which showed a very similar UV-vis spectra (H⁺/EtOH, λ_{max} 613 nm) to the *p*-toluenesulfonate salt 15. Addition of an excess (69-72%) perchloric acid gave no bisprotonation since the same UV-vis spectrum was recorded [H⁺/EtOH, λ_{max} 613 nm). The failure to bisprotonate in perchloric acid differed from that of the quinoxalino[2,3-b]phenazines,^{11,12} indicating that the triazino system was by comparison less basic.

Reactions with active methylenes

Our earlier work⁴ attempts to condense malononitrile with the benzotriazinone **1** led to complex highly coloured reaction mixtures, from which no stable product could be isolated. Similar complex reaction mixtures were obtained with another active methylene ethyl 2-cyanoacetate, however, the reaction of benzotriazinone **1** with dimethyl malonate (1.04 equiv.) in the presence of Hünig's



Fig. 5 A comparison of the absorption spectra of the free base 1,3,11-triphenyl-1*H*-[1,2,4]triazino[5,6-*b*]phenazin-11-ium-6-ide (16) (λ_{max} 624 nm) and the monoprotonated 1,3,11-triphenyl-1,6-dihydro-[1,2,4]triazino[5,6-*b*]phenazin-11-ium 4-methylbenzenesulfonate (15) (λ_{max} 613 nm) in ethanol.

base (1 equiv.) gave 6-(methoxycarbonyl)-7-oxo-1,3-diphenyl-7*H*-benzofuro[5,6-e][1,2,4]triazin-1-ium-4-ide (17) in 74% yield (Scheme 7).



6-(Methoxycarbonyl)-7-oxo-1,3-diphenyl-7*H*-benzofuro[5,6-*e*] [1,2,4]triazin-1-ium-4-ide (**17**) is deep blue green in solution (λ_{max} 629 nm) suggesting a high degree of conjugation and displayed negative solvatochromism¹⁰ typical of a charge separated ground state (Fig. 6).¹⁹ The compound crystallized as green needles and



Fig. 6 Correlation between solvent polarity $E_{\rm T}(30)^{19}$ and the maximium π - π^* absorption of 6-(methoxycarbonyl)-7-oxo-1,3-diphenyl-7*H*-benzofuro[5,6-*e*][1,2,4]triazin-1-ium-4-ide (17) (n = 8; $r^2 = 0.93$; slope = -2.42).

gave a correct elemental analysis for the formula $C_{23}H_{15}N_3O_4$, which supported a molecular parent ion of m/z 397 Da (100%) from EI mass spectrometry. FTIR spectroscopy indicated the presence of a methyl ester group with a moderately strong carbonyl stretch at v(C=O) 1761 cm⁻¹ and this was also supported by ¹H and ¹³C NMR spectroscopy which showed the presence of a single methoxy group at δ_H 3.92 ppm and δ_C 51.7 ppm. Furthermore, NMR spectroscopy indicated the absence of the H6 benzotriazinone hydrogen and the presence of at least 10 quaternary *C* signals. The data was in agreement with the proposed fused furanone structure.

As such this compound was potentially an additional rare example of a non symmetrical biscyanine. DFT studies [UB3LYP/6-31G(d)] indicated the molecule strongly preferred the singlet over the possible triplet ground state (ΔE_{sT} –18.7 kcal mol⁻¹). The HOMO and LUMO are similar to those reported for other zwitterionic biscyanines (Fig. 7), however, the plot of electrostatic surface potential (ESP) (Fig. 8) suggests considerable positive charge is located at the triazine and that considerable negative charge is located near the furanone.



Fig. 7 HOMO (-6.61 eV) and LUMO (-3.36 eV) orbitals of 6-(methoxy-carbonyl)-7-oxo-1,3-diphenyl-7*H*-benzofuro[5,6-*e*][1,2,4]triazin-1-ium-4-ide (**17**) [DFT UB3LYP/6-31G(d)].



Fig. 8 The electrostatic surface potential (ESP) mapped on the electron density surface of 6-(methoxycarbonyl)-7-oxo-1,3-diphenyl-7*H*-benzofuro [5,6-*e*][1,2,4]triazin-1-ium-4-ide (**17**) [DFT UB3LYP/6-31G(d)].

In light of the ESP data, the zwitterionic biscyanine motif may not account fully for the structure of this zwitterion. An analysis of the bond lengths and NICS values of the DFT [UB3LYP/6-31G(d)] computed ground state structure showed somewhat

Table 3NICS (0) and NICS (1) values for rings A, B, and C calculated atthe B3LYP/6-31G* level for the singlet ground state of the benzofuro[5,6-e][1,2,4]triazin-7(4H)-one 17

	A	В	С
NICS (0)	-5.2	-6.1	-3.3
NICS (1)	-5.0	-8.0	-6.7

conflicting information: the two C–C bonds that separated the possible cyanine fragments were separated by relatively long C–C bonds (C5a–C8a, 145.4 and C4a–C9a, 147.0 pm) typical of zwitterionic biscyanines.^{11–18} However, NICS values of the individual rings that comprise the tricycle supported the central benzene (ring *B*) being markedly aromatic [NICS (1) (ring *B*) –8.0] and in contrast to the [1,2,4]triazino[5,6-*b*]phenazine **16** which had a non-aromatic triazine ring [Fig. 4, Table 2, NICS (1) (ring *D*) +3.4] the NICS (1) value of the triazine ring of the benzofuro[5,6-*e*][1,2,4]triazin-7(4*H*)-one **17** was clearly of opposite sign and mildly aromatic [NICS (1) (ring *C*) –6.7] (Fig. 9, Table 3).



Fig. 9 Compound numbering and selected bond lengths (pm).

As before, we calculated the HOMA²⁰ value for the central arene (HOMA, ring B = 0.48) which was similar to that determined for the equivalent central arene in the [1,2,4]triazino[5,6-*b*]phenazine **16** (HOMA, ring C = 0.47) and supported a low level π -orbital overlap within ring C as expected for a zwitterion biscyanine. In light of this we propose that the benzofuro[5,6-*e*][1,2,4]triazin-7(4*H*)-one **17** is probably best represented by the biscyanine motif but that there may very well be a significant contribution of resonance structure **17a** (Scheme 8).



As a final consideration of the nature of the charge separation in compounds **17** we calculated and compared the dipoles (magnitude and vector) for both zwitterions **16** and **17** from the computational structures (Fig. 10).

Perfectly symmetrical zwitterionic biscyanines such as the 5,7-diphenylquinoxalino[2,3-*b*]phenazine $18^{11,12}$ are expected to have a dipole moment that lines up with the *y*-axis (Fig. 10), and contributions of non-biscyanine charge separated resonance forms such as that depicted in structure 17a should lead to the dipole moment deviating from the *y*-axis. As can be seen, the calculated dipole moments of both structures 16 and 17 (Fig. 10) deviate from the *y*-axis, the former showing only a minor deviation, and the latter showing a considerable deviation. This adds further support for there being a reasonable



Fig. 10 Dipole moments of 5,7-diphenylquinoxalino[2,3-*b*]phenazine 18, the [1,2,4]triazino[5,6-*b*]phenazine 16 and the benzofuro [5,6-*e*][1,2,4]triazin-7(4*H*)-one 17 expressed as vectors orientated to an imaginary *y*-axis to enable direct comparison. Charges are fitted to the ESP calculated at the B3LYP/6-31G(d) level and constrained to reproduce the dipole moment.^{21,22}

contribution of a charge separated non-biscyanine resonance form in compound 17 (*cf.* structure 17a) and only a minor one in compound 16, in line with the calculated electrostatic surface potentials (Fig. 3 and 8).

Interestingly, the reaction between dimethyl malonate and the benzotriazinone **1** to give the benzofuro[5,6-e][1,2,4]triazin-7(4*H*)one **17** could occur *via* two different pathways: (Path A) the dimethyl malonate could regioselectively add to the benzotriazinone at C6 to give intermediate **19** and subsequent intramolecular cyclization could occur *via* the benzotriazinone carbonyl, which was expected to be strongly nucleophilic owing to the strong contribution of the benzotriazinone's zwitterionic resonance forms; or (Path B) the reverse could occur, with the dimethyl malonate reacting first with the carbonyl to give intermediate **20** followed by an intramolecular cyclization onto the benzotriazinone C6 position (Scheme 9).

At this stage we are unable to differentiate between these two mechanistic possibilities and this cyclization is now under further investigation.

This new fused heterocycle has structural similarities with benthocyanins **21** (Scheme 10) that act as inhibitors of lipid peroxidation in rat microsomes²³ and also showed inhibitory effects on rat erythrocyte hemolysis;²⁴ as such the benzofurotriazine **17** and related compounds could also show promising biological properties.

Reaction of benzotriazinone 1 with S_4N_4

To check if the double bond between C5 and C6 on the benzotriazinone **1** was susceptible to cycloaddition reactions, benzotriazinone **1** was reacted with various enophiles: the reaction with phenyl azide gave only complex mixtures, while N,N'-bis(trimethylsilyl)sulfur diimide in DMF at *ca*. 100 °C for 12 h gave only 6-aminobenzotriazinone and unreacted starting material (by TLC). Fortunately, the reaction of benzotriazinone **1** with S₄N₄ (5 equiv.) in DMF at reflux 1 h gave the cyclized [5,6-*c*]thiadiazolo-7-oxo-1,3-diphenyl-1,2,4-benzotriazine (**22**) (15%) together with





6-amino-1,2,4-benzotriazinone **23** in 48% yield (Scheme 11). The alternative use of PhCl or xylene as solvents gave very complex reactions, while with PhMe only starting material was recovered from the reaction.



Compound **22** was brown in solution (λ_{max} 541 nm), tentatively indicating the extensive conjugation of the starting quinonimine had been maintained, and was isolated as brown needles that gave a correct elemental analysis for the formula C₁₉H₁₁N₅OS, which supported a molecular parent ion of m/z 357 Da (47%) from EI mass spectrometry. ¹H and ¹³C NMR spectroscopy indicated the absence of the H5 and H6 benzotriazinone hydrogens and the replacement of two aromatic *C*H for two quaternary *C* assignments supporting functionalization at the C5 and C6 carbon positions. The data was in agreement with the proposed fused 1,2,5-thiadiazole structure.

The mechanism of the reaction of S_4N_4 with activated double and triple bonds is based on the reagent's ability to cyclo-add and subsequently fragment to give thermodynamically stable heteroarenes such as 1,2,5-thiadiazoles.^{25,26} Rees and Daley^{27,28} have conducted extensive studies on these reactions. It is known²⁹ that in the reactions with S_4N_4 , elemental sulfur and ammonia are nearly always formed as side products and the presence of the latter could explain the formation of the 6-aminobenzotriazinone **23**, which can be prepared directly from ammonia and benzotriazinone **1**.⁴

3. Conclusions

1,3-Diphenylbenzo[e][1,2,4]triazin-7(1H)-one (1) reacts with bisnucleophiles, 1,2-benzenediamine, 2-aminobenzenethiol and N-phenyl-1,2-benzenediamine, regioselectively at C6 and these adducts on treatment with TsOH·H2O undergo intramolecular cyclocondensation at the C7 carbonyl to afford highly coloured tetracenes 1,3-diphenyl-1,6-dihydro-[1,2,4]triazino[5,6-b]phenazin-4-ium 4-methylbenzenesulfonate (12), 1,3-diphenyl-1*H*-[1,2,4]triazino[6,5-*b*]phenothiazine (14) and 1,3,11-triphenyl-1,6-dihydro[1,2,4]triazino-[5,6-b]phenazin-11ium 4-methylbenzenesulfonate (15), respectively. Neutralization of the latter with alkali gave the free base 1,3,11-triphenyl-1H-[1,2,4]triazino[5,6-b]phenazin-11-ium-6-ide (16). A similar cyclo-condensation reaction occurred between dimethyl malonate and benzotriazinone 1 affording 6-(methoxycarbonyl)-7-oxo-1,3-diphenyl-7*H*-benzofuro[5,6-*e*][1,2,4]triazin-1-ium-4-ide (17) in 74% yield. Finally, an intermolecular cycloaddition across the C5–C6 bond of benzotriazinone 1 with S_4N_4 gave [5,6*c*]thiadiazolo-7-oxo-1,3-diphenyl-1,2,4-benzotriazine (22)in 15% yield. The free bases 16 and 17 are zwitterions and DFT calculations at the UB3LYP/6-31G(d) level afford ΔE_{sT} values of -13.6 and -18.7 kcal mol⁻¹, respectively that strongly favour the singlet ground state.

4. Experimental

4.1. Computational procedure

The geometries of the singlet and triplet states of molecules **16–18** were fully optimized, and analytical second derivatives were computed using vibrational analysis to confirm each stationary point to be a minimum by yielding zero imaginary frequencies at the UB3LYP/6-31G(d) level of theory. The possibility of internal instability in the singlet wave function was investigated using stability calculations. All the energies were corrected after zero-point energies (ZPE) were scaled by 0.981.³⁰ All the above computations were performed using the Gaussian 03 suite of programs.³¹

Nucleus independent chemical shifts (NICS) were evaluated by using the gauge invariant atomic orbital³² (GIAO) approach, at the B3LYP/6-31G* level. The NICS probes (bq's) were placed above the geometric centers of the systems at each ring at distances 0.0 Å

(*i.e.*, at the center of the molecular plane) and 1.0 Å perpendicular to the molecular plane.

HOMA²⁰ values for an all carbon system were calculated using eqn (1), where 257.7 is the normalization value, n = number of C–C bonds, $d_{opt} =$ the optimized bond length (138.8 pm)²⁰ and $d_i =$ the computed bond length from DFT calculations performed at the UB3LYP/6-31G(d) level of theory.

HOMA =
$$1 - 257.7/n \sum_{i}^{n} (d_{opt} - d_{i})^{2}$$
, (1)

Dipole moments of [1,2,4]triazino[5,6-b]phenazine **16** and benzofuro[5,6-e][1,2,4]triazin-7(4*H*)-one **17** and 5,7-diphenylquinoxalino[2,3-b]phenazine **18** are expressed as vectors, after ESP calculation on G03 at B3LYP/6-31G(d) level of theory to produce charges fit to the electrostatic potential at points selected according to the Merz-Singh-Kollman scheme^{21,22} and constrain them to reproduce the dipole moment [pop = (MK, dipole)]. The dipole moment vectors are visualized using GaussView 5.

4.2. General methods and materials

Solvents: DMF was azeotropically distilled with PhH then distilled under vacuum from anhydrous MgSO4 and stored over 4 Å molecular sieves. Reactions were protected by CaCl₂ drying tubes. Decomposition points (decomp.) and mp >250 $^{\circ}$ C were determined using a TA Instruments DSC Q1000 with samples hermetically sealed in aluminium pans under an argon atmosphere, using heating rates of 5 °C min⁻¹. Anhydrous Na₂SO₄ was used for drying organic extracts and all volatiles were removed under reduced pressure. All reaction mixtures and column eluents were monitored by TLC using commercial glass backed thin layer chromatography (TLC) plates (Kieselgel 60 F₂₅₄). The plates were observed under UV light at 254 and 365 nm. The technique of dry flash chromatography was used throughout for all non-TLC scale chromatographic separations using silica gel 60 (less than 0.063 mm).³³ Melting points were determined using a hotstage microscope apparatus. Solvents used for recrystallization are indicated after the melting point. Inflections in the UV spectra are identified by the abbreviation "inf". FTIR spectra were recorded using a Ge ATR accessory and strong, medium and weak peaks are represented by s, m and w respectively. ¹H NMR spectra were recorded at either 300 or 500 MHz and ¹³C NMR spectra were recorded at either 75 and 125 MHz, respectively. DEPT 135 or APT NMR studies identified quaternary and tertiary carbons, which are indicated by (s) and (d) notations, respectively. Deuterated solvents were used for homonuclear lock and the signals are referenced to the deuterated solvent peaks. Low resolution (EI) mass spectra were recorded on a GCMS with direct inlet probe.

4.3. Substitution at benzotriazinone C-6 position

4.3.1. 6-(**2**-Aminophenylamino)-**1,3**-diphenylbenzo[*e*][**1,2,4**]triazin-7(1*H*)-one (**9**). To a stirred solution of 1,3-diphenylbenzo[*e*][1,2,4]triazin-7(1*H*)-one (**1**) (214 mg, 0.72 mmol) in EtOH (8 ml), Hünig's base (136 μ L, 0.79 mmol) and phenylenediamine (155.5 mg, 1.44 mmol) were added and the reaction mixture was heated at reflux for 25 h. The reaction mixture was then allowed to cool to *ca*. 20 °C and the precipitate was filtered and washed with cold hexane to afford the *title compound* **9** (216.4 mg, 75%) as orange needles, mp 278–282 °C (from PhCl); $R_{\rm f}$ 0.23 (*t*-BuOMe); (found: C, 74.0, H, 4.6; N, 17.2. $C_{25}H_{19}N_5O$ requires C, 74.1; H, 4.7; N, 17.3%); $\lambda_{\rm max}$ (DCM)/nm 229 (log ε 3.46), 277 inf (3.52), 300 (3.53), 330 inf (3.28), 431 (3.10); $v_{\rm max}/cm^{-1}$ 3194m (Ar NH), 1631m, 1568m, 1542s, 1516m, 1489s, 1473m, 1455m, 1448m, 1393m, 1379m, 1313m, 1299m, 1272m, 990m, 766m, 747s; $\delta_{\rm H}$ (300 MHz, TFA- d_1) NH and NH₂ exchanged 8.18 (2H, d, *J* 7.7), 7.77–7.62 (9H, m), 7.57–7.52 (1H, m), 7.45 (2H, dd, *J* 7.5, 7.5), 7.18 (2H, dd, *J* 5.5, 5.1); $\delta_{\rm C}$ (75 MHz; TFA- d_1) 160.9 (*C*==O), 159.4 (s), 152.7 (s), 150.1 (s), 142.2 (s), 138.3 (s), 138.2 (s), 135.1 (d), 134.4 (d), 133.8 (d), 132.8 (d), 131.9 (d), 131.5 (s), 130.8 (d), 130.2 (d), 129.5 (d), 127.1 (s), 127.0 (d), 126.5 (d), 101.8 (d), 100.5 (d); *m*/*z* (EI) 406 (M⁺+1, 12%), 405 (M⁺, 39), 388 (100), 300 (11), 180 (13), 104 (7), 77 (36), 65 (12), 51 (10).

4.3.2. 1,3-Diphenyl-6-[2-(phenylamino)phenylamino]benzo[e]-[1,2,4]triazin-7(1H)-one (10). To a stirred solution of 1,3diphenylbenzo[e][1,2,4]triazin-7(1H)-one (1) (100 mg, 0.33 mmol) in EtOH (4 ml), at ca. 20 °C, protected with a CaCl₂ drying tube, N-phenylbenzene-1,2-diamine (123 mg, 0.67 mmol) and Hünig's base (64.7 μ l, 0.37 mmol) were added and the reaction mixture was refluxed for 48 h until no starting material remained (TLC). The reaction mixture was then diluted (DCM, 25 ml) and washed (5% HCl, 25 ml) to remove unreacted amine. The organic layer was separated, dried (Na₂SO₄) and adsorbed onto silica. Chromatography (t-BuOMe–DCM–hexane, 1:6:3) gave the title compound 10 (58.8 mg, 51%) as red needles, mp 243-245 °C (from PhH), R_f 0.80 (t-BuOMe); (found C, 77.4; H, 4.6; N, 14.4. $C_{31}H_{23}N_5O$ requires C, 77.3; H, 4.8; N, 14.5%); $\lambda_{max}(DCM)/nm$ 234 (log ε 3.39), 289 (3.62), 345 inf (3.06), 430 (3.22), 465 inf (3.20); v_{max} /cm⁻¹ 3200m (N–H), 3065w (Ar CH), 1589m, 1568m, 1549m, 1541m, 1514m, 1487s, 1456m, 1447m, 1396m, 1377m, 1315m, 1290m, 1277m, 989m, 745m, 714m; $\delta_{\rm H}$ (300 MHz, CDCl₃) 8.30 (1H, br s, NH), 8.26-8.22 (2H, m), 7.62-7.54 (5H, m), 7.48-7.40 (5H, m), 7.29-7.23 (3H, m), 7.08-7.02 (3H, m), 6.98-6.93 (2H, m), 6.19 (1H, s), 5.94 (1H, br s, NH); $\delta_{\rm C}$ (75 MHz, CDCl₃) one Ar C missing 173.4 (C=O), 153.1 (s), 152.6 (s), 150.1 (s), 142.5 (s), 141.8 (s), 138.9 (s), 136.2 (s), 135.2 (s), 130.3 (d), 130.2 (d), 130.1 (d), 129.5 (d), 128.7 (d), 127.7 (d), 127.1 (d), 126.1 (d), 125.4 (d), 122.0 (d), 121.5 (d), 119.3 (d), 118.1 (d), 98.7 (d), 94.6 (d); m/z(EI) 482 (M⁺+1, 6%), 481 (M⁺, 15), 464 (100), 389 (9), 207 (9), 180 (7), 167 (6), 77 (25), 51 (6).

4.3.3. 6 - (2 - Aminothiophenyl) - 1,3 - diphenylbenzo[e][1,2,4]triazin-7(1H)-one (11). To a stirred solution of 1,3diphenylbenzo[e][1,2,4]triazin-7(1H)-one (1) (107.2 mg, 0.36 mmol) in EtOH (4 ml), Hünig's base (69 µl, 0.39 mmol) and 2-aminothiophenol (89.8 mg, 0.72 mmol) were added and the mixture was heated at reflux for 22 h. The reaction mixture was then allowed to cool to ca. 20 °C and the precipitate was filtered and recrystallized to afford the title compound 11 (149.1 mg, 99%) as brown needles, mp >300 °C (from PhCl), $R_{\rm f}$ 0.34 (t-BuOMe-hexane, 3:1); (found: C, 71.2; H, 4.2; N, 13.2. C₂₅H₁₈N₄OS requires C, 71.1; H, 4.3; N, 13.3%); λ_{max}(DCM)/nm 234 (log ε 3.52), 271 inf (3.43), 323 (3.53), 413 (3.15), 520 (2.73), 566 inf (2.68), 602 inf (2.49); $v_{\text{max}}/\text{cm}^{-1}$ 3335w (Ar NH), 3201w (Ar NH), 3057w (Ar CH), 1588s, 1576s, 1554m, 1524s, 1511s, 1497s, 1492m, 1483m, 1452m, 1372m, 1314s, 1197m, 1142m, 1004s, 864m, 845m, 838m, 821m, 815m, 778m, 750s, 728m; $\delta_{\rm H}$ (300 MHz, TFA-d₁) NH₂ exchanged 8.32 (2H, d, J 8.0), 7.94–7.67 (9H,

m), 7.56–7.43 (3H, m), 7.40 (1H, s), 7.31 (1H, s); $\delta_{\rm C}$ (75 MHz, TFA- d_1) 164.1 (s), 163.0 (s), 152.3 (s), 151.3 (s), 142.2 (s), 140.6 (d), 138.2 (s), 135.8 (d), 135.2 (d), 134.7 (d), 134.3 (d), 133.6 (s), 132.8 (s), 132.0 (d), 130.7 (d), 129.7 (d), 127.4 (d), 126.5 (d), 126.2 (d), 122.7 (s), 99.6 (d); *m*/*z* (EI) 422 (M⁺, 22%), 420 (M⁺-2, 39), 405 (33), 389 (60), 299 (35), 271 (21), 211 (10), 168 (17), 125 (74), 97 (14), 93 (25), 84 (22), 77 (100), 65 (18), 63 (25), 56 (26), 51 (37).

4.4. Intramolecular cyclocondensation reactions

4.4.1. 1,3-Diphenyl-1,6-dihydro-[1,2,4]triazino[5,6-b]phenazin-4-ium 4-methylbenzenesulfonate (12). To a stirred solution of 6-(2-aminophenylamino) - 1,3 - diphenylbenzo[e] - [1,2,4]triazin-7(1H)-one (9) (150 mg, 0.37 mmol) in EtOH (5 ml), TsOH·H₂O was added (70.0 mg, 0.37 mmol) and the mixture heated at reflux for 10 min. The volatiles were removed in vacuo and the residue crystallized to afford the title compound 12 (160.9 mg, 78%) as blue needles, mp >300 °C (from DCM-MeOH, 1:2), R_f 0.31 (t-BuOMe); (found: C, 68.8; H, 4.4; N, 12.4. C₃₂H₂₅N₅O₃S requires C, 68.7; H, 4.5; N, 12.5%); λ_{max} (DCM)/nm 229 (log ε 3.45), 242 inf (3.40), 297 (3.72), 560 (3.43), 620 inf (3.09); $v_{\text{max}}/\text{cm}^{-1}$ 3063w (Ar CH), 1524s, 1504s, 1493m, 1391m, 1333m, 1151s, 1123m, 1030m, 1007s, 872m, 854m, 797m; $\delta_{\rm H}$ (300 MHz, TFA- d_1) NH exchanged 7.77 (2H, d, J 7.7), 7.65-7.43 (12H, m), 7.39-7.31 (3H, m), 7.17 (2H, d, J 7.9), 6.46 (1H, s, H-12), 3.00 (3H, s, CH₃); $\delta_{\rm C}(75 \text{ MHz}, \text{TFA-}d_1) 151.1 \text{ (C=O)}, 146.2 \text{ (s)}, 146.0 \text{ (s)}, 145.3 \text{ (s)},$ 144.6 (s), 142.8 (s), 141.1 (s), 138.4 (s), 135.4 (d), 134.4 (d), 133.7 (d), 132.5 (d), 132.2 (d), 131.5 (s), 131.0 (d), 130.9 (d), 129.6 (s), 128.0 (s), 128.0 (d), 127.2 (d), 126.0 (d), 120.6 (d), 119.8 (d), 99.5 (d), 95.5 (d), 21.2 (CH₃); m/z (EI) 388 (M⁺+1, 34%), 387 (M⁺, 100), 310 (7), 296 (7), 283 (13), 128 (9), 77 (16).

4.4.2. 1,3-Diphenyl-1,6-dihydro-[1,2,4]triazino[5,6-b]phenazine (13). To a stirred solution of 6-(2-aminophenylamino)-1.3-diphenylbenzo[e][1,2,4]triazin-7(1H)-one (9) (55.3 mg, 0.136 mmol) in EtOH (4 ml), TsOH·H₂O was added (26.0 mg, 0.137 mmol) and the mixture heated at reflux for 10 min, then cooled to ca. 20 °C and poured into iced water (20 ml). The precipitate that formed (44.3 mg) was filtered, dissolved in DCM (20 ml) and washed with NaOH 10% (15 ml). The organic layer was dried (Na₂SO₄), filtered and concentrated in vacuo to give the *title compound* **13** (22.8 mg, 43%) as blue needles, mp >300 °C (from PhH); (found: C, 77.4; H, 4.4; N, 18.0. C₂₅H₁₇N₅ requires C, 77.5; H, 4.4; N, 18.1%); λ_{max} (DCM)/nm 253 (log ε 3.92), 290 (3.97), 514 (3.60), 612 inf (2.87) v_{max} /cm⁻¹ 1569m, 1516m, 1490m, 1449s, 1332m, 1321m, 890m, 772m, 753m; m/z (EI) 388 (M++1, 25%), 387 (M⁺, 100), 103 (19), 77 (C₆H₅⁺, 42), 71 (14), 69 (17), 57 (18), 55 (19), 51 (15).

4.4.3. 1,3 - Diphenyl - 1H - [1,2,4]triazino[6,5 - *b*]phenothiazine (14). To a solution of 6-(2-aminophenylthio)-1,3-diphenylbenzo[*e*][1,2,4]triazin-7(1*H*)-one (11) (155.5 mg, 0.37 mmol) in EtOH (9 ml) TsOH·H₂O (72.0 mg, 0.38 mmol) was added and the mixture was heated at reflux for 20 min then cooled to *ca.* 20 °C and poured into iced water (20 ml). The precipitate that formed was filtered, dissolved in DCM (25 ml) and washed with NaOH 10% (20 ml). The organic layer was dried (Na₂SO₄), filtered and concentrated *in vacuo* to give the *title compound* 14 (121.3 mg, 82%) as green needles, mp 256–260 °C (from PhCl), $R_{\rm f}$ 0.84 (*t*-BuOMe–hexane, 3 : 1); (found: C, 74.3; H, 4.1; N, 14.0. C₂₅H₁₆N₄S

requires C, 74.2; H, 4.0; N, 13.9%); $\lambda_{\text{max}}(\text{DCM})/\text{nm}$ 245 (log ε 3.42), 304 (3.52), 315 inf (3.49), 349 inf (3.18), 399 inf (2.80), 463 inf (2.89), 488 (2.58), 517 (3.15), 674 (2.52), 623 inf (2.56); $v_{\text{max}}/\text{cm}^{-1}$ 3065w (Ar CH), 1591m, 1518s, 1493m, 1476m, 1452s, 1310m, 972m, 862m, 847m, 781m; $\delta_{\text{H}}(300 \text{ MHz}, \text{TFA-}d_1)$ 7.96 (2H, d, *J* 8.8), 7.82 (1H, br s), 7.73–7.61 (5H, m), 7.53–7.47 (3H, m), 7.43–7.32 (2H, m), 7.26–7.20 (2H, m), 6.70 (1H, br s); $\delta_{\text{c}}(75 \text{ MHz}, \text{TFA-}d_1)$ 154.1 (s), 153.8 (s), 146.9 (s), 143.9 (s), 143.3 (s), 141.2 (s), 135.7 (d), 135.1 (d), 134.3 (d), 133.6 (s), 132.2 (d), 131.0 (d), 130.8 (d), 128.7 (s), 128.5 (d), 127.9 (d), 125.8 (d), 122.0 (s), 122.0 (d), 115.2 (d), 96.8 (d); *m*/*z* (EI) 405 (M⁺+1, 39%), 404 (M⁺, 100), 196 (25), 77 (23), 51 (11).

4.4.4. 1,3,11-Triphenyl-1,6-dihydro-[1,2,4]triazino[5,6-b]phenazin-11-ium 4-methylbenzenesulfonate (15). To a stirred solution of 6-[2-(N-phenylamino)anilino]-1,3-diphenylbenzo[e][1,2,4]triazin-7(1H)-one (10) (54.7 mg, 0.11 mmol) in EtOH (3 ml), TsOH·H₂O (19.5 mg, 0.11 mmol) was added and the mixture heated at reflux for 15 min. The reaction mixture was cooled to 0 °C and then filtered to give the title compound 15 (69.0 mg, 99%) as blue needles, mp 245–248 °C (from EtOH), $R_{\rm f}$ 0.57 (t-BuOMe); (found: C, 71.0, H, 4.8, N, 10.6. C₃₈H₂₉N₅O₃S·1/2 EtOH requires C, 71.1; H, 4.9; N, 10.6%); $\lambda_{max}(DCM)/nm$ 308 $(\log \varepsilon 3.77)$, 320 inf (3.67), 401 (2.61), 534 inf (3.17), 574 (3.50), 620.1 (3.59); λ_{max}(EtOH)/nm 305 (log ε 4.11), 428 (3.06), 530 inf (3.50), 569 (3.80), 613 (3.86); v_{max}/cm^{-1} 3414w (NH), 3061w (Ar CH), 1514s, 1499m, 1468m, 1393m, 1161m, 1121m, 1034m, 1007m; $\delta_{\rm H}$ (300 MHz, CDCl₃) 13.09 (1H, s, NH), 8.06 (2H, d, J 7.1), 7.86 (2H, d, J 8.0), 7.62 (2H, dd, J 7.5, 7.5), 7.52-7.34 (12H, m), 7.14 (2H, d, J 7.9), 7.07 (1H, s), 6.75 (1H, dd, J 7.2, 7.2), 6.55 (1H, dd, J 7.5, 7.5), 6.07 (1H, d, J 8.1), 5.31 (1H, s, H-12), 3.71 (1H, q, J 7.0, CH₃CH₂OH), 2.32 (3H, s, CH₃), 1.23 (1.5H, t, CH₃CH₂OH); $\delta_{\rm C}$ (75 MHz; CDCl₃) one Ar C missing 159.3 (s), 154.4 (s), 145.4 (s), 144.3 (s), 143.5 (s), 140.3 (s), 139.6 (s), 138.8 (s), 135.8 (s), 133.7 (s), 131.8 (d), 131.5 (d), 130.9 (d), 130.6 (d), 130.4 (s), 130.0 (d), 128.9 (d), 128.6 (d), 128.1 (d), 127.6 (d), 127.5 (d), 126.4 (d), 125.8 (d), 125.2 (d), 118.5 (d), 116.5 (d), 102.9 (d), 92.3 (d), 21.6 (CH₃); m/z (EI) 464 (M⁺+1, 33%), 463 (M⁺, 100), 386 (8), 372 (8), 255 (23), 231 (8), 178 (6), 128 (11), 77 (22).

4.4.5. 1,3,11-Triphenyl-1*H*-[1,2,4]triazino[5,6-*b*]phenazin-11ium-6-ide (16). To a stirred solution of 6-[2-(N-phenylamino)anilino]-1,3-diphenylbenzo[e][1,2,4]triazin-7(1H)-one (10) (64 mg, 0.12 mmol) in EtOH (3 ml), TsOH·H₂O (22.8 mg; 0.12 mmol) was added and the mixture heated at reflux for 20 min. On cooling to ca. 20 °C the reaction mixture was then diluted (DCM, 30 ml) and washed (10% KOH, 15 ml). The organic layer was separated, dried (Na₂SO₄) and evaporated in vacuo. The residue obtained was triturated (DCM-MeOH 1:3) to give the title compound 16 (55.1 mg; 87%) as blue needles, mp >300 °C (from PhH), R_f 0.30 (t-BuOMe); (found: C, 80.3, H, 4.4, N, 15.0. $C_{31}H_{21}N_5$ requires C, 80.3; H, 4.6; N, 15.1%); $\lambda_{max}(CCl_4)/nm$ 407 (2.31), 426 (log ε 2.40), 480 (2.18), 513 (2.18), 564 inf (2.26), 607 (2.39), 657 (2.37); λ_{max} (PhMe)/nm 307 (log ε 2.86), 316 (2.78), 403 (2.33), 426 (2.43), 478 (2.22), 510 (2.23), 556 inf (2.28), 601 (2.43), 650 (2.40); $\lambda_{max}(1,4\text{-dioxane})/\text{nm}$ 307 (log ε 3.44), 313 inf (3.37), 403 inf (2.80), 426 (2.92), 477 (2.63), 508 (2.67), 550 inf (2.76), 593 (2.98), 643 (2.95); λ_{max} (CHCl₃)/nm 306 (log ε 3.70), 406 inf (3.02), 427 (3.13), 477 (2.81), 508 (2.80), 550 inf (3.02), 591 (3.29), 637 (3.29); λ_{max} (DCM)/nm 307 (log ε 3.97), 404 inf

(3.27), 426 (3.39), 477 (3.09), 506 (3.12), 548 inf (3.29), 590 (3.55), 635 (3.55); λ_{max} (MeCN)/nm 304 (log ε 3.51), 402 inf (2.83), 425 (2.93), 476 (2.68), 505 (2.74), 541 inf (2.85), 584 (3.09), 628 (3.08); λ_{max} (EtOH)/nm 303 (log ε 3.48), 406 (2.79), 427 (2.86), 476 (2.60), 541 inf (2.82), 583 (3.09), 624 (3.10); λ_{max} (MeOH)/nm 302 (log ε 3.43), 404 (2.72), 426 (2.78), 475 (2.59), 537 inf (2.81), 574 (3.07), 615 (3.09); λ_{max} (H⁺/EtOH)/nm 305 (log ε 3.88), 368 (2.75), 527 inf (3.29), 567 (3.61), 613 (3.67); v_{max}/cm^{-1} 3049w, 1514s, 1393m; $\delta_{\rm H}(300 \,{\rm MHz};{\rm TFA-}d_1)$ 7.27 (2H, d, J 7.4), 7.07–7.01 (5H, m), 6.97– 6.84 (7H, m), 6.79-6.76 (3H, m), 6.71-6.68 (2H, m), 6.20 (1H, d, J 7.9), 5.17 (1H, s, H-12); $\delta_{\rm C}$ (75 MHz; TFA- d_1) 151.8 (s), 146.3 (s), 145.1 (s), 144.5 (s), 144.4 (s), 140.8 (s), 136.0 (s), 135.9 (d), 134.7 (s), 134.4 (d), 133.8 (d), 133.6 (d), 133.5 (d), 132.4 (d), 131.8 (d), 131.0 (d), 129.8 (s), 128.0 (d), 127.7 (s), 127.7 (d), 125.6 (d), 121.1 (d), 119.7 (d), 99.2 (d), 96.7 (d); m/z (EI) 464 (M⁺+1, 32%), 463 (M⁺, 100), 255 (24), 232 (12), 178 (7), 77 (36).

4.4.6. 6 - (Methoxycarbonyl) - 7 - oxo - 1,3 - diphenyl-7*H*-benzofuro[5,6-e][1,2,4]triazin-1-ium-4-ide (17). To a stirred solution of 1,3-diphenylbenzo[e][1,2,4]triazin-7(1H)-one (1) (50 mg, 0.167 mmol) in MeOH (1.5 ml), dimethyl malonate (20 μ l, 0.174 mmol) and Hünig's base (28 μ l, 0.167) were added. The mixture was refluxed for 6 h. TLC (t-BuOMe-hexane, 3:1) showed the absence of the starting material and the presence of a new less polar green product. Dry flash chromatography (t-BuOMe-hexane, 2:1) of the residue gave the *title compound* 17 (49 mg, 74%) as green needles, mp 272–268 °C (DCM–MeOH, 1:3), R_f 0.29 (t-BuOMe– hexane, 3:1); (found: C, 69.5; H, 3.7; N, 10.6. C₂₃H₁₅N₃O₄ requires C, 69.5; H, 3.8; N, 10.6%); λ_{max} (CCl₄)/nm 282 (log ε 3.20), 297 inf (3.09), 357 (2.98), 376 (2.94), 432 (2.44), 457 (2.47), 554 inf (2.40), 600 (2.51), 651 (2.52), 732 inf (2.37); λ_{max} (PhMe)/nm 358 (log ε 3.24), 374 (3.23), 429 (2.66), 457 (2.74), 550 inf (2.62), 592 inf (2.80), 645 (2.88), 711 inf (2.74); $\lambda_{max}(1,4\text{-dioxane})/\text{nm}$ 280 (log ε 3.45), 297 inf (3.33), 353 (3.27), 368 (3.27), 419 inf (2.65), 449 (2.74), 580 inf (2.81), 628 (2.88), 688 inf (2.75); λ_{max} (CHCl₃)/nm 280 (log ɛ 3.44), 298 inf (3.33), 354 (3.27), 366 (3.27), 427 inf (2.69), 453 (2.80), 585 (2.80), 635 (2.86), 698 inf (2.74); $\lambda_{max}(DCM)/nm$ 279 (log ε 3.40), 298 inf (3.29), 353 (3.22), 364 (3.21), 429 inf (2.64), 452 (2.74), 586 inf (2.75), 629 (2.81), 686 inf (2.69); λ_{max} (MeCN)/nm 275 (log ε 3.42), 295 inf (3.34), 352 (3.29), 444 (2.82), 606 (2.89); λ_{max} (EtOH)/nm 277 (log ε 3.42), 295 inf (3.32), 351 (3.27), 444 (2.83), 600 (2.86); λ_{max} (MeOH)/nm 257 inf (log ε 3.50), 276 (3.58), 295 inf (3.47), 348 (3.44), 443 (3.01), 594 (3.03); $v_{\rm max}/{\rm cm}^{-1}$ 3065w, 1761m, 1468s, 1421s, 1396m, 1261m, 1217m, 1144m, 982m, 781m; $\delta_{\rm H}$ (300 MHz, CDCl₃) 8.44 (2H, dd, J 7.8, 1.6), 8.09 (1H, s), 7.80–7.75 (3H, m), 7.71–7.68 (2H, m), 7.58–7.51 (3H, m), 6.92 (1H, s, *H*-9), 3.92 (OC H_3); δ_C (75 MHz, CDCl₃) one Ar C missing 166.2 (s), 164.6 (s), 161.1 (s), 159.2 (s), 148.6 (s), 148.0 (s), 141.5 (s), 135.7 (s), 133.9 (s), 132.2 (d), 130.6 (d), 129.2 (d), 128.2 (d), 125.7 (d), 107.3 (d), 92.8 (d), 88.0 (s), 51.7 (CH₃); m/z (EI) 398 (M⁺+1, 25%), 397 (M⁺, 100), 366 (82), 339 (55), 282 (17), 180 (9), 103 (9), 77 (57), 51 (18).

4.5. Intermolecular cycloaddition reaction

4.5.1. [5,6-*c*]-Thiadiazolo-1,3-diphenylbenzo[*e*][1,2,4]triazin-7(1*H*)-one (22). To a stirred solution of 1,3-diphenylbenzo[*e*][1,2,4]triazin-7(1*H*)-one (1) (40.0 mg, 0.133 mmol) in DMF (2 ml), S_4N_4 (122.4 mg, 0.665 mmol) was added and the reaction mixture was heated at reflux for 1 h or until all the starting

material was consumed (by TLC). The mixture was allowed to cool to ca. 20 °C, diluted with DCM and washed with H₂O. The organic layer was separated, dried and loaded on silica. Dry flash chromatography (ether-DCM, 1:1) gave the title compound 22 (7 mg, 15%) as brown crystals, mp 285–290 °C (from PhCl); (found: C, 63.9; H, 3.1; N, 19.7. C₁₉H₁₁N₅OS requires C, 63.9; H, 3.1; N, 19.6%); λ_{max} (DCM)/nm 271 (log ε 3.69), 309 (3.81), 407 (3.39), 541 (2.73); $v_{\text{max}}/\text{cm}^{-1}$ 1619s (C=O), 1601m, 1589m, 1573m, 1520s, 1505s, 1489m, 1464m, 1454m, 1438m, 1412m, 1354m, 1250m, 1239s, 1160m, 1153m, 904m, 855m, 833s, 826s, 796m, 790m, 782s, 770s; $\delta_{\rm H}$ (300 MHz; CDCl₃) 8.42–8.32 (2H, m), 7.70–7.57 (5H, m), 7.57–7.48 (3H, m), 6.25 (1H, s, H-5); δ_c(75 MHz; CDCl₃) 173.1 (C=O), 157.8 (s), 152.7 (s), 150.8 (s), 150.0 (s), 141.2 (s), 139.8 (s), 132.9 (s), 131.2 (d), 130.5 (d), 130.4 (d), 128.9 (d), 127.0 (d), 124.9 (d), 98.3 (d); m/z (EI) 358 (M⁺+1, 15%), 357 (M⁺, 47), 340 (13), 226 (24), 174 (13), 142 (19), 103 (29), 86 (14), 77 (C₆H₅⁺, 100), 63 (14), 51 (55). Further elution (ether) gave the orange 6-amino-1,3diphenylbenzo[e][1,2,4]triazin-7-(1H)-one (23) (20 mg, 48%) mp 279-282 °C (lit.,⁴ 279-282 °C) (from PhH), R_f 0.21 (t-BuOMehexane, 3:1); (found: C, 72.7; H, 4.4; N, 17.9. C₁₉H₁₄N₄O requires C, 72.6; H, 4.5; N, 17.8%); λ_{max} (DCM)/nm 274 (log ε 3.49), 302 inf (3.46), 312 (3.48), 332 inf (3.29), 401 inf (3.25), 417 (3.30), 504 (2.60); v_{max}/cm^{-1} 3416w (Ar NH), 1581m, 1566m, 1555s, 1541s, 1491m, 824m; $\delta_{\rm H}$ (300 MHz; TFA- d_1) NH peak missing 8.09 (2H, d, J 7.6), 7.78–7.64 (7H, m), 7.58–7.48 (3H, m); m/z (EI) 315 $(M^++1, 23\%), 314 (M^+, 100), 286 (12), 104 (13), 77 (100), 51 (61)$ identical to an authentic sample.

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