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REACTIVITY OF 3-ALKYNYLTHIO-1-ETHYL-1,2,4-TRIAZINIUM SALTS IN INTRAMOLECULAR DIELS-ALDER REACTIONS

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Quaternization of 3-(3-butynylthio) and 3-(4-pentynylthio) substituted 1,2,4-triazines with triethyloxonium tetrafluoroborate in CH_2Cl_2 at room temperature occurs exclusively at N-1 yielding 3-alkynylthio-1-ethyl-1,2,4-triazinium salts, as unequivocally shown by the ^{13}C NMR and X-ray crystallographic data. 3-Alkynylthio-1-ethyl-5-phenyl-1,2,4-triazinium salts undergo the intramolecular Diels-Alder reaction into the corresponding thieno [2,3-b]- and thiopyrano [2,3-b]pyridines under considerably milder conditions than the corresponding neutral 1,2,4-triazines.

INTRODUCTION

Inverse electron demand Diels-Alder reactions of pyrimidines[1,2] pyrazines[3,4], 1,2,4-triazines[5,6] and other heterocyclic azadienes proved to be efficient and useful synthetic routes to a variety of new heterocyclic compounds (for reviews see[7,8]). Specially the intramolecular version of these reactions has recently received considerable attention because of the enhanced reactivity of azadienes containing a dienophilic fragment in their molecules[2,4,5,6,8]. Particularly, 1,2,4-triazines with appropriate dienophilic side chains at C-3 or C-6 were found to participate in intramolecular [4+2] cycloadditions across C3/C6 of the 1,2,4-triazine ring with subsequent extrusion of molecular nitrogen to yield fused pyridines, pyrazines and other heterocyclic systems[5,6]. It is known that introduction of electron withdrawing substituents into the azaaromatic ring decreases the LUMO energy thus making the azadiene substrate more reactive in inverse electron demand Diels-Alder reactions due to a lower HOMO/LUMO energy separation[8]. Indeed, it has recently been reported that 3-(3-butynylthio) and 3-(4-pentynylthio) substituted 1,2,4-triazines undergo intramolecular Diels-Alder cyclizations into thieno [2,3-b]- and thiopyrano [2,3-b]pyridines, and that the reactivity of these 3-alkynylthio-1,2,4-triazines was found to increase substantially after oxidation of the sulphur atom in the side-chain at C-3 into the corresponding sulfoxide or sulfone derivatives[6a].

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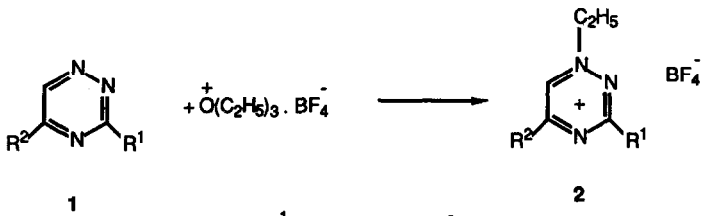
A new way to facilitate intramolecular Diels-Alder reactions of 1,2,4-triazines was supposed to be the use of 1,2,4-triazinium cations. For this reason quaternization of some 1,2,4-triazines with triethyloxonium tetrafluoroborate was studied and the behaviour of 3-alkynylthio-1-ethyl-1,2,4-triazinium salts in intramolecular cyclizations was investigated.

RESULTS AND DISCUSSION

In order to compare the behaviour of quaternary 1,2,4-triazinium salts in intramolecular cyclizations with that of the corresponding neutral species the following triazines were chosen as starting materials for the quaternization reaction: 3-(3-butynylthio)-1,2,4-triazine (**1a**), 3-(3-butynylthio)-5-phenyl-1,2,4-triazine (**1b**) and 3-(4-pentynylthio)-5-phenyl-1,2,4-triazine (**1c**) and 3-benzylthio-5-phenyl-1,2,4-triazine (**1d**). Triethyloxonium tetrafluoroborate (Meerwein reagent) was chosen as alkylating agent for quaternization of these 1,2,4-triazines. The quaternary salt of **1d** which is unable to undergo the intramolecular cyclization, was used as reference compound.



	R^1	R^2
a	$SCH_2CH_2C{\equiv}CH$	H
b	$SCH_2CH_2C{\equiv}CH$	C_6H_5
c	$SCH_2CH_2CH_2C{\equiv}CH$	C_6H_5
d	$SCH_2C_6H_5$	C_6H_5

Scheme I

Addition of the Meerwein reagent (1 equiv.) to a solution of **1a** in methylene chloride or acetone immediately gave the 1-ethyl-1,2,4-triazinium salt **2a**. The position of the ethyl group was established by the ^1H and ^{13}C NMR spectral data (Tables 2 and 3); attempts to isolate the salt **2a** as crystalline solid failed. However, the 5-phenyl substituted 1,2,4-triazines **1b-d** on treatment with the Meerwein reagent in methylene chloride at room temperature gave crystalline quaternary salts **2b-d** in excellent yields (Table 1). The ^1H and ^{13}C NMR spectral parameters of the 1,2,4-triazines **1a-d** and the quaternary salts **2a-d** are summarized in Tables 2 and 3 (see experimental part).

Analysis of the spectral data effects caused by quaternization led us to the conclusion that the N-1 is the site of ethylation. In the ^{13}C NMR spectra of the salts **2a-d** the signal of C-6 undergoes a 4.6-6.2 upfield shift compared to the C-6 signal in the compounds **1a-d.** The signal of C-6 is easily to identify in the ^{13}C NMR spectra of 5-phenyl substituted 1,2,4-triazines **1b-d** and their salts **2b-d** due to a large one-bond ^{13}C-^1H coupling constant. Upfield shifts of that magnitude for the α-

carbon resonances in the ^{13}C NMR spectra of azinium salts have also been observed in the series of pyridines[9], quinolines[10], pyridopyrazines[11], pteridines[12], pyrazines[13], 1,2,4-triazines[14] and other azine derivatives.

The coupled ^{13}C NMR spectrum of the 5,6-unsubstituted salts **2a** provides further evidence for the structure under consideration. As known in the literature a decrease in two-bond coupling constants between C-β and H-α is one of the characteristic changes in NMR spectral parameters caused by quaternization of azines[11-14]. In the ^{13}C NMR spectrum of **2a** the chemical shifts of C-5 and C-6 can be assigned on basis of the ones established for this series (Table 3); the decrease in the ^{13}C-^{1}H coupling constant ^{2}J(C-5, H-6) of about 3 Hz indicates that the N-1 nitrogen is the site of quaternization.

The ^{1}H NMR spectral data for the 1-ethyl-1,2,4-triazinium salts **2a-d** feature broadening of the H-6 and N-CH_2 proton signals due to the long range coupling ^{4}J(H-6, NCH_2), as shown by using the double resonance decoupling technique. This result is certainly a strong argument for the presence of the ethylgroup at N-1, and against its presence at N-2 or at N-4.

Although a huge amount of data on the reactivity of 1,2,4-triazines is available in the literature[15], a little is hitherto known concerning the formation and behaviour of N-alkyl-1,2,4-triazinium cations (for a recent review see 15d). Only a few papers on the formation of 1-alkyl-1,2,4-triazinium salts with NMR structural identification have so far been published[13,14,16]. Although the ^{1}H and ^{13}C NMR spectral data for the salts **2a-d** are in full agreement with the previously reported data for 1-alkyl-1,2,4-triazinium salts[13,14,16], the X-ray analysis of 3-(3-butynylthio)-1-ethyl-5-phenyl-1,2,4-triazinium tetrafluoroborate (**2b**) has been performed not only to approve the conclusions made on the basis of the NMR data, but also to get an insight into the stereo-structure of the 3-alkynylthio substituted 1-ethyl-1,2,4-triazinium salts. A picture of molecule **2b** is given in Figure 1. The atomic coordinates are present in Table IV. The bond distances and angles are listed in Table V. The X-ray analysis showed unequivocally the position of the N-ethyl group at N-1 It also revealed that in the sulfur containing side chain C_9 (Fig. 1) is oriented in the same plane as N_2 and N_4 as illustrated in the Newman projections along S-C_3 (Fig. 2).

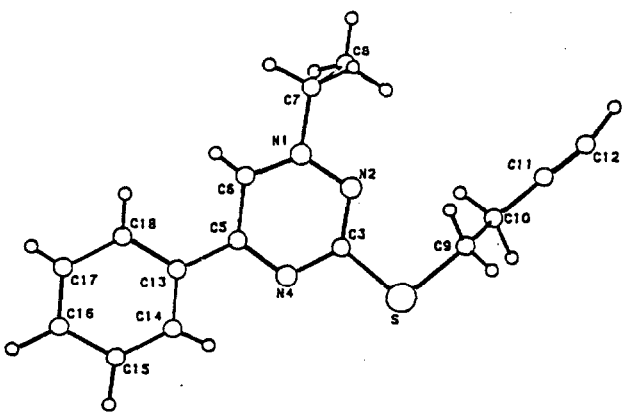


Fig. 1 Drawing of the molecule showing the atomic numbering

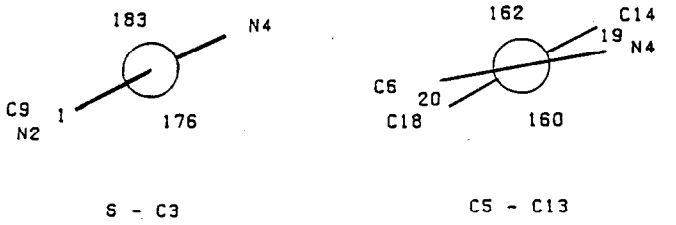


Fig. 2 Newman-projections along S-C3 and C5-C13

Salt **2b** is rather stable in the crystalline state, but when dissolved in acetone or ethanol it converts gradually into 2,3-dihydro-6-phenylthieno [2,3-b]-pyridinium tetrafluoroborate **4**. Compound **4** was isolated, converted into the free base **5** and identified by means of elemental analysis, NMR and mass spectroscopy data (see Table 1 and experimental section) and melting point. The process can easily be followed by either UV or NMR spectroscopy. At room temperature it takes about two weeks to convert salt **2b** into thienopyridine **4** in ethanol, as illustrated in Figure 3. It shows that the absorption of the salt **2b** with the maximum at 276 nm is gradually decreasing with a simultaneous growth of the new band at 233 nm which belongs to the absorption of **4** (Fig. 3b). The isobestic points observed indicate that no intermediary product was present.

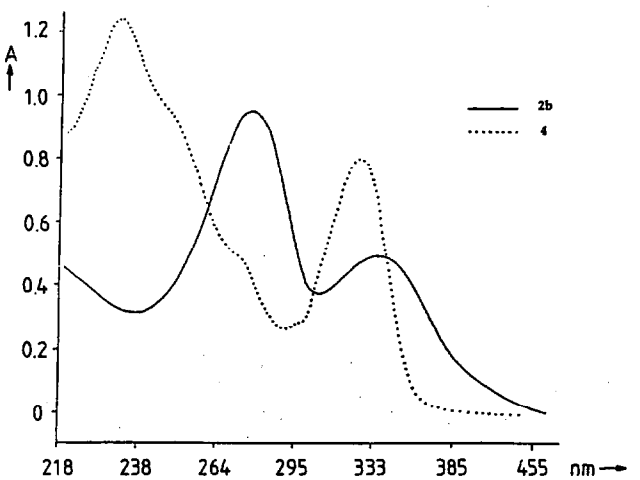
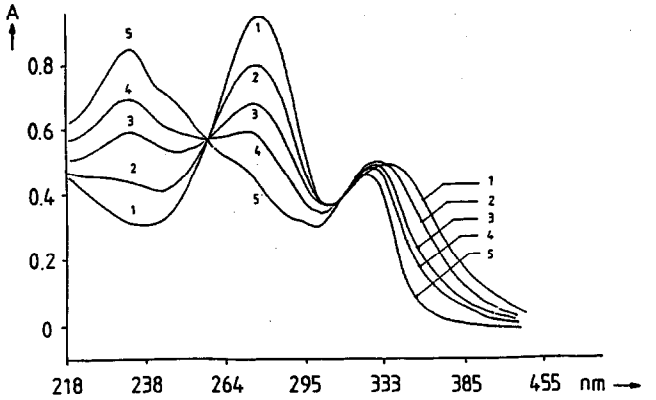
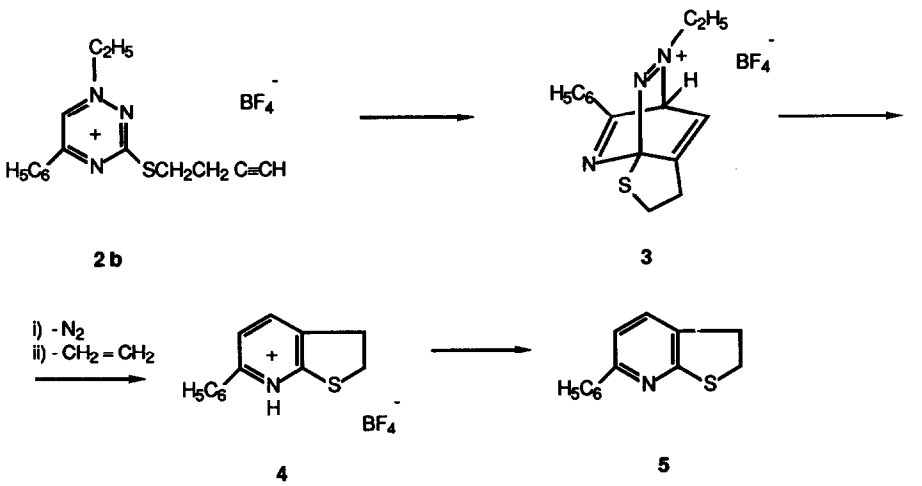


Fig. 3 A. The UV and VIS spectra of the compounds **2b** ($c = 1.04 \times 10^{-3}$ mol/1) and **4** ($c = 1.27 \times 10^{-3}$ mol/l) in ethanol



B. The conversion of the salt **2b** into **4** in ethanol at 23°C. The spectra were taken after 0(1), 24(2), 48(3), 72 hours (4) and 12 days (5).



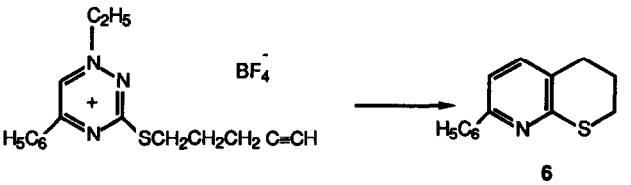
Scheme II

In acetone-d_6 the conversion of **2b** into **4** was complete after 12 days at room temperature or after one hour of heating in a sealed tube at 70°C. When this reaction was carried out on preparative scale, 7 hours of heating in refluxing acetone was found to be sufficient to obtain thienopyridines **4** and **5** in good yields (see experimental section). These conditions are considerably milder than those for the conversion of the neutral 3-(3-butynylthio)-5-phenyl-1,2,4-triazine (**1b**) into thienopyridine **5** (24 hours of heating in refluxing dioxane at 101 °C)[6a].

The scheme suggested for this reaction involves the formation of cycloadduct **3** followed by the elimination of molecular nitrogen and ethylene (scheme II). It is based on the accepted mechanism postulated for the intramolecular Diels-Alder reactions[7,8] although the behaviour of

the positively charged 1,2,4-triazinium cations in intramolecular cyclizations has never been investigated before. According to the ^1H NMR spectra the conversion of **2b** into **4** in acetone-d_6 in a sealed tube is accompanied by the appearance of the singlet peak at 5.35 ppm, which can be assigned to the resonance of ethylene protons; however more evidence has still to be obtained concerning the chemical species eliminating from the intermediate.

In a similar way 3-(4-pentynylthio)-5-phenyl-1,2,4-triazinium tetrafluoroborate (**2c**) could be converted on heating in refluxing dioxane (101°C, 20 hours) into 3,4-dihydro-7-phenyl-2*H*-thiopyrano[2,3-b)pyridine (**6**) in 40% yield (Scheme III).



2c **6**

Scheme III

Transformations of 3-alkynylthio-1-ethyl-1,2,4-triazinium salts into condensed pyridines result in the same products as those obtained with the neutral 1,2,4-triazines. However, the conditions are considerally milder. This simple and convienient method of activation of azadienes for intramolecular cyclizations will stimulate new investigations into the area of cycloaddition reactions.

Experimental section

Melting points are uncorrected. The ^1H NMR spectra were recorded on a Varian (90 MHz) EM 390 spectrometer with Me_4Si as internal standard (δ = 0 ppm). The ^{13}C NMR spectra were recorded at 75.46 MHz on a Bruker CXP-300 spectrometer. Mass spectral data were obtained on a AEI MS 902 spectrometer equipped with VG ZAB console.

The X-ray analysis was performed on a NONIUS CAD4 diffractometer. The cyrstalls of 3-(3-butynylthio)-1-ethyl-5-phenyl-1,2,4-triazinium tetrafluorobarate (**2b**) are triclinic, space group PI with 2 molecules in a unit cell of dimensions: a = 14.408(2), b=12.889(2), c=7.766(2) Å, α=107.95(2), β=106.09(2), γ=63.82(2)°. V=877.2(5) Å^3; d_{calc} = 1.28 gcm^{-3}. A number of 3324 intensities were measured using graphite monochromatized CuKα radiation. Among them 930 were below the 2.5 σ level and were treated as unobserved. The structure was solved in a straightforward application of the symbolic addition program system SIMPEL[17] and refined by means of block-diagonal least-squares calculation, anisotropic for the non-hydrogen atoms and isotropic for the hydrogen atoms which were located in a ΔF-synthesis. The empirical absorbtion correction was applied[18]. The anomalous scattering of S was taken into account and a weighting scheme $w=1/(2.5 + F_o + 0.008F_o^2)$ was employed. The final R-value was 0.102 (R_w=0.141) for the 2394 observed reflexions. The relatively high R-value is mainly due to disorder of the BF_4 group for which no satisfactory model could be found (see Fig. 4 for the electron density at a sphere of radius 1.35 Å around B). In order to suppress as much as possible the effect of the disorder on the rest of the structure **2b** six fluoro atoms were introduced in an ad hoc manner and refined anisotropically with variable population parameters. Not much physical meaning can therefore be attached to the F parameters. The final coordinates are listed in Table IV. A picture of the molecule showing the atomic numbering is given in Fig. 1. The bond distances and angles are listed in Table V.

Starting materials. 3-(3-Butynylthio)-1,2,4-triazine(**1a**), 3-(3-butynylthio)-5-phenyl-1,2,4-triazine (**1b**) and 3-benzylthio-5-phenyl-1,2,4-triazine (**1d**) were synthesized as described in the literature[6a,19].

3-(4-pentynylthio)-5-phenyl-1,2,4-triazine (**1c**). 5-Phenyl-1,2,4-triazine-3-thione[19,20] (1.9 g, 10 mmol) and triethylamine (1.5 ml, 10.6 mmol) were dissolved in 30 ml of anhydrous tetrahydrofuran and 5-iodo-1-pentyne (2.0 g, 10.5 mmol) was added at room temperature. The reaction mixture was stirred at room temperature overnight. A saturated solution of sodium bicarbonate (50 ml) was then added and the resulting mixture was extracted with ether (50 ml) and then with methylene chloride (2 x 60 ml). The combined extracts were dried by anhydrous magnesium sulphate and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (100 g) with ether-petroleum ether (2:3) to yield 2.4 g (77%) of a white solid, mp 77°C.
The elemental analyses, the ^1H and ^{13}C NMR spectral data for the compound **1c** are given in Tables I-III. Ms Calcd. for $C_{14}H_{13}N_3S$ (M^+): m/e 255.0830. Found: m/e 255.0830.

General procedure for quaternization of 3-alkynylthio-1,2,4-triazines **1a-d**
Triethyloxonium tetrafluoroborate (5.5 mmol) was added to a solution of 3-alkynylthio-1,2,4-triazine (5 mmol) in 10 ml of methylene chloride. The resulting yellow solution was stirred at room temperature for 15 min. and then cooled in a refregirator. Salts **2b-d** were separated by filtration and recrystallized from ethanol. Their melting points, yields, the ^1H and ^{13}C NMR spectral data are listed in Tables I-III. Compound **2a** could not be isolated as crystalline solid after a prolonged cooling at - 30°C. In order to identify the product, the solution was evaporated under reduced pressure and the ^1H and ^{13}C NMR spectra of the residue in acetone-d_6 were taken. They provided unequivocal evidence for the formation of quaternary salt **2a** (Tables 2 and 3).

Intramolecular transformation of 3-(3-butynylthio)-1-ethyl-5-phenyl-1,2,4-triazinium tetrafluoroborate (**2b**) into 6-phenyl-2,3-dihydrothieno[2,3-b]pyridinium tetrafluoroborate (**4**) and its neutral base **5**.
A. A solution of quaternary salt **2b** (0.54 g, 1.5 mmol) in acetone (15 ml) was heated at reflux for 7 hours. Acetone was removed from the resulting solution by evaporation under reduced pressure and the residual solid (0.46 g) was recrystallized from isopropanol to give the analytically pure tetrafluoroborate salt **4** as a white crystalline solid (0.25 g, 56%), mp 173-175°C (with decomp.); ^1H NMR (methanol-d_4) 3.4-3.9 (m, 4H), 7.5-7.9 (m, 6H), 8.14 (d, J= 8.5 Hz, 1H). ^1H NMR (acetone-d_6 with several drops of CF_3COOH): 3.5-4.1 (m, 4H), 7.6-7.8 (m, 3H), 7.9-8.1 (m, 3H), 8.40 (d, J=8.5 Hz, 1H). The elemental analysis data for compound **4** are presented in Table 1.
B. A solution of the quaternary salt **2b** (0.54 g, 1.5 mmol in acetone (15 ml) was heated at reflux for 7 hours. The resulting solution was cooled to room temperature, worked up with a saturated solution of sodium bicarbonate (25 ml) and this aqueous mixture was extracted with ether (3 x 60 ml). The extracts were combined, dried with magnesium sulfate and evaporated under reduced pressure to yield an yellow oil (270 mg), which was purified by column chromatography on silica gel (approx 80 g) using as eluant ether/petroleum ether (1:2). The eluate was concentrated to a volume of approximately 10 ml and cooled in a refrigerator to afford 6-phenyl-2,3-dihydrothieno-[2,3-b]pyridine (**5**) as white crystalline solid (200 mg, 63%). Recrystallization from n-hexane gave white needles with mp 83°C (lit. mp 82-83°C[6a]). ^1H NMR ($CDCl_3$): 3.1-3.5 (m, 4H), 7.1-7.6 (m, 5H), 7.7-8.1 (m, 2H).

Intramolecular transformation of 3-(4-pentynylthio)-1-ethyl-5-phenyl-1,2,4-triazinium tetrafluoroborate (**2c**) into 7-phenyl-3,4-dihydro-2*H*-thiopyrano[2,3-b]pyridine (**6**)
A solution of quaternary salt **2c** (0.7 g, 1.89 mmol) in dry dioxane (20 ml) was heated at reflux for 20 hours. The resulting solution was cooled to room temperature, worked up with a saturated solution of sodium bicarbonate (30 ml) and the mixture was extracted with ether (3 x 60 ml). The extracts were combined, dried with magnesium sulfate, evaporated and the residual oil was passed through a column with silica gel using as eluent - ether/petroleum ether (1:2). The first fraction was collected and evaporated under reduced pressure to afford 170 mg (40%) of the crude material as a light yellow oil. The second elution through a silica gel column gave 80 mg of analytically pure 7-phenyl-3,4-dihydro-2H-thiopyrano-[2,3-b]pyridine (**6**) (Table 1). MS calcd for $C_{14}H_{13}NS$ (M^+): m/e 227.0769. Found: 227.0754. ^1H NMR ($CDCl_3$): 1.8-2.3 (m, 2H), 2.6-2.8 (m, 2H), 3.0-3.2 (m, 2H), 7.1-7.5 (m, 5H), 7.8-8.1 (m, 2H). ^{13}C NMR ($CDCl_3$): 22.35, 28.72, 29.26, 115.77, 126.80, 128.44, 128.55, 128.74, 137.52, 138.85, 155.40 and 156.43.

Table 1. Melting points, yields and elemental analyses data for compounds **1c, 2b-d, 4, 5** and **6**

Compound	M.p., °C	Found, %			Formula	Calculated			Yield, %
		C	H	N		C	H	N	
1c	77	65.77	5.12	16.67	$C_{14}H_{13}N_3S$	65.85	5.13	16.45	77
2b	152-153*	50.19	4.58	12.06	$C_{15}H_{16}BF_4N_3S$	50.43	4.51	11.76	88
2c	105-107*	51.92	4.99	11.57	$C_{16}H_{18}BF_4N_3S$	51.76	4.88	11.32	80
2d	150-152	54.58	4.75	10.92	$C_{18}H_{18}BF_4N_3S$	54.69	4.59	10.63	95
4	173-175*	51.68	4.82	4.09	$C_{13}H_{11}NS\ HBF_4$	51.84	4.65	4.01	56
5	83**	72.96	5.13	6.48	$C_{13}H_{11}NS$	73.20	5.19	6.56	63

* with decomposition; ** lit mp 82-83[4];

Table 2. ^1H NMR spectral data for 1,2,4-triazines **1a-d** and their quaternary salts **2a-d**

Compound[a]	Solvent	^1H Chemical Shifts, (ppm) and coupling constants, Hz		
		H-6	R^1	R^2
1a	acetone-d_6	9.07 (d, J=2.4)	2.43 (t, J=2.6, 1H), 2.67 (dt, J=2.6 and 7.0, 2H), 3.41 (t, J=7.0, 2H)	8.53 (d, J=2.4)
2a	acetone-d_6	9.59[b] (d, J=3.3)	2.49 (t, J=2.6, 1H), 2.76 (dt, J=2.6 and 7.0, 2H), 3.45 (t, J=7.0, 2H)	9.49[b] (d, J=3.3)
1b	acetone-d_6	9.70 (s, 1H)	2.46 (t, J=2.6, 1H), 2.73 dt, J=2.6 and 7.0, 2H), 3.50 (t, J=7.0, 2H)	7.4-7.7 (m, 3H), 8.2-8.4 (m, 2H)
2b	acetone-d_6	10.21 (s, 1H)	2.49 (t, J=2.6, 1H), 2.75 (dt, J=2.6 and 7.0, 2H), 3.57 (t, J=7.0, 2H)	7.6-8.0 (m, 3H), 8.4-8.7 (m, 2H),
1c	$CDCl_3$	9.38 (s, 1H)	2.02 (t, J=2.6, 1H), 2.13 (m, 2H), 2.42 (m, 2H), 3.45 (t, J=7.0, 2H)	7.4-7.7 (m, 3H), 8.0-8.3 (m, 2H)
2c	$CDCl_3$	9.87 (s, 1H)	1.9-2.2 (m, 3H), 2.40 (m, 2H), 3.41 (t, J=7.0, 2H)	7.4-7.8 (m, 3H), 8.2-8.5 (m, 2H)
	acetone-d_6	10.27 (s, 1H)	1.9-2.6 (m, 5H), 3.56 (t, J=7.0, 2H)	7.5-7.9 (m, 3H) 8.3-8.6 (m, 2H)
1d	acetone-d_6	9.70 (s, 1H)	4.60 (s, 2H), 7.1-7.6 (m, 5H)[c]	7.1-7.6 (m, 3H)[c], 8.2-8.4 (m, 2H)
2d	acetone-d_6	10.20 (s, 1H)	4.71 (s, 2H), 7.2-7.9 (m, 5H)[c]	7.2-7.9 (m, 3H)[c] 8.3-8.6 (m, 2H)

[a] =N-C_2H_5: CH_3 1.63-1.77 (t, J=7.3 Hz); CH_2 (4.91-4.96(q, J=7.3 Hz)
[b] The signals may be interchanged.
[c] These multipletes are overlapped.

Table 3. ^{13}C NMR spectral data for 1,2,4-triazines **1a-d** and their quaternary salts **2a-d** in acetone-d_6 (quaternization effects are given in parentheses)

Compound	^{13}C Chemical shifts for the ring carbons, (ppm) C-3	C-5	C-6	Coupling constants, (Hz)	Other signals
1a	173.7	149.7	146.9	^1J(C-5, H-5)= 190.5 ^1J(C-6, H-6)= 190.4 ^2J(C-5, H-6)= 9.8 ^2J(C-6, H-5)= 9.7	19.3, 31.4, 71.1 (J=249) and 82.6 (S-butynyl)
2a	179.7 (6.0)	161.3 (11.6)	140.7 (-6.2)	^1J(C-5, H-5)= 205 (14.5) ^1J(C-6, H-6)= 205 (14.6) ^2J(C-5, H-6)= 7 (-2.8) ^2J(C-6, H-5)= 11 (1.3) ^3J(C-3, H-5)= 7	18.8, 31.2, 72.1 (J=249) and 82.2 (S-butynyl), 14.4 and 63.1 (N-ethyl)
1b	174.8	155.5	143.6	^1J(C-6, H-6)= 188.7	19.7, 30.2, 71.3 (J=248) and 83.0 (S-butynyl), 128.7, 130.2, 133.5 and 134.2 (phenyl)
2b	179.0 (4.2)	166.5 (11.0)	139.0 (-4.6)	^1J(C-6, H-6)= 200.2 (11.5)	19.2, 31.3, 72.1 (J=249) and 82.4 (S-butynyl) 14.8 and 63.4 (N-ethyl), 130.3, 130.9, 132.2 and 136.7 (phenyl)
1c	173.6	155.3	143.4	^1J(C-6, H-6)= 188.7	18.0, 29.0, 30.0, 70.6 (J=249) and 83.8 (S-pentynyl), 128.7, 130.2, 133.5 and 134.2 (phenyl)
2c	178.1 (4.5)	166.4 (11.1)	138.7 (-4.7)	^1J(C-6, H-6)= 200.2 (11.5)	14.8 and 63.3 (N-ethyl), 18.1, 28.4, 31.1, 71.0 (J=249) and 83.7 (S-pentynyl), 130.4, 130.9, 131.1 and 136.7 (phenyl)
1d	173.4	155.4	143.5	^1J(C-6, H-6)= 190.5	35.2, 128.1, 128.7, 129.4, 129.9, 130.1, 133.5, 134.2 and 138.3 (two phenyl groups)
2d	177.5 (4.1)	166.2 (10.8)	138.7 (-4.8)	^1J(C-6, H-6)= ± 200 (9.5)	14.8 and 63.1 (N-ethyl), 36.1, 128.7, 129.5, 129.9, 130.1, 130.7, 136.4 and 136.6 (two phenyl groups)

Table 4. Final co-ordinates, (equivalent) isotropic parameters (Å^2) and population parameters (for F atoms).

S	.96904 (16)	.02684 (13)	.25548 (22)	.0634 (8)	
N1	.7298 (6)	.3593 (5)	.2883 (9)	.076 (3)	
N2	.8501 (5)	.2614 (5)	.3059 (7)	.066 (3)	
C3	.8270 (6)	.1619 (5)	.2350 (7)	.057 (3)	
N4	.6985 (5)	.1529 (4)	.1549 (6)	.056 (2)	
C5	.5840 (6)	.2523 (5)	.1409 (7)	.056 (3)	
C6	.6020 (6)	.3616 (5)	.2125 (9)	.068 (4)	
C7	.7548 (10)	.4722 (7)	.3864 (16)	.116(7)	
C8	.8349 (21)	.4885 (13)	.2880 (23)	.202 (16)	
C9	1.1175 (7)	.0720 (6)	.3781 (9)	.067 (3)	
C10	1.1837 (8)	.0998 (7)	.2543 (10)	.081 (4)	
C11	1.3023 (8)	.1363 (6)	.3590 (10)	.080 (4)	
C12	1.3984 (10)	.1625 (9)	.4444 (13)	.105 (6)	
C13	.4415 (6)	.2472 (5)	.0539 (8)	.059 (2)	
C14	.4328 (7)	.1430 (6)	-.0572 (9)	.067 (3)	
C15	.3014 (8)	.1337 (6)	-.1368 (10)	.079 (4)	
C16	.1742 (8)	.2314 (7)	-.1021 (11)	.085 (5)	
C17	.1812 (8)	.3356 (7)	.0071 (13)	.094 (5)	
C18	.3148 (7)	.3450 (6)	.0857 (11)	.082 (4)	
B1	.7034 (9)	.3072 (6)	.7419 (12)	.072 (4)	
F1	.6027 (9)	.3746 (8)	.8483 (12)	.206 (8)	.97 (2)
F2	.7983 (11)	.3525 (10)	.7566 (15)	.195 (11)	.83 (2)
F3	.7125 (17)	.2209 (10)	.5998 (14)	.224 (13)	.76 (2)
F4	.6170 (12)	.3654 (11)	.6037 (15)	.207 (11)	.75 (2)
F5	.7061 (22)	.2142 (11)	.7756 (22)	.226 (18)	.56 (2)
F6	.8029 (15)	.2588 (19)	.8808 (18)	.212 (12)	.49 (2)
H6	.530 (10)	.426 (8)	.221 (12)	.14 (3)	
H71	.655 (10)	.544 (8)	.423 (13)	.16 (4)	
H72	.852 (6)	.477 (5)	.485 (8)	.06 (1)	
H81	.930 (0)	.412 (0)	.260 (0)	.19	
H82	.762 (0)	.498 (0)	.147 (0)	.19	
H83	.848 (0)	.566 (0)	.353 (0)	.19	
H91	1.080 (7)	.147 (5)	.479 (9)	.08 (2)	
H92	1.180 (7)	.009 (6)	.435 (9)	.09 (2)	
H101	1.227 (10)	.016 (8)	.134 (13)	.15 (3)	
H102	1.105 (7)	.171 (5)	.188 (9)	.08 (2)	
H12	1.465 (9)	.208 (7)	.518 (11)	.13 (3)	
H14	.517 (7)	.086 (5)	-.086 (9)	.08 (2)	
H15	.286 (7)	.052 (6)	-.230 (9)	.09 (2)	
H16	.068 (8)	.224 (6)	-.172 (10)	.10 (2)	
H17	.108 (9)	.396 (7)	.025 (11)	.12 (3)	
H18	.320 (6)	.420 (5)	.184 (8)	.06 (1)	

Table 5. Bond distances (Å) and bond angles (°) with e.s.d.'s in parentheses

N1-N2	1.340(6)	N2-N1-C6	115.5(5)
N1-C6	1.288(7)	N2-N1-C7	112.7(6)
N1-C7	1.519(8)	C6-N1-C7	121.5(6)
N2-C3	1.329(6)	N1-N2-C3	113.4(5)
C3-S	1.735(4)	N2-C3-N4	126.6(5)
C3-N4	1.349(6)	N2-C3-S	119.7(4)
N4-C5	1.318(5)	N4-C3-S	113.6(4)
C5-C6	1.422(6)	C3-N4-C5	117.2(5)
C5-C13	1.471(7)	N4-C5-C6	118.8(5)
C7-C8	1.388(17)	N4-C5-C13	119.4(5)
S-C9	1.808(6)	C6-C5-C13	121.9(5)
C9-C10	1.525(8)	C5-C6-N1	118.5(5)
C10-C11	1.458(9)	N1-C7-C8	108.6(10)
C11-C12	1.160(10)	C3-S-C9	101.8(3)
C13-C14	1.381(6)	C9-C10-C11	111.1(6)
C13-C18	1.382(7)	C10-C11-C12	178.1(6)
C14-C15	1.378(8)	C5-C13-C14	120.1(5)
C15-C16	1.388(8)	C5-C13-C18	120.8(5)
C16-C17	1.371(8)	C14-C13-C18	119.1(5)
C17-C18	1.398(9)	C13-C14-C15	121.8(5)
		C15-C16-C17	119.7(7)
		C16-C17-C18	121.0(6)
		C13-C18-C17	119.3(6)

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