Synthesis of a series of 2,3-disubstituted 4*H*-1,4-benzothiazines and X-ray crystal structure of ethyl 7-chloro-3-methyl-4*H*-1,4-benzothiazine-2-carboxylate

Anshu Dandia[a]*, Pritima Sarawgi[a], Michael B. Hursthouse[b], Ann L. Bingham[b], Mark E. Light[b], John E. Drake[c] and Raju Ratnani[d]

[a]*Department of Chemistry, University of Rajasthan, Jaipur – 302 016, India*

[b]*Department of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, UK*

[c]*Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ontario, N9B 3P4, Canada*

[d]*Department of Pure & Applied Chemistry, M.D.S. University, Ajmer – 305 009 India*

The reaction between 2-aminobenzenethiol and ethyl acetoacetate is studied under a variety of conditions, and a procedure for the exclusive synthesis of 1,4-benzothiazines by the neat reaction of substituted aminothiols with β-ketoesters and β-dicarbonyl compounds in 85–96% yield is described. With microwave heating, even when both the reactants are solid, yields are high, reaction times brief, and work-up easy. A facile reaction is also observed even in a solid-state reaction. The molecular structure of ethyl 7-chloro-3-methyl-4*H*-1,4-benzothiazine-2-carboxylate (**4d**) was determined by single-crystal X-ray diffraction.

Keywords: 1,4-benzothiazines, *o*-aminobenzenethiols, crystal structures, β-ketoesters, 1,3-diones

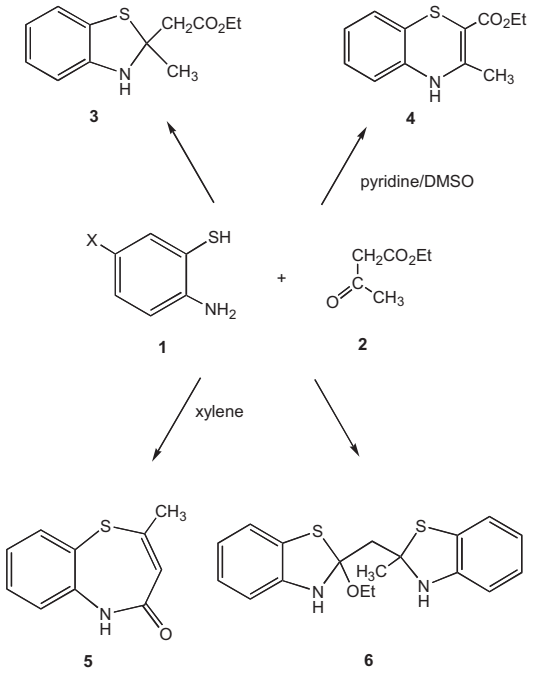
1,4-Benzothiazine is an analogue of phenothiazine in which an *o*-phenylene group is replaced by an ethylene linkage. The molecule is folded along the nitrogen–sulfur axis, which is one of the structural features responsible for a wide variety of biological activities.[1] Luciferin and Rafanycin are 1,4-benzothiazine derivatives possessing pharmacological activity.

Literature survey shows many different protocols that have been developed for the synthesis of 1,4-benzothiazines.[2-9] The most commonly employed methods involve the reaction of 2,3-dihydro-1,3-benzothiazoles with sulfuryl chloride, in toluene,[4] in anhydrous dichloromethane under nitrogen atmosphere,[5] by the oxidative cyclocondensation of 2-aroylmethyl-1*H*-benzimidazoles with *o*-aminothiophenol, in which a mixture of DMSO, acetic acid and water is used as oxidant and solvent giving isomeric product,[6] by the oxidative ring expansion of *N*-substituted benzothiazolines in refluxing dimethylsulfoxide under nitrogen atmosphere.[7] This straightforward method suffers from low yields due, in part, to competitive benzothiazoline thermal decomposition in which 2-substituted benzothiazoles were formed. Besides these, 1,4-benzothiazines are usually prepared by the reaction of 2-aminobenzenethiols with α-haloketones or α-haloesters or oxidative cyclocondensation of 2-aminobenzenethiols with 1,3-dicarbonyl compounds. The former method requires the use of lachrymatory α-haloketones as one of the reactants, and the products isolated are in low yields and as isomeric mixtures[1] and the latter reaction, *e.g.* **1** with **2**, has been studied extensively earlier and has been reported to give either dihydrobenzothiazoles[8] (**3**) or bisdihydrobenzothiazoles[8] (**6**), while formation of benzothiazepinone (**5**) occurred in refluxing xylene.[9] Synthesis of 1,5-benzothiazines (**4**) has been reported in lower yield using DMSO at 150 ºC, a dipolar aprotic solvent with several unfavourable properties, was necessary to act as both solvent and oxidant.[8, 9] (Scheme 1)

Earlier reported methods suffer from various drawbacks, *e.g.* multistep pathways, formation of mixture of products, lower yield, longer reaction period, use of lachrymatory reactants, *etc*. These methods do therefore need to be improved.

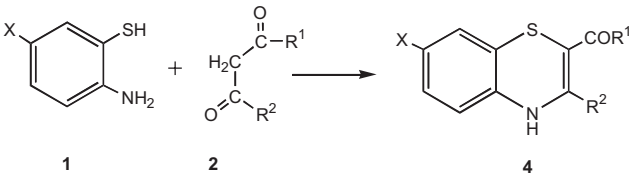
The immense chemotherapeutic applications of 1,4-benzothiazines generated great interest in a detailed study of this class of compound. Microwave irradiation (MWI) is well known to promote the synthesis of a variety of compounds,[10] where chemical reactions are accelerated because of selective absorption of microwaves by polar molecules. Recently, the combination of MWI with solid supports under solvent free conditions has received attention.[10b,11]

With a view to the development of expeditious methods under solvent-free conditions using microwave irradiation and encompassing "green chemistry",[12] we extended our studies to solvent-free reactions for the one-pot selective synthesis of 1,4-benzothiazines by the reaction of substituted 2-aminothiophenols with β-ketoester or β-dicarbonyl compounds under microwaves in 2–4 min with improved yields without catalyst, since the reaction using solid support requires an appreciable amount of solvent for adsorption of reactants and elution of products. Crystalline products in reasonably purity (TLC) were isolated using microwaves under neat conditions with no need of further purification (Scheme 2).



Scheme 1

* Correspondent. E-mail: dranshudandia@eth.net



1 2 4

X = H, Cl, CH_3, OMe, OEt, Br

R^1= CH_3, OEt, $C_6H_4OMe(m)$, $C_6H_4OEt(p)$, C_6H_5; R^2=C_6H_5, CH_3

Scheme 2

In view of the above, we studied the title reaction extensively using different reaction conditions (Table 1). The reaction was studied: (a) without solvent at room temperature by intimate mixing in a mortar; (b) under neat conditions with microwave heating; (c) as a neat reaction in an oil bath; (d) neat, with a few drops of DMF under microwaves, with or without an alumina bath; (e) using various inorganic solid supports under microwaves; (f) in ethanol (i) thermally, (ii) with microwave heating, and (iii) in an ultrasonic bath. Under all conditions benzothiazine **4** was formed exclusively and the best yield was obtained under neat conditions with microwaves and in solution in an ultrasonic bath. Fairly good yields were obtained, with separation of pure crystalline product, even during the progress of the reaction under microwaves or ultrasonic radiation was also observed in case of reactions carried out in ethanol.

We also describe our extension of this facile route to the heterocyclic system involving the neat reaction of 2-aminobenzenethiols and β-ketoester or β-dicarbonyl compounds without any added oxidising agent or catalyst under microwaves (Scheme 2). This reaction finds general applicability for ethyl acetoacetate, acetylacetone, benzoylacetone, dibenzoylmethane, ethyl benzoylacetate, in reaction with substituted *o*-aminobenzenethiols (Table 2). In few cases reaction also occurred by neat mixing of the reactants at room temperature. Facile reaction may occur by aerial oxidation, since the reactions are carried out in open vessels.

The products of the condensation were found to be 2,3-disubstituted 1,4-benzothiazines and their melting points and spectral data are in good agreement with those reported in the literature. The structure of a representative compound, ethyl 7-chloro-3-methyl-4*H*-1,4-benzothiazine-2-carboxylate (**4d**), is confirmed by X-ray crystallography (see below).

The IR spectrum of ethyl 7-chloro-3-methyl-4*H*-1,4-benzothiazine-2-carboxylate (**4d**) showed characteristic bands at 3340 (NH), 1635 (C=O), 1600 and 1575 (aromatic C–C), 1300 and 1260 (C-O) cm^{-1}. The abnormally low ester C=O frequency can be explained on the basis of the X-ray structure. In the crystalline state compound **4d** is hydrogen-bonded (N–H···O=C) in chains parallel to the *b*-axis, thus stabilising the 1*H*- in preference to the 3*H*-tautomer.

Table 1 Comparative study for synthesis of ethyl 7-chloro-3-methyl-4*H*-1,4-benzothiazine-2-carboxylate (**4d**)

Reaction conditions	Method	Time/min	Yield/%
Neat	MW	2	96
Solid state	RT (mixing)	10	90
Neat	Δ (oil bath)	30	90
Neat + DMF	MW	2	60
Neat + DMF (alumina bath)	MW	2	58
Montmorillonite KSF	MW	7	50
Montmorillonite K10	MW	7	57
Basic alumina	MW	6	80
Neutral Al_2O_3	MW	5	90
Acidic Al_2O_3	MW	8	60
Silica gel	MW	5	60
Zeolite	MW	8	40
Ethanol	RT (stirring)	4380	78
Ethanol	MW	4	96
Ethanol	Ultrasonic bath	30	95
Ethanol	Δ, reflux	120	82

X-Ray crystal structure of $C_{12}H_{12}ClNO_2S$ (**4d**)

Compound **4** crystallises in the space group *C*2/*c*. A strong intermolecular hydrogen bond is observed between the N–H bond of one molecule and carbonyl oxygen atom of another molecule as can be seen in the ORTEP diagram (Fig. 1). All the bond lengths and angles are in the expected ranges.

The six-membered heterocyclic ring adopts a shallow boat conformation with S(1) and N(1) displaced 0.258(4) and 0.118(4) Å, respectively, from the best mean-plane of C (1,2,4,9). However, a half-chair conformation is a consistent feature of 1,4-benzothiazine heterocyclic ring systems and has been seen in a few corresponding derivatives, *viz*. the spiro(1,4-benzothiazine-pyrrolo-pyrimidine) derivative $C_{20}H_{24}N_4O_5S$ (**7**),[13] the spiro(4*H*-1,4-benzothiazine-cyclohexadiene) derivative $C_{27}H_{30}N_2O_3S$ (**8**),[14] and the analogous 2-acetyl-3-methyl-4*H*-1,4-benzothiazine $C_{11}H_{11}NOS$ (**9**).[15] The S(1)–C(1) distance of 1.783(3)Å is slightly shorter than those found in **7** (1.830(4)Å) or **8** (1.821(2)Å) but is quite comparable with **9** (1.7896Å). The N(1)–C(2) distance of 1.364(4)Å found is similar to that observed in **9** (1.359Å), whereas this N–C distance in both reduced 1,4-benzothiazine ring systems **7** (an amide) and **8** is seen as 1.347(6)Å and 1.458(3)Å respectively. Similarly, C(1)–C(2) bond length of 1.364(4)Å confirms the presence of double bond between the two carbon atoms, quite comparable to the value of 1.3722Å found for the analogous **9**; these distances in **7** (1.517(6)Å) and **8** (1.565(3) Å) are consistent with the presence of single bonds between the corresponding carbon atoms of the heterocyclic ring system. The C(1)–S(1)–C(9) bond angle of 101.3(1)° is very close to that found for other 1,4-benzothiazine systems such as **7** (99.8(2)°), **8** (101.0(1)°), and **9** (102.51°). Similarly, C(2)–N(1)–C(4) bond angle of 126.6(3)° is comparable to a bond angle value of 127.7(4)° for **7**, 123.8(2)° for **8**, and 126.66° for **9**. Slightly higher than 120° values for all remaining bond angles of the heterocyclic ring system are found. Bond lengths and angles are listed in Table 3.

In conclusion: we have developed a simple, economic and eco-friendly synthetic strategy for the synthesis of 4*H*-1,4-benzothiazines without use of solvent, catalyst, added oxidising agent, or inorganic solid support. The product separation is simple and involves only ethanol (an environmentally benign solvent) as an auxiliary. The operational simplicity and high yields in significantly short reaction times recommends this procedure as an attractive alternative to the currently available methods.

Experimental

Melting points were determined using a Toshniwal apparatus. Purity of compounds was checked on thin layers of silica gel in various non-aqueous solvent systems, typically benzene: ethyl acetate (9: 1) or benzene: dichloromethane (8: 2). IR spectra (KBr) were recorded on a Magna FT IR–550 spectrophotometer. The microwave induced reactions were carried out in an open borosil glass vessel under atmospheric pressure in a multimode MW oven (Panasonic-NN-781JF) equipped with inverter technology (generating fixed frequency throughout the required time) for realistic control of the microwave operating at 1000W generating 2450 MHz frequency (power = 600 watt) An ultrasonic bath (Bandelin sonorex) generating 33 KHz output frequency was used.

The 2-aminobenzenethiols (**1a–e**) were prepared according to literature methods.[17]

General procedures for the synthesis of 4H-1,4-benzothiazines

(a) Neat/RT: intimate mixing of equimolar amounts of 2-aminobenzenethiol (**1**) (1 mmol), and β-ketoester or β-dicarbonyl

Table 2 Synthesis of substituted 4*H*-1,4-benzothiazines (**4a–q**)

Cpd	X	R^1	R^2	M.P./°C		Time/min (a/b/c)	Yield/% method*		
				Lit.	Found		a	b	c
4a	H	OEt	CH_3	144 [b]	144–145	3/10/35	92	70	62
4b	H	C_6H_5	CH_3	190 [b]	190–191	3/12/40	90	60	67
4c	H	CH_3	CH_3	195 [b]	195–196	4/14/45	93	78	71
4d	Cl	OEt	CH_3	184 [a]	184–185	2/10/60	96	90	60
4e	Cl	C_6H_5	CH_3	119 [c]	119–121	3/14/45	95	88	65
4f	Cl	CH_3	CH_3	180 [a]	180–182	2/15/60	98	78	50
4g	CH_3	OEt	CH_3	178 [a]	178–179	3/–/60	90	–	50
4h	CH_3	CH_3	CH_3	186 [a]	186–188	2/–/60	92	–	75
4i	CH_3	C_6H_5	CH_3	136 [c]	136–137	3/–/45	89		65
4j	OEt	OEt	CH_3	101 [a]	101–102	4/–/60	88	–	50
4k	OMe	OEt	CH_3	114 [a]	114–116	3/–/60	86	–	45
4l	OMe	C_6H_5	CH_3	140 [c]	140–141	2.5/–/60	87		60
4m	OMe	C_6H_5	C_6H_5	171 [a]	171–172	4/–/60	90	–	65
4n	Br	CH_3	CH_3	108 [a]	108–110	3/–/60	92	–	60
4o	Br	*p*-$MeOC_6H_4$	CH_3	193 [d]	193–194	3.5/–/45	90		55
4p	Br	*p*-$CH_3C_6H_4$	CH_3	122 [d]	122–123	3/–/–45	88		58
4q	Cl	C_6H_5	C_6H_5	85 [a]	85–86	4/–/60	90	–	60

[a] Ref. 16b, [b] Ref. 8b, [c] Ref. 16a, [d] Ref. 16c.
* a = MW method, b = solid state method, c = conventional method using DMSO

compound (**2**) (1 mmol), was carried out in a mortar for 8–10 min. The colour of the reaction mixture changed from yellow to orange-red. The progress of reaction was monitored by TLC and after completion of the reaction 3–4 ml of ethanol was added. The crystalline solid that separated was filtered and found to be pure on TLC with no need of further recrystallisation in some cases (ethyl acetoacetate). In a few cases, when both the reactants were solid, a few drops of ethanol were added as homogeniser. This method is not preferred because in some cases the reaction was found to be incomplete and the unreacted thiol tends to crystallise together with the product.

(b) Neat/MW: a neat equimolar (1 mmol) mixture of **1** and **2** was placed in the microwave oven and irradiated for 2–4 min (TLC). The reaction mixture was cooled to room temperature. After completion of the reaction, 3–4 ml of ethanol was added to the reaction mixture. The product that separated out was filtered off and found to be pure by TLC with no need of further recrystallisation in any case.

(c) Solid support/MW: The appropriate 2-aminobenzenethiol (**1**) (1 mmol) and β-ketoester or β-diketone (**2**) (1 mmol) were introduced in a beaker and dissolved in ethanol. Suitable inorganic solid support (2–3 g) was then added and swirled for a while followed by removal of solvent under gentle vacuum. The dry powder thus obtained was irradiated in a microwave oven at power output of 600 W for an appropriate time (monitored by TLC). The inorganic support (which can be reused 3–4 times without any loss of activity) was separated by filtration after eluting the product with ethanol. The filtrate was concentrated and kept in a refrigerator overnight and the product, obtained after removal of the solvent, was crystallised from methanol as coloured crystals.

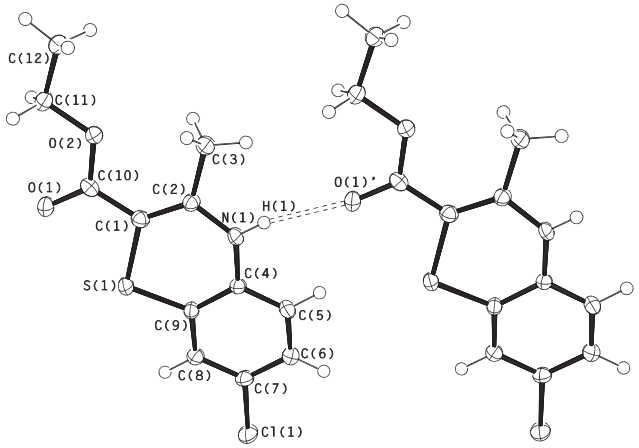


Fig. 1 ORTEP plot of $C_{12}H_{12}ClNO_2S$ (**4d**) showing the intermolecular hydrogen bond. The non-hydrogen atoms are drawn with 50% probability ellipsoids.

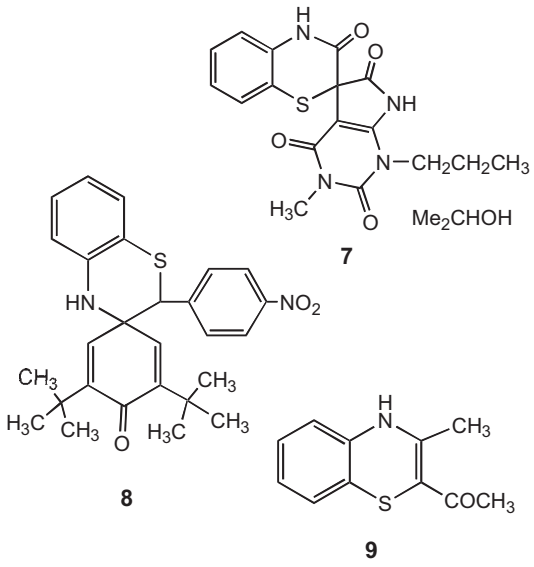
(d) Ethanol/MW: The appropriate 2-aminobenzenethiol (**1**) (1 mmol) and β-ketoester or β-diketone (**2**) (1 mmol) were introduced in a beaker and minimum quantity of ethanol sufficient to make slurry was added. The mixture was placed in the microwave oven and irradiated intermittently for 4–5 min (TLC) at power output 360 watts. The product started to separate out immediately after cooling the reaction mixture to room temperature (or in some cases during the course of the heating). The crystalline solid that separated out was filtered off and found pure by TLC.

(e) Using ultrasonic bath: In a conical flask appropriate 2-aminobenzenethiol (**1**) (1 mmol) and β-ketoester or β-diketone (**2**) (1 mmol) dissolved in 5 ml ethanol were immersed in the water bath of an ultrasonic cleaner. The flask was positioned 0.5 cm above the bottom of the bath and the level of the water was adjusted to that of the solvent level inside the flask. The mixture was treated with ultrasound (operating at 230 V generating 33 KHz output frequencies) for 30–40 min (TLC) at room temperature. The product started to

Table 3 Bond distances [Å] and angles [θ] for compound **4d**[a]

Distances			
S(1)–C(1)	1.783(3)	S(1)–C(9)	1.763(3)
C(1)–C(2)	1.364(4)	C(4)–C(9)	1.398(4)
N(1)–C(2)	1.364(4)	N(1)–C(4)	1.412(4)
N(1)–H(1)	0.80(3)	N(1)–O(1)	2.999(3)
H(1)–O(1)	2.22(4)	C(2)–C(3)	1.502(4)
C(1)–C(10)	1.452(4)	C(10)–O(1)	1.228(3)
C(10)–O(2)	1.343(3)	O(2)–C(11)	1.452(4)
C(11)–C(12)	1.498(4)	C(4)–C(5)	1.385(4)
C(5)–C(6)	1.390(4)	C(6)–C(7)	1.385(4)
C(7)–C(8)	1.391(4)	C(8)–C(9)	1.388(4)
C(7)–Cl(1)	1.740(3)		
Angles			
S(1)–C(1)–C(2)	123.2(2)	C(1)–C(2)–N(1)	122.1(3)
C(2)–N(1)–C(4)	126.6(3)	N(1)–C(4)–C(9)	121.2(3)
C(4)–C(9)–S(1)	122.2(2)	C(9)–S(1)–C(1)	101.3(1)
C(2)–N(1)–H(1)	114(2)	C(4)–N(1)–H(1)	119(2)
N(1)–H(1)–O(1)	164(3)	N(1)–C(2)–C(3)	113.0(3)
C(1)–C(2)–C(3)	124.9(3)	C(2)–C(1)–C(10)	127.1(2)
S(1)–C(1)–C(10)	109.5(2)	C(1)–C(10)–O(1)	122.3(3)
O(1)–C(10)–O(2)	122.1(3)	C(1)–C(10)–O(2)	115.6(2)
C(10)–O(2)–C(11)	117.3(2)	O(2)–C(11)–C(12)	107.1(2)
N(1)–C(4)–C(5)	119.2(3)	C(4)–C(5)–C(6)	121.1(3)
C(5)–C(6)–C(7)	118.7(3)	C(6)–C(7)–C(8)	121.1(3)
C(7)–C(8)–C(9)	119.6(3)	C(8)–C(9)–C(4)	119.8(3)
S(1)–C(9)–C(8)	117.8(2)	C(5)–C(4)–C(9)	119.6(2)
Cl(1)–C(7)–C(6)	119.9(2)	Cl(1)–C(7)–C(8)	119.0(2)

[a] Symmetry equivalent position (*x*, –1 + *y*, *z*) given by a prime. See Fig. 1 for atom numbering scheme.



(Structures 7–9)

separate out during the course of reaction. The crystalline solid that separated out was filtered and found pure by TLC.

Crystal structure determination

A translucent orange triangular crystal of **4d** was mounted on a glass fiber. Data were collected on a Bruker-Nonius Kappa CCD area detector diffractometer, with N and T scans chosen to give a complete asymmetric unit. Cell refinement[18] gave cell constants corresponding to a monoclinic cell. An absorption correction was applied.[19]

Crystal data and structure refinement: Empirical formula $C_{12}H_{12}ClNO_2S$; Formula weight 269.74; Temperature, 120(2)K; Wavelength, 0.71073Å; Crystal system: monoclinic; Space group: *C*2/*c*; *a*, 13.559(3)Å; *b*, 7.548(2)Å; *c*, 23.138(5)Å; *β*, 92.71(3)°; Volume: 2365.5(8)Å^3; *Z*: 8; Density (calculated): 1.515 g/cm^3; Absorption coefficient: 0.487 mm^{-1}; *F(000)*: 1120; Crystal size: 0.08 × 0.08 × 0.04 mm^3; θ range for data collection: 3.01 to 27.44°; Index ranges: $-15\leq h\leq 17$, $-9\leq k\leq 9$, $-29\leq l\leq 29$; Reflections collected: 12876; Independent reflections: 2651 [R_{int} = 0.080]; Observed reflections [$F^2>4\sigma(F^2)$]: 1956; Max. and min. transmission: 0.981 and 0.962; Refinement method: Full-matrix least-squares on F^2; Data/restraints/parameters: 2651/0/160; Goodness-of-fit on F^2: 1.074; Final *R* indices [$F^2>4\sigma(F^2)$]: R_1 = 0.054, wR_2 = 0.125; *R* indices (all data): R_1 = 0.081, wR_2 = 0.137; Largest diff. peak and hole: 1.50 and –0.35 e.Å^{-3}.

The structure was solved by direct methods[20] and was refined using the WinGX version[21] of SHELX-97.[22] All of the non-hydrogen atoms were treated anisotropically. The hydrogen atom attached to N(1) was located in the difference map and refined. The remaining hydrogen atoms were included in idealised positions with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they were attached. The final cycle of full-matrix least squares refinement (to convergence) was based on 2651 reflections and 160 variable parameters.

Bond distances and angles are given in Table 3. The molecule is displayed as ORTEP diagram in Fig. 1. Additional material available from the Cambridge Crystallographic Data Centre (CCDC no. 280708) comprises the final atomic coordinates for all atoms, thermal parameters, and a complete listing of bond distances and angles. Copies of this information may be obtained free of charge on application to The Director, 12 Union Road, Cambridge CB2 2EZ, UK (fax: + 44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: http: //www.ccdc.cam.ac.uk).

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