# Reactions of S-Alkyl-NN-disubstituted Thioamide Salts. Part 5.[1] Diamidinium Salts

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3-(α-Dialkylaminoarylidene)-1-alkylthiotriazenes (**2**; R[1] = aryl), readily obtainable from thioamide salts, give with iodomethane at room temperature the diamidinium iodides (**3**) (*NN*-dialkyl-3-dialkylamino-1,3-diaryl-2-azapropenylideneammonium iodides) in moderate to good yields. Their properties have been investigated and the structure of the corresponding chloride (**4**; R[1] = Ph, R[2] = Me, A = Cl) has been investigated by *X*-ray crystal analysis.

Recently[1,2] we described the preparation of the sulphenamidines (**1**) by catalytic extrusion of nitrogen with copper(I) cyanide at room temperature or below from the readily available 3-(α-dialkylaminoarylidene)-1-alkylthiotriazines (**2**). We now report that the triazenes (**2**; R[1] = aryl), with iodomethane in acetone at room temperature, give moderate to good yields of the diamidinium iodides (**3**) (*NN*-dialkyl-3-dialkylamino-1,3-diaryl-2-azapropenylideneammonium iodides).
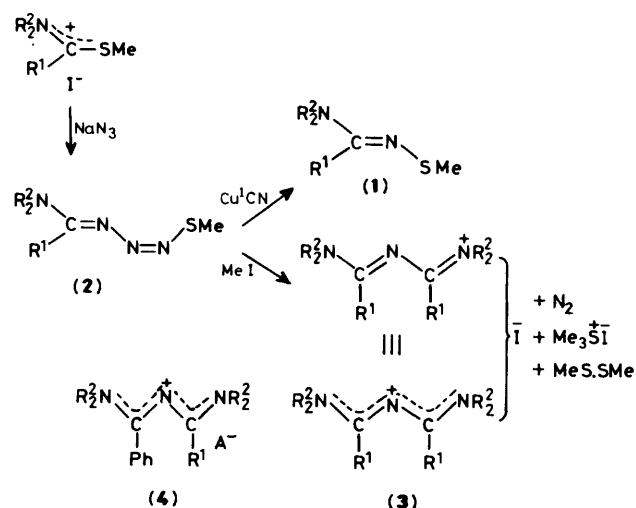
The course of the slightly exothermic reaction was monitored by measuring nitrogen evolution, and was complete in *ca.* 2 h, during which time trimethylsulphonium iodide crystallised out and could be filtered off or removed later by water-washing of the product. The symmetrical diamidinium iodides (**3**) readily formed yellow crystals on cooling with scratching of the solution, and were pure after washing with acetone and then ice–water. They could be recrystallised from boiling water (Table 1). Diamidinium salts were also formed, less conveniently, from the triazenes by reaction in acetone with iodine, or by stirring in acetonitrile solutions with mercury(II)- or silver-cyanide. The reaction with these cyanides is in contrast to that with copper(I) cyanide. The iodomethane reaction was general for the aryl-

Table 1. Diamidinium iodides (**3**)

Compound	Yield (%)	M.p. (°C)	Elemental analysis (%)[a]		
			C	H	N
(**3a**)	62[b]	247—248	54.0	5.3	8.5
	33[c]		(53.8)	(5.3)	(8.55)
(**3b**)	54[b]	223—224	53.2	5.5	10.2
			(53.1)	(5.4)	(10.3)
(**3c**)	54[b]	206	45.6	4.2	8.9
			(45.4)	(4.2)	(8.8)
(**3d**)	39[b]	183—184	51.3	5.6	8.9
			(51.4)	(5.6)	(9.0)
(**3e**)	45[c]	225	43.3	4.0	13.9
			(43.5)	(4.0)	(14.1)

[a] Required values in parentheses. [b] Yield pure to [1]H n.m.r. but not recrystallised. [c] Yield recrystallised from water.

substituted triazenes, but was more complex, as was also the mercury(II) cyanide reaction, with the benzyl compound (**2**; R[1] = CH$_2$Ph, NR$_2^2$ = morpholino).

No gas other than nitrogen was detected in the iodomethane reaction, and the presence of dimethyl disulphide in the malodorous mother liquor was shown by g.c.–m.s. examination of the ether-soluble fraction, and by comparison of the chemical shift of its [1]H n.m.r. singlet with that of the authentic compound. That free radicals are involved in this mechanism, as in that of sulphenamidine formation, was indicated by preliminary e.s.r. examination during the reaction. The initial step may be loss of nitrogen with formation of amidino and methylthio radicals, the former then attacking another triazene molecule.

Unsymmetrical diamidinium salts (**4**; R[1] = H or Me, NR$_2^2$ = NMe$_2$ or heterocyclic, A = I$_3$ or I) have previously been synthesised[3] in several steps from thiobenzamide and diethyl acetals of *NN*-dialkyl-formamide or -acetamide.

The iodide (**3b**) in aqueous methanol was converted, by passage through an ion-exchange column, into the corresponding chloride (**4**; R[1] = Ph, R[2] = Me, A = Cl), the structure of which was determined by *X*-ray crystallography (Figure). It has approximate 2-fold symmetry about the bisector of the central C(2)–N(1)–C(12) bonds. The non-planar zig-zag chain N(3)–C(2)–N(1)–C(12)–N(13) thus has the phenyl substituents overlapping to some extent, and with their normals inclined at 70° to the plane of C(2)–N(1)–C(12). The phenyl groups are mutually inclined at an angle of 26°. The groups C(2), N(3), C(4), C(5) and C(12), N(13), C(14), C(15) are essentially planar (sum of angles at N, 359.9 and 360° respectively) and are each inclined at 34° to the C(2)–N(1)–C(12) plane. The non-planarity of the zig-zag presumably arises from the attempt of C(5) and C(15) to minimise interaction with the lone pair on N(1).

Table 2. Spectral properties of the diamidinium iodides (3)

Mass (m/z) (b = base)	U.v. ($\lambda_{max.}$) (nm; EtOH)[a]	I.r. ($\nu_{max.}$) (cm^{-1}; Nujol)	^{1}H N.m.r. $\delta(J/Hz)$ (CDCl$_3$ except where shown)
(3a) 364 (M^+ and b)	260 (11 500), 305 (16 000)	1 520, 1 110, 1 030, 780	7.1 (10 H, complex m, ArH), 4.35 (4 H, m, 2CH$_2$O), 4.05 (4 H, m, 2CH$_2$N), 3.68 (8 H, s, morpholinium)
(3b) 280 (M^+) 118 (b)	260 (10 100), 295 (15 600)	1 550, 800, 760	7.28 (2 H, d, ArH p), 7.20 (4 H, t, ArH m), 6.89 (4 H, d, ArH o), 3.60 (6 H, s, 2NMe), 3.22 (6 H, s, 2NMe)
(3c) 348 (M^+) 152 (b)	270 (14 100), 298 (15 000)	1 560, 1 100, 1 020, 830	7.2 (8 H, m, ArH), 3.60 (6 H, s, 2NMe), 3.23 (6 H, s, 2NMe)
(3d) 340 (M^+) 142 (b)	248 (14 800), 283 (24 900)	1 550, 1 260, 1 180, 1 020, 840	6.8 (8 H, m, ArH), 3.76 (6 H, s, 2OMe), 3.51 (6 H, s, 2NMe), 3.22 (6 H, s, 2NMe)
(3e) 354.1209 ($M^+ - CH_4$) 163 (b)	255 (25 200), 322 (8 400)	1 570, 1 520, 1 220, 1 100, 870	[(CD$_3$)$_2$SO] 8.0 (4 H, d, J 10, ArH o to NO$_2$), 7.20 (4 H, d, J 10, other ArH), 3.44 (6 H, s, 2NMe), 3.23 (6 H, s, 2NMe)

[a] ε In parentheses
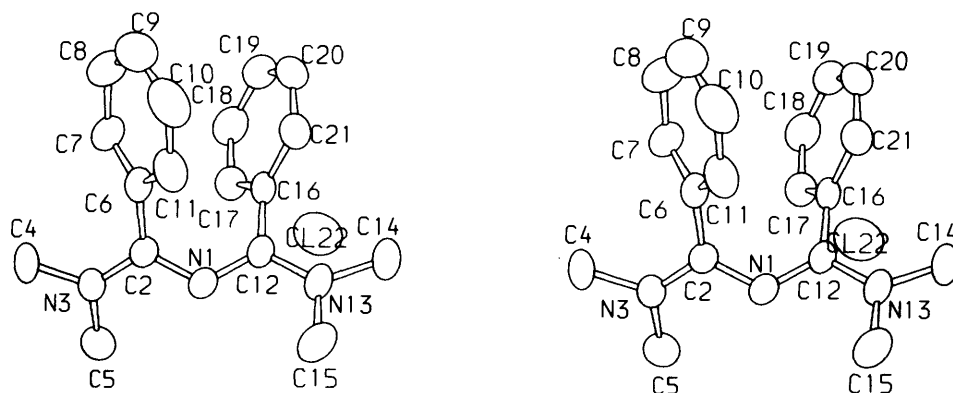
Figure. Stereoscopic view of (4; R^1 = Ph, R^2 = Me, A = Cl)

The C–N distances along the 5-membered delocalised chain vary between 1.315 and 1.346 Å, mean 1.330 Å; the remaining four N–C distances vary between 1.442 and 1.463 Å, mean 1.455 Å.

We can find no other recorded example of X-ray structural data for this kind of chain. There is no significantly short intermolecular distance.

Mild alkaline hydrolysis of the iodide (3a) gave, in poor yield, the expected N^1-benzoyl-N^2N^2-dimethylbenzamidine, and in aqueous ethanol it yielded the corresponding picrate with sodium picrate. Reaction of iodide (3b) with ethanolic iodine gave the tri-iodide.

Spectral data for the diamidinium iodides are shown in Table 2. The u.v. spectra in ethanol show peaks at 250—270 nm, but also more variable absorptions at 280—320 nm, the position and intensity of which depend on the nature of the aryl substituent. The two absorptions are not completely separated, and only a shoulder may appear between them. It seems likely that the substituent-dependent absorptions are due to charge-transfer interactions between the two overlying aromatic rings. Such interactions have only rarely been observed between identical species, though they have been postulated for benzene, provided the the nuclei lie over each other and are staggered,[4] as found here, at least in the solid state.

The ^{1}H n.m.r. spectra of the bis-dimethylamino salts show two sharp methyl singlets, since although the terminal groups are identical, each has two methyl groups almost rigidly fixed in different environments, and each shows nuclear Overhauser

effects, but to different extents, with the neighbouring *ortho*-protons.[5]

Mass spectra of the iodides all show prominent peaks for the molecular cation, except for the nitro-compound where the highest m/z value corresponds to $M^+ - CH_4$, as shown by accurate mass measurement. Other dimethylamino, but not morpholino, iodides also give peaks at $M^+ - CH_4$. The i.r. spectra, as Nujol mulls, show strong absorptions at 1 520—1 570 cm^{-1}.

Experimental

U.v. and i.r. spectra were recorded on Perkin-Elmer 402 and Pye-Unicam SP3-200 instruments, respectively. ^{1}H N.m.r. spectra at 60 and 300 MHz were obtained using Perkin-Elmer R 12B and Varian Associates XL-300 spectrometers, respectively.

Preparation of Diamidinium Iodies (3).—(a) *General procedure.* The triazenes (2a—e)[1,6] (10 mmol) were suspended in a mixture of iodomethane (5.7 g, 40 mmol) and acetone (8 ml) in a flask surrounded by water at room temperature to act as a heat sink. Nitrogen evolution began slowly, but then accelerated and was complete in *ca.* 2 h, accompanied by dissolution of the triazene and separation of trimethylsulphonium iodide. After being kept for a further 1 h, the pale brown mixture was cooled in ice with scratching, and the yellow product was filtered off washed with small amounts of cold acetone to remove brown mother liquor, and then several times with ice–water to remove the sulphonium

iodide, and dried (SiO_2 gel). Alternatively, the sulphonium salt can usually be filtered off first and the product obtained by cooling with scratching of the filtrate. Any sulphonium iodide remaining was removed by filtering it off from a solution of the product in chloroform (*ca.* 50 ml); evaporation of the solvent then gave a pure (to n.m.r.) yellow product. The salts can be crystallised from a little boiling water, though with loss of yield.

The trimethylsulphonium iodide formed colourless crystals which sublimed without melting above 200 °C (Found: C, 17.9; H, 4.6. Calc. for C_3H_9IS: C, 17.65; H, 4.4%).

In one experiment, the mother liquor was evaporated to small volume, the remaining ionic salts precipitated by addition of an excess of ether, the mixture filtered, and the ether filtrate examined by g.c.–m.s. (2.7 m column, i.d. 4 mm, stationary phase SP 1 000 at 150 °C, with an A.E.I. MS 30 spectrometer at 70 e.v.). The dimethyl disulphide fraction showed m/z 94 (M^+ and base) and 79 ($M^+ - $ Me). After evaporation of ether, the residue in $CDCl_3$ showed a [1]H n.m.r. singlet at δ 2.40, identical with that given by authentic dimethyl disulphide.

(*b*) *Preparation of iodide* (**3a**) *using iodine.* The triazene (**2a**) (0.66 g, 2.5 mmol) suspended in acetone (10 ml) was stirred in a bath of water at room temperature whilst iodine (0.32 g, 2.5 mg-atom) was added in small portions over 1.5 h. Nitrogen evolution, quickly ceasing, occurred after each addition, and solid separated, yellow at first then darkening, perhaps due to the tri-iodide. The acetone was evaporated, the residue dissolved in chloroform, the solution shaken with sodium thiosulphate solution and then with water, dried (Na_2SO_4) and the solvent evaporated. The remaining yellow oil crystallised completely on cooling and its [1]H n.m.r. spectrum was identical with that of the iodide (**3a**).

Preparation of the Diamidinium Picrate (**4**; R^1 = Ph, NR_2^2 = morpholino, A = $C_6H_2N_3O_7$).—(*a*) The triazene (**2a**) (0.66 g, 2.5 mmol) in acetonitrile (10 ml) was stirred with mercury(II) cyanide (0.70 g, 2.8 mmol) at room temperature for 1.5 h, and the resulting grey solid, perhaps containing mercury(II) azide, was cautiously filtered off and the filtrate evaporated to *ca.* 4 ml. Water (25 ml) was added, the solution was filtered, and excess of aqueous picric acid solution was added to the filtrate, to give a yellow oil which crystallised on scratching. The *picrate* formed yellow rods from ethanol, m.p. 164—165 °C (Found: C, 56.55; H, 4.7; N, 14.2. $C_{28}H_{28}N_6O_9$ requires C, 56.75; H, 4.7; N, 14.2%). The same picrate was obtained from reaction of the triazene with silver cyanide in acetonitrile.

(*b*) The iodide (**3a**) was dissolved in the minimum amount of ethanol, then diluted with twice the volume of water and treated with aqueous sodium picrate solution, to give a picrate, m.p. 163 °C, identical with that obtained above.

Preparation of the Diamidinium Tri-iodide (**4**; R^1 = Ph, R^2 = Me, A = I_3).—The iodide (**3b**) (0.41 g, 1 mmol) and iodine (0.25 g, 2 mg-atom) in ethanol (30 ml) were stirred at room temperature for 1 h and the small dark red crystals of the *tri-iodide* were filtered off, washed with ethanol, and dried (SiO_2 gel), m.p. 126 °C (Found: C, 32.7; H, 3.35; N, 6.3. $C_{18}H_{22}I_3N_3$ requires C, 32.7; H, 3.3; N, 6.3%).

Hydrolysis of Iodide (**3a**).—The iodide (1.0 g) was shaken at room temperature for 70 h with a mixture of aqueous sodium hydroxide solution (1M; 2 ml), water (1 ml), and chloroform (10 ml). The chloroform layer was washed with water, dried, and the solvent evaporated. The residual brown gum in ethanol was scratched to give a brown amorphous solid which was filtered off; the filtrate was then cooled in ice and again scratched, to yield N^1-benzoyl-N^2N^2-dimethylbenzamidine (0.11 g) as pale yellow cubes from ethanol, m.p. 153—154 °C (lit.,[6] m.p. 153—

154 °C), identical with the compound obtained by benzoylation of the amidine.

Preparation of the Diamidinium Chloride (**4**; R^1 = Ph, R^2 = Me, A = Cl).—The iodide (**3b**) (1.0 g) was dissolved in methanol (4 ml), water (16 ml) was added, and the solution was passed through a column of Amberlite IRA 400 resin (chloride form; 20 g), [eluant: 20% aqueous methanol (250 ml)]. The eluate was evaporated to dryness and the solid was triturated with ethyl acetate, filtered off, and dried (0.69 g). The *chloride* formed small colourless cubes from cyclohexanone, m.p. 253—254 °C (Found: C, 68.5; H, 7.0; N, 13.05. $C_{18}H_{22}ClN_3$ requires C, 68.45; H, 7.0; N, 13.3%); δ($CDCl_3$) 7.0 (10 H, m, ArH), 3.57 (6 H, s, $2NMe_3$), and 3.22 (6 H, s, 2NMe). Its solution in a few drops of water gave a precipitate of the less soluble iodide with potassium iodide.

Structure Determination of the Chloride.—An Enraf-Nonius CAD4 four-circle diffractometer was used to measure accurate lattice parameters and for data collection.

Table 3. Atomic co-ordinates for structure (**4**; R^1 = Ph, R^2 = Me, A = Cl)

Atom	x/a	y/b	z/z
N(1)	0.430 3(3)	0.182 8(2)	0.152 0(2)
C(2)	0.322 5(3)	0.182 6(2)	0.182 7(2)
N(3)	0.230 7(3)	0.107 4(2)	0.157 9(2)
C(4)	0.125 4(5)	0.089 0(3)	0.199 3(3)
C(5)	0.221 0(5)	0.038 9(3)	0.079 4(3)
C(6)	0.315 9(4)	0.260 0(2)	0.248 9(2)
C(7)	0.175 6(4)	0.308 7(3)	0.216 7(3)
C(8)	0.174 3(5)	0.384 5(3)	0.275 7(4)
C(9)	0.310 3(6)	0.411 6(3)	0.367 2(4)
C(10)	0.449 8(6)	0.363 7(3)	0.400 1(3)
C(11)	0.454 0(4)	0.288 4(2)	0.340 8(3)
C(12)	0.487 0(3)	0.261 4(2)	0.134 0(2)
N(13)	0.631 7(3)	0.257 1(2)	0.147 9(2)
C(14)	0.697 4(5)	0.331 6(3)	0.111 8(4)
C(15)	0.732 6(4)	0.176 1(3)	0.199 2(3)
C(16)	0.391 6(4)	0.349 0(2)	0.092 5(2)
C(17)	0.240 2(4)	0.344 1(2)	0.003 4(3)
C(18)	0.147 4(4)	0.424 6(3)	−0.031 1(3)
C(19)	0.201 5(5)	0.509 2(3)	0.021 7(3)
C(20)	0.350 0(5)	0.514 3(2)	0.110 3(4)
C(21)	0.446 5(4)	0.435 1(2)	0.145 7(3)
Cl(22)	0.870 3(1)	0.286 9(1)	0.454 4(1)
H(7)	0.088 3(41)	0.289 1(22)	0.151 6(27)
H(8)	0.076 8(54)	0.423 0(31)	0.249 2(36)
H(9)	0.311 2(51)	0.464 8(29)	0.407 0(35)
H(10)	0.552 0(45)	0.384 2(26)	0.464 6(31)
H(11)	0.549 4(45)	0.253 6(26)	0.362 8(29)
H(17)	0.203 0(41)	0.285 9(23)	−0.031 7(28)
H(18)	0.046 4(45)	0.419 5(25)	−0.092 1(30)
H(19)	0.134 5(52)	0.566 9(29)	−0.003 7(34)
H(20)	0.392 0(48)	0.570 9(28)	0.152 2(32)
H(21)	0.546 6(37)	0.436 9(21)	0.209 3(25)
H(41)	0.001 8(65)	0.110 5(37)	0.140 3(43)
H(42)	0.156 0(46)	0.126 5(27)	0.262 6(32)
H(43)	0.130 7(45)	0.022 3(27)	0.215 1(31)
H(51)	0.320 7(68)	0.033 5(38)	0.085 5(44)
H(52)	0.143 9(50)	0.060 4(28)	0.009 0(32)
H(53)	0.192 0(54)	−0.023 3(31)	0.095 1(37)
H(141)	0.771 6(49)	0.364 4(28)	0.175 1(33)
H(142)	0.618 7(52)	0.376 9(30)	0.058 9(35)
H(143)	0.746 4(50)	0.297 8(28)	0.071 6(33)
H(151)	0.675 9(48)	0.117 1(28)	0.199 8(32)
H(152)	0.801 3(66)	0.186 3(35)	0.266 2(45)
H(153)	0.773 9(57)	0.158 0(32)	0.150 7(38)

Table 4. Selected parameters for structure (4; R^1 = Ph, R^2 = Me, A = Cl)

Bond lengths (Å)

N(1)–C(2)	1.346(4)	N(1)–C(12)	1.321(4)
C(2)–N(3)	1.315(4)	C(12)–N(13)	1.336(4)
N(3)–C(4)	1.463(4)	N(13)–C(14)	1.459(4)
N(3)–C(5)	1.456(5)	N(13)–C(15)	1.442(5)
C(2)–C(6)	1.474(4)	C(12)–C(16)	1.477(4)
C(6)–C(7)	1.391(5)	C(16)–C(17)	1.389(5)
C(7)–C(8)	1.371(5)	C(17)–C(18)	1.378(5)
C(8)–C(9)	1.373(7)	C(18)–C(19)	1.365(5)
C(9)–C(10)	1.378(6)	C(19)–C(20)	1.370(6)
C(10)–C(11)	1.377(5)	C(20)–C(21)	1.380(5)
C(11)–C(6)	1.391(5)	C(21)–C(16)	1.387(4)

Bond angles (°)

N(1)–C(2)–N(3)	117.4(3)	N(1)–C(12)–N(13)	117.3(3)
N(1)–C(2)–C(6)	121.4(3)	N(1)–C(12)–C(16)	122.1(3)
N(3)–C(2)–C(6)	121.1(3)	N(13)–C(12)–C(16)	120.4(3)
C(2)–N(3)–C(4)	124.2(3)	C(12)–N(13)–C(14)	123.3(3)
C(2)–N(3)–C(5)	120.3(3)	C(12)–N(13)–C(15)	120.9(3)
C(4)–N(3)–C(5)	115.3(3)	C(14)–N(13)–C(15)	115.8(3)

C(2)–N(1)–C(12)	123.4(3)

Torsion angles (°)

C(12)–N((1)–C(2)–N(3)	154	C(2)–N(1)–C(12)–N(13)	153
N(1)–C(2)–N(3)–C(4)	170	N(1)–C(12)–N(13)–C(14)	168
N(1)–C(2)–N(3)–C(5)	−14	N(1)–C(12)–N(13)–C(15)	−11

N(1)–C(2)–C(6)–C(7)	127	N(1)–C(12)–C(16)–C(21)	126

Crystal data. $(C_{18}H_{22}N_3)^+Cl^-$, M = 315.5, monoclinic, a = 9.852(1), b = 14.037(2), c = 14.517(2) Å, β = 120.73(4)°, V = 1 726 Å^3, Z = 4, ρ_c = 1.21, μ = 2.3 cm^{-1}, Mo-K_α radiation, λ = 0.710 69 Å, $P2_1/c$ (No. 14), R = 0.050 for 1 865 reflexions with $F_{obs} > 3\sigma(F)$.

The chloride formed clear, colourless crystals and a specimen of dimensions (0.29 × 0.23 × 0.35) mm was used for data

* For details of the Supplementary Publications scheme, see Instructions for Authors (1986), *J. Chem. Soc., Perkin Trans. 1*, 1986, Issue 1.

collection to a θ value of 25° with Mo-K_α radiation. No absorption correction was applied. Of the 3 188 unique reflexions measured, 1 865 had $F > 3\sigma(F)$ and were used in structure refinement. Standard reflexion monitoring indicated no crystal deterioration during data collection. The structure was solved by direct methods using the MULTAN suite of programs.[7] With the 288 highest E-values (> 1.57), all expected non-hydrogen atoms were located. The co-ordinates and isotropic thermal parameters of these 22 atoms were refined to R = 0.14 before inclusion of hydrogen atoms attached to the phenyl groups and anisotropic thermal motion refinement. At R = 0.07, a difference Fourier synthesis enabled all the remaining methyl hydrogen atoms to be located. Final convergence (all atomic positions, anisotropic treatment for heavy atoms, isotropic treatment of hydrogen atoms) was at R = 0.05. The weighting scheme $\omega^{-1} = (0.6 - 0.026F + 0.0019F^2)$ was applied to obtain a uniform $\omega\Delta F^2$ distribution over the F-range.

The atomic co-ordinates are given in Table 3 and selected bond lengths, angles, and torsion angles in Table 4. Tables of thermal parameters and hydrogen bond lengths and angles are available as a Supplementary Publication [SUP no. 56464 (3 pp.)].* Copies of the structure factors are available from the Editorial Office.

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