

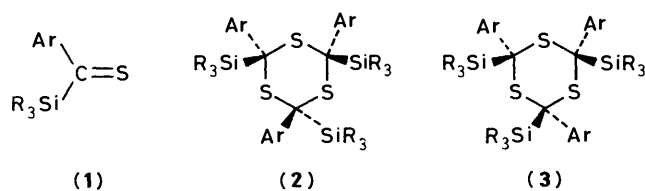
## Chemistry of Silyl Thioketones. Part 4.† 2,4,6-Triaryl-2,4,6-tris(trimethylsilyl)-1,3,5-trithianes from Silyl Thioketones: Crystal Structure of 2,4,6-Triphenyl-2,4,6-tris(trimethylsilyl)-1,3,5-trithiane and Stereochemistry of Desilylation with Fluoride Ion

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Silyl thioketones are easily converted into the corresponding trimers (1,3,5-trithianes) under acidic conditions. Both the  $\alpha$ -(*cis,trans*)- and the  $\beta$ -(*cis,cis*)-isomers were isolated. The  $\beta$ -diastereoisomers predominate over the  $\alpha$ -form. The major isomer from the trimerisation of trimethylsilylphenyl thioketone, upon X-ray analysis, shows a chair-like conformation with the silyl groups all equatorial. Desilylation of the  $\alpha$ - and  $\beta$ -trimers of the trimethylsilylphenyl thioketone with fluoride ion affords, stereospecifically, the two isomeric 2,4,6-triphenyl-1,3,5-trithianes.

The preparation of thiocarbonyl compounds under a variety of conditions (neutral, acidic, basic, photochemical, thermochemical)<sup>1</sup> is often complicated by the concomitant formation of by-products, trimers being the main ones. Thioaldehydes, especially, have such a great tendency to polymerise that, normally, their attempted syntheses have given rise only to oligomers. The constitution of many trimers derived from thioaldehydes and thioketones was first elucidated by Baumann and Fromm.<sup>2</sup> Stereochemical assignments to the so called  $\alpha$ - and  $\beta$ -isomers of trimeric thioaldehydes, however, gave rise to some conflicting reports.<sup>2-4</sup> It was only in 1947 that Hassel and Viervoll,<sup>5</sup> by means of electron diffraction investigations, were able to assign unambiguously the chair conformation to a number of 1,3,5-trithiane rings and the *eq,eq,ax* and the *eq,eq,eq* stereochemistry to the three substituents of the  $\alpha$ - and  $\beta$ -trimers of thioaldehydes (*cis,trans* and *cis,cis* stereoisomers respectively).

Following that pioneering paper many reports appeared in the literature dealing with the molecular structure and stereochemistry of 1,3,5-trithiane derivatives<sup>1c,6,7</sup> obtained either from trimerisation of the corresponding thiocarbonyls, mainly thioaldehydes,<sup>1c,6</sup> or from substitution at the trithiane carbons.<sup>7</sup>



- a; R = Me, Ar = Ph  
 b; R = Me, Ar = 4-MeC<sub>6</sub>H<sub>4</sub>  
 c; R = Ph, Ar = Ph

During work on the synthesis and reactivity of silyl substituted thiones (1),<sup>1d,8</sup> we obtained in several instances oligomeric mixtures of such thiones which were particularly

abundant (up to 70% based on the starting material) when the sulphurisation reaction of the acylsilanes was carried out at higher temperature than usual (0 °C instead of -20 °C).

All the oligomeric fractions consisted of two principal products (*ca.* 90% of total) plus some unidentified by-products.

In order to clarify both the structure of these products and to study the stereochemistry of their protodesilylation, we examined in detail the oligomers obtained from the phenyl trimethylsilyl thioketone (1a) which together with the other reported (see Experimental section) represent the first examples of trimerisation of thioacylsilanes.

The acid-catalysed reaction of phenyl trimethylsilyl ketone with hydrogen sulphide at 0 °C<sup>1d</sup> and subsequent thick layer chromatography on silica gel gave, besides some blue phenyl trimethylsilyl thioketone (1a), two main white crystalline products. The <sup>1</sup>H and <sup>13</sup>C n.m.r. spectra of the higher *R<sub>F</sub>* fraction (m.p. 130–132 °C from EtOH) showed two types of carbon substituents in the ratio 2:1 typical of a trimer with a *cis,trans* structure ( $\alpha$ -form) (2a). The lower *R<sub>F</sub>* fraction (m.p. 180–181 °C from EtOH) had the n.m.r. spectra typical of a fully symmetrical structure with a *cis,cis* arrangement of substituents as in compound (3a) (see Experimental section).

N.m.r. data was not sufficient either to assign the conformation to the two trimers or to determine the stereochemistry of the phenyl and trimethylsilyl substituents. On the other hand, literature data was abundant in the case of trimers of thioaldehydes,<sup>1c,5,7</sup> but surprisingly lacking in the case of trimers of thioketones. We have, therefore, carried out an X-ray structural analysis on crystals of the symmetrical trimer (3a). Tables 1 and 2 list fractional atomic co-ordinates, relevant bond lengths, angles, and dihedral angles respectively; the molecule is shown in the Figure. The 1,3,5-trithiane ring adopts a chair-like conformation with the most bulky silyl substituents all equatorial and the phenyl groups all axial.

In order to relieve the diaxial 1,3 interactions the three phenyl nuclei adopt a basket shaped conformation as can be seen in the Figure and by the dihedral angles listed in Table 2. Moreover the overall steric crowding flattens the ring (see Table 2) with respect to the less substituted trithiane derivatives.<sup>9</sup>

Finally it should be noted that, probably again in order to relieve the steric crowding, the silicon-ring carbon bond lengths are higher than usual.<sup>8b</sup>

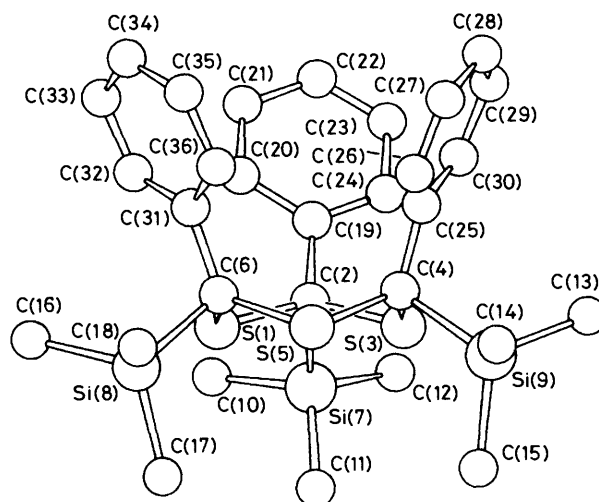
† For Parts 2 and 3 see refs. 8d and e.

**Table 1.** Fractional atomic co-ordinates

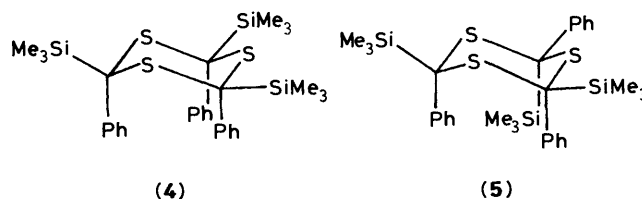
Atom	x	y	z
S(1)	0.293 22(12)	0.074 58(10)	0.378 00
S(3)	0.332 2(1)	0.162 5(1)	0.007 0(2)
S(5)	0.235 0(1)	0.030 9(1)	0.532 4(2)
Si(7)	0.436 9(1)	0.168 3(1)	0.385 0(3)
Si(8)	0.299 4(2)	0.108 1(1)	0.851 1(2)
Si(9)	0.238 8(2)	-0.064 6(1)	0.424 8(3)
C(2)	0.320 6(4)	0.159 9(4)	0.436 7(7)
C(4)	0.247 5(4)	0.118 4(3)	0.686 9(7)
C(6)	0.216 3(5)	0.031 0(4)	0.464 2(7)
C(10)	0.436 3(9)	0.158 4(8)	0.211 7(14)
C(11)	0.500 0(6)	0.100 4(5)	0.458 9(9)
C(12)	0.477 4(7)	0.253 5(5)	0.425 2(11)
C(13)	0.307 2(6)	0.196 0(4)	0.916 4(10)
C(14)	0.234 0(7)	0.053 6(6)	0.953 3(12)
C(15)	0.402 6(6)	0.068 8(5)	0.840 6(11)
C(16)	0.215 7(7)	-0.080 0(6)	0.256 5(11)
C(17)	0.343 6(5)	-0.085 7(5)	0.457 5(10)
C(18)	0.166 1(6)	-0.118 5(5)	0.521 6(9)
C(20)	0.224 4(4)	0.211 4(2)	0.274 7(6)
C(21)	0.183 4(4)	0.267 5(2)	0.223 0(6)
C(22)	0.189 3(4)	0.331 6(2)	0.279 8(6)
C(23)	0.236 0(4)	0.339 6(2)	0.388 3(6)
C(24)	0.276 9(4)	0.283 4(2)	0.440 0(6)
C(19)	0.271 1(4)	0.219 3(2)	0.383 2(6)
C(26)	0.099 8(4)	0.124 6(2)	0.760 4(6)
C(27)	0.029 5(4)	0.161 5(2)	0.795 4(6)
C(28)	0.026 6(4)	0.232 2(2)	0.776 7(6)
C(29)	0.093 9(4)	0.265 9(2)	0.723 1(6)
C(30)	0.164 2(4)	0.229 0(2)	0.688 1(6)
C(25)	0.167 2(4)	0.158 4(2)	0.705 8(6)
C(32)	0.111 9(3)	0.065 5(3)	0.299 8(5)
C(33)	0.030 7(3)	0.074 5(3)	0.258 2(5)
C(34)	-0.035 4(3)	0.065 2(3)	0.340 3(5)
C(35)	-0.020 4(3)	0.047 0(3)	0.464 0(5)
C(36)	0.060 8(3)	0.038 0(3)	0.505 6(5)
C(31)	0.127 0(3)	0.047 2(3)	0.423 5(5)

**Table 2.** Relevant bond lengths (Å), bond angles (°), and dihedral angles (°) of compound (3a)

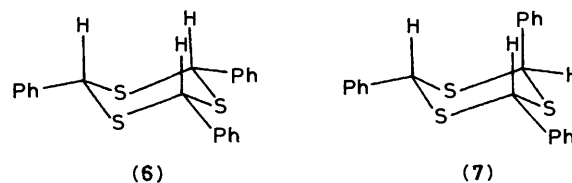
S(1)-C(2)	1.817(8)	S(5)-C(6)	1.828(7)
S(1)-C(6)	1.823(8)	Si(7)-C(2)	1.963(7)
S(3)-C(2)	1.835(8)	Si(8)-C(4)	1.961(7)
S(3)-C(4)	1.829(7)	Si(9)-C(6)	1.948(8)
S(5)-C(4)	1.816(7)	Si-Me	1.86(1)
C(2)-S(1)-C(6)	113.3(3)	S(3)-C(4)-Si(8)	98.6(3)
C(2)-S(3)-C(4)	112.1(3)	S(5)-C(4)-Si(8)	103.9(3)
C(4)-S(5)-C(6)	109.6(3)	S(3)-C(4)-C(25)	117.3(4)
S(1)-C(2)-S(3)	113.0(4)	S(5)-C(4)-C(25)	115.6(5)
S(3)-C(4)-S(5)	112.1(4)	Si(8)-C(4)-C(25)	106.8(4)
S(1)-C(6)-S(5)	112.4(4)	S(1)-C(6)-Si(9)	101.7(4)
S(1)-C(2)-Si(7)	99.7(4)	S(5)-C(6)-Si(9)	100.5(4)
S(3)-C(2)-Si(7)	100.4(3)	S(1)-C(6)-C(31)	116.0(5)
S(1)-C(2)-C(19)	117.6(5)	S(5)-C(6)-C(31)	115.7(5)
S(3)-C(2)-C(19)	114.0(5)	Si(9)-C(6)-C(31)	108.1(4)
Si(7)-C(2)-C(19)	109.4(5)		
C(6)-S(1)-C(2)-S(3)	47.4	S(1)-C(6)-C(31)-C(32)	28.8
C(2)-S(1)-C(6)-S(5)	-51.8	S(5)-C(6)-C(31)-C(36)	-156.9
S(1)-C(2)-S(3)-C(4)	-48.5	S(5)-C(4)-C(25)-C(26)	40.4
C(2)-S(3)-C(4)-S(5)	54.5	S(3)-C(4)-C(25)-C(30)	-12.7
S(3)-C(4)-S(5)-C(6)	-57.8	S(1)-C(2)-C(19)-C(20)	-14.2
C(4)-S(5)-C(6)-S(1)	56.2	S(3)-C(2)-C(19)-C(24)	33.9

**Figure.** Perspective view of the molecule (3a) through the mean plane of the heterocycle, with atomic numbering

and (5) with that of other already known 1,3,5-trithianes we protidesilylated the two diastereoisomers with tetrabutylammonium fluoride in aqueous tetrahydrofuran (THF). Clean substitution at silicon occurred with both isomers, compound



(4) affording the  $\beta$ -trimer<sup>6b</sup> of thiobenzaldehyde (6) and compound (5) the  $\alpha$ -trimer<sup>6b,c</sup> (7); no cross contamination was observed (t.l.c. and n.m.r. measurements of the two crude products). Yields ranged from 70% to quantitative. The physical data of compounds (6) and (7) were identical with those already reported.<sup>6b,c</sup>



It is noteworthy that the protidesilylation proceeds with complete stereospecificity not only in the obvious case of the  $\beta$ -isomer but also for the less stable  $\alpha$ -form. Two explanations are, in principle, possible. The first is that desilylation occurs with retention of configuration at the carbon atoms. In this case it is very likely that the phenyl groups of 2,4,6-triphenyl-1,3,5-trithianes adopt the more stable *eq,eq,eq* and *eq,eq,ax* conformations with respect to the *ax,ax,ax* and *ax,ax,eq* conformations held in the parent silylated chairs. For this reason we have indicated the two desilylated products (6) and (7) as inverted chairs with respect to the two silylated parents (4) and (5).

Although the energy of activation for ring inversion has not been measured for 2,4,6-triphenyl-1,3,5-trithiane, a rapid equilibration at room temperature is in line with the  $\Delta G^\ddagger$  value

Having given to trimer (3a) the structure (4), the other isomer (2a) should have the conformation (5).

In order to correlate the stereochemistry of compounds (4)

of 11.1 kcal mol<sup>-1</sup> measured with the coalescence method for 1,3,5-trithiane itself.<sup>10</sup> Another possible explanation for the observed stereospecificity, would be a complete inversion at the carbon atoms during the desilylation. This would lead directly to the stable conformations *eq,eq,eq* and *eq,eq,ax*. This hypothesis is not in agreement with the stereochemical outcome of other desilylations in cyclic systems,<sup>11</sup> which proceed with retention of configuration at carbon and, moreover, is mechanistically hardly conceivable.

The total stereospecificity of the desilylation observed in the present case would also exclude the formation of a free intermediate carbanion unless asymmetric solvation phenomena are operative.<sup>11</sup> It is known that formation of a carbanion, obtained in the presence of a strong base in highly polar solvents, in trimer (7)<sup>6c</sup> followed by reprotonation, leads to the *cis, cis*-isomer (6).

## Experimental

M.p.s and  $\delta$  values are uncorrected. The routine n.m.r. spectra (60 MHz) were obtained with a Varian EM 360 L instrument. <sup>13</sup>C N.m.r. spectra were recorded at 75.46 MHz (Bruker CXP 300 spectrometer of the High Field n.m.r. Service of CNR in Bologna). Mass spectra were recorded with a V.G. 7070-E spectrometer.

Diethyl ether was distilled from P<sub>2</sub>O<sub>5</sub>. Light petroleum refers to the fraction, b.p. 40–70 °C.

*Preparation of Trimers of Silyl Thioketones. General Procedure.*—Hydrogen chloride and hydrogen sulphide were bubbled into a solution of the silyl ketone (1 g) in anhydrous ether (30 ml) at 0 °C. The solution first turned green, then blue, then red (in order to obtain the thioketones, as main products, the reaction must be carried out at lower temperature).<sup>8b</sup> The solution was concentrated under reduced pressure and chromatographed on silica [light petroleum–benzene (10:1) as eluant]. On coming into contact with silica the red solution became blue (thioketone). The first fraction (blue) consisted of monomeric thioketone.<sup>8b</sup> The second fraction (red) consisted of a mixture of the two trimers of the thione.

*2,4,6-Triphenyl-2,4,6-tris(trimethylsilyl)-1,3,5-trithianes (2a) and (3a).*—The mixture of the two trimers of the trimethylsilylphenyl thioketone, after separation by preparative t.l.c. [light petroleum–benzene (15:1) as eluant], afforded (2a) as the higher R<sub>F</sub> fraction (0.2 g, 18.6% yield) and (3a) as the lower R<sub>F</sub> fraction (0.42 g, 38.5% yield).

Compound (2a), m.p. 130–132 °C (from MeOH) (Found: C, 61.5; H, 7.4; S, 16.4. C<sub>30</sub>H<sub>42</sub>S<sub>3</sub>Si<sub>3</sub> requires C, 61.8; H, 7.3; S, 16.5%);  $\delta_{\text{H}}(\text{CDCl}_3)$  -0.08 (18 H, s, SiMe<sub>3</sub>), 0.12 (9 H, s, SiMe<sub>3</sub>), and 6.9–8.26 (15 H, m, ArH);  $\delta_{\text{C}}(\text{CDCl}_3)$  144.9, 141.4, 130.0, 129.5, 127.4, 126.3, 125.3, 124.9 (ArC), 43.56, 42.17 (q carbons), and -1.94 (SiMe<sub>3</sub>). All the signals were split except that of SiMe<sub>3</sub>. Spectra recorded in deuteriated benzene also showed two signals for the trimethylsilyl group at -1.77 and -1.70;  $m/z$  388 ( $M^+$  - PhCSSiMe<sub>3</sub>), 356 (dimer - S), and 315 (dimer - SiMe<sub>3</sub>).

Compound (3a), m.p. 180–181 °C (from EtOH) (Found: C, 61.6; H, 7.2; S, 16.5. C<sub>30</sub>H<sub>42</sub>S<sub>3</sub>Si<sub>3</sub> requires C, 61.8; H, 7.3; S, 16.5%);  $\delta_{\text{H}}(\text{CDCl}_3)$  0.2 (27 H, s, SiMe<sub>3</sub>) and 6.7–7.9 (15 H, m, ArH);  $\delta_{\text{C}}(\text{CDCl}_3)$  141.1, 130.2, 126.1, 124.8 (ArC), 38.6 (q, carbons), and -2.7 (SiMe<sub>3</sub>);  $m/z$  388 (dimer), 356 (dimer - S), and 315 (dimer - SiMe<sub>3</sub>).

*2,4,6-Tri-p-tolyl-2,4,6-tris(trimethylsilyl)-1,3,5-trithianes (2b) and (3b).*—Following the same procedure as described for compounds (2a) and (3a), (2b) and (3b) were obtained in the ratio 1:1.2.

Compound (2b), m.p. 170–172 °C (from EtOH) (Found: C, 63.1; H, 7.8; S, 15.5. C<sub>33</sub>H<sub>48</sub>S<sub>3</sub>Si<sub>3</sub> requires C, 63.4; H, 7.7; S, 15.4%);  $\delta_{\text{H}}(\text{CDCl}_3)$  -0.08 (18 H, s, SiMe<sub>3</sub>), 0.1 (9 H, s, SiMe<sub>3</sub>), 2.2 (6 H, s, CH<sub>3</sub>), 2.35 (3 H, s, CH<sub>3</sub>), 6.77 and 7.50 (8 H, AB quartet, *J* 8 Hz, ArH), and 7.15 and 7.90 (4 H, AB quartet, *J* 8 Hz, ArH);  $m/z$  624 ( $M^+$ ), 551 ( $M^+$  - SiMe<sub>3</sub>), 416 (dimer), 384 (dimer - S), and 343 (dimer - SiMe<sub>3</sub>).

Compound (3b), m.p. 229–230 °C (from EtOH) (Found: C, 63.2; H, 7.6; S, 15.5. C<sub>33</sub>H<sub>48</sub>S<sub>3</sub>Si<sub>3</sub> requires C, 63.4; H, 7.7; S, 15.4%);  $\delta_{\text{H}}(\text{CDCl}_3)$  0.2 (27 H, s, SiMe<sub>3</sub>), 2.1 (9 H, s, CH<sub>3</sub>), 6.67 and 7.55 (12 H, AB quartet, *J* 8 Hz, ArH);  $m/z$  551 ( $M^+$  - SiMe<sub>3</sub>), 416 (dimer), 384 (dimer - S), and 343 (dimer - SiMe<sub>3</sub>).

*2,4,6-Triphenyl-2,4,6-tris(triphenylsilyl)-1,3,5-trithianes (2c) and (3c).*—Following the same procedure as described for compounds (2a) and (3a), (2c) and (3c) were obtained as a mixture. An attempt to separate the products by preparative t.l.c. [light petroleum–ethyl acetate (10:1) as eluant] afforded a crystalline solid (from EtOH) with a melting range 170–235 °C;  $m/z$  760 (dimer), 728 (dimer - S), 682 (dimer - C<sub>6</sub>H<sub>6</sub>), 501 (dimer - SiPh<sub>3</sub>), 380 (PhCSSiPh<sub>3</sub>), 303 (Ph<sub>3</sub>SiCS), 259 (SiPh<sub>3</sub>), 121 (PhCS), and 105 (SiPh).

*Desilylation of the Trimer (2a).*—A solution (1M) of tetrabutylammonium fluoride in THF (0.52 ml, 0.52 mmol) was added to a solution of compound (2a) (0.1 g, 0.52 mmol) in THF (10 ml) and water (1 ml) at 0 °C. After 15 min, the solution was quenched with water, extracted with ether and the extract dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated; chromatography of the residue [preparative t.l.c., light petroleum–benzene (1:1) as eluant] gave compound (4) (0.044 g, 70.6%), m.p. 168 °C (lit.<sup>6b</sup> 168 °C);  $\delta_{\text{H}}(\text{CDCl}_3)$  5.5 (2 H, s, CH), 5.8 (1 H, s, CH), and 7.06–8.16 (15 H, m, ArH);  $m/z$  366 ( $M^+$ ), 365 ( $M^+$  - H), 244 (PhCHS)<sub>2</sub>, 212 (PhCHSCHPh), 180 (PhCHCHPh), and 121 (PhCS).

*Desilylation of the Trimer (3a).*—Employing the same procedure as described for (4), the product (5) was obtained in 100% yield, m.p. 230 °C (EtOH) (lit.<sup>6b</sup> 229–230 °C);  $\delta_{\text{H}}(\text{CDCl}_3)$  5.43 (3 H, s, CH) and 7.3–7.7 (15 H, m, ArH);  $m/z$  366 ( $M^+$ ), 365 ( $M^+$  - H), 212 (PhCHSCHPh), 180 (PhCHCHPh), and 121 (PhCS).

*Crystal Data for (β)-2,4,6-Triphenyl-2,4,6-tris(trimethylsilyl)-1,3,5-trithiane (3a).*—C<sub>30</sub>H<sub>42</sub>S<sub>3</sub>Si<sub>3</sub>, *M* 583.1, orthorhombic, space group *Pna*2<sub>1</sub>, *a* = 16.132(1), *b* = 19.526(2), *c* = 10.723(1) Å, *V* = 3379.6 Å<sup>3</sup>, *Z* = 4, *D*<sub>C</sub> = 1.17 g cm<sup>-3</sup>, *F*(000) = 1248, *Mo-K*<sub>α</sub> λ = 0.710 69 Å, μ(*Mo-K*<sub>α</sub>) = 3.3 cm<sup>-1</sup>. Intensity data were collected using a CAD4 diffractometer [monochromatized *Mo-K*<sub>α</sub> radiation, ω–2θ scan, scan width 1.1°, scan speed 0.9–8° min<sup>-1</sup>]. For 3011 independent reflections with 2.5° ≤ θ ≤ 25°, 2440 having *I* > 2.5σ(*I*) were considered as observed. Cell constants were obtained from a diffractometer setting of 25 reflections with 11.5° ≤ θ ≤ 17.5°. The structure was solved by direct methods and refined by full-matrix least-squares methods, using the SHELX-76 program system.<sup>12</sup> Anisotropic thermal parameters were used only for S and Si atoms. The carbon atoms of the phenyl rings and the methyl groups were refined as rigid groups. The hydrogen atoms were located geometrically (C–H 1.08 Å) and constrained to refine riding on their attached carbon atoms. Two overall temperature factors were refined for the methyl and phenyl H atoms.

The final agreement index was *R* = 0.055. Programs XANADU<sup>13</sup> and SCHAKAL<sup>14</sup> were used for geometrical calculations and graphics.

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