

## Structure of the 3-(Methoxycarbonylamino)phenyl Ester of *N*-(3-Chlorophenyl)carbamate

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(Received 7 November 1989; accepted 14 February 1990)

**Abstract.** Methyl *N*-{3-[*N*-(3-chlorophenyl)carbamoyloxy]phenyl}carbamate,  $C_{15}H_{13}ClN_2O_4$ ,  $M_r = 320.7$ , monoclinic,  $P2_1/c$ ,  $a = 11.240$  (1),  $b = 14.669$  (2),  $c = 9.084$  (1) Å,  $\beta = 98.13$  (1)°,  $V = 1482.7$  (5) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.437$  g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $\mu = 24.83$  cm<sup>-1</sup>,  $F(000) = 664$ ,  $T = 293$  K, final  $R = 0.038$  for 2383 unique reflections. One intramolecular C—H...O interaction is observed. Two N—H...O hydrogen bonds maintain intermolecular cohesion.

**Introduction.** This work is the second part of a study on the structural properties of a series of bis(*N*-phenylcarbamate) compounds. Here we describe the structure of the *m*-chloro derivative, and compare it with the methyl derivative (Thozet, Ramiliarisoa, Perrin, Bavoux & Meallier, 1990).

**Experimental.** Colourless hexagonal plates (0.39 × 0.06 × 0.2 mm) were obtained from ethyl acetate by slow evaporation. Intensities were collected on an Enraf–Nonius CAD-4 four-circle diffractometer operating in the  $\omega/2\theta$  scan mode with Cu  $K\alpha$  radiation. For measuring lattice parameters, 25 reflections in the range  $11 \leq \theta \leq 44^\circ$  were used. Semi-empirical absorption correction applied using  $\psi$  scans. Maximum value of  $\sin\theta/\lambda = 0.620$  Å<sup>-1</sup>;  $h, k, l$  range  $-13$  to  $13$ ,  $-18$  to  $18$ ,  $0$  to  $11$ . Number of reflections measured 6709; 2383 unique reflections with  $I > 2.5\sigma(I)$ ; value of  $R_{\text{int}} = 0.015$ . No significant variation in the net intensities of three reference reflections (244, 151 and 300) measured every 3600 s.

The structure was solved by direct methods using *MULTAN82* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and refined by least squares (based on  $F$ ) with anisotropic thermal parameters for all non-H atoms. All H atoms were located on the difference Fourier map and refined isotropically. C—H bonds for methyl groups were constrained at 1.08 Å while H—C—H angles were kept constant at 109.5°. All calculations were performed with *SDP* (Frenz, 1980) and *SHELX76* (Sheldrick, 1976). Final  $R = 0.038$ ,  $S = 0.66$ ,  $(\Delta/\sigma)_{\text{av}}$

$= 0.012$ ,  $(\Delta/\sigma)_{\text{max}} = 0.061$  for  $x$  of C(14);  $-0.10 \leq \Delta\rho \leq 0.10$  e Å<sup>-3</sup>. Unit weights used. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV).

**Discussion.** Fig. 1 shows the molecule and the atom-numbering scheme, and Fig. 2 shows a stereoscopic view of the structure. Table 1 gives the final atomic coordinates and equivalent isotropic thermal parameters for the non-H atoms.\* Bond lengths and bond angles are listed in Table 2.

In both rings, three bonds are rather short C(1)—C(2) = 1.376 (3), C(3)—C(4) = 1.378 (3),

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53059 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

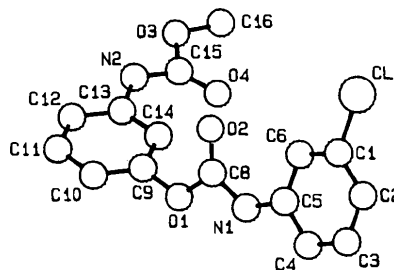


Fig. 1. View of a molecule along [001] with numbering scheme.

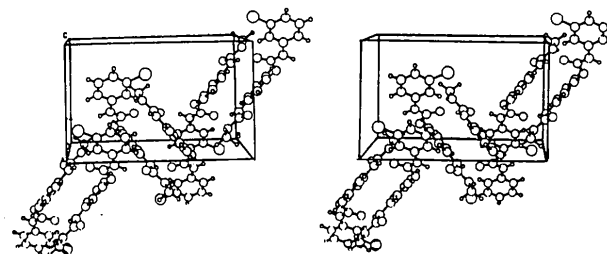


Fig. 2. Stereoscopic view of the structure along [100] drawn by *PLUTO* (Motherwell & Clegg, 1978).

Table 1. *Positional parameters and equivalent isotropic temperature factors with e.s.d.'s in parentheses*

$$B_{\text{eq}} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (2abc\cos\gamma)\beta_{12} + (2accos\beta)\beta_{13} + (2bccos\alpha)\beta_{23}]$$

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}$ (Å <sup>2</sup> )
Cl	0.5439 (6)	0.4438 (4)	0.6959 (8)	4.93 (2)
O(1)	0.1133 (2)	0.2609 (1)	0.1646 (2)	3.95 (4)
O(2)	0.1911 (2)	0.3840 (1)	0.2973 (2)	4.19 (4)
O(3)	0.1106 (2)	0.5578 (1)	-0.3812 (2)	4.44 (4)
O(4)	0.2086 (1)	0.4475 (1)	-0.2406 (2)	4.24 (4)
N(1)	0.2737 (2)	0.2407 (1)	0.3272 (2)	3.25 (4)
N(2)	0.0100 (2)	0.4798 (1)	-0.2333 (2)	3.60 (4)
C(1)	0.4971 (2)	0.3378 (2)	0.6220 (3)	3.50 (5)
C(2)	0.5539 (2)	0.2606 (2)	0.6825 (3)	4.13 (6)
C(3)	0.5139 (2)	0.1774 (2)	0.6232 (3)	4.31 (6)
C(4)	0.4208 (2)	0.1720 (2)	0.5072 (3)	3.67 (5)
C(5)	0.3659 (2)	0.2514 (1)	0.4472 (2)	3.01 (4)
C(6)	0.4041 (2)	0.3356 (2)	0.5052 (3)	3.27 (5)
C(8)	0.1938 (2)	0.3038 (2)	0.2676 (2)	3.22 (5)
C(9)	0.0276 (2)	0.3141 (2)	0.0757 (2)	3.42 (5)
C(10)	-0.0909 (2)	0.3018 (2)	0.0889 (3)	4.20 (6)
C(11)	-0.1757 (2)	0.3503 (2)	-0.0061 (3)	4.46 (6)
C(12)	-0.1406 (2)	0.4078 (2)	-0.1127 (3)	3.89 (5)
C(13)	-0.0201 (2)	0.4187 (1)	-0.1242 (2)	3.16 (5)
C(14)	0.0663 (2)	0.3721 (2)	-0.0283 (2)	3.16 (5)
C(15)	0.1173 (2)	0.4901 (2)	-0.2796 (1)	3.41 (5)
C(16)	0.2188 (3)	0.5761 (2)	-0.4426 (3)	5.08 (7)

Table 2. *Bond lengths (Å) and bond angles (°) with e.s.d.'s in parentheses*

Cl—C(1)	1.746 (2)	C(1)—C(6)	1.380 (3)
O(1)—C(8)	1.360 (3)	C(2)—C(3)	1.382 (4)
O(1)—C(9)	1.403 (3)	C(3)—C(4)	1.378 (3)
O(2)—C(8)	1.209 (3)	C(4)—C(5)	1.393 (3)
O(3)—C(15)	1.351 (3)	C(5)—C(6)	1.386 (3)
O(3)—C(16)	1.434 (4)	C(9)—C(10)	1.366 (4)
O(4)—C(15)	1.210 (3)	C(9)—C(14)	1.387 (3)
N(1)—C(5)	1.401 (3)	C(10)—C(11)	1.387 (4)
N(1)—C(8)	1.348 (3)	C(11)—C(12)	1.383 (4)
N(2)—C(13)	1.413 (3)	C(12)—C(13)	1.383 (3)
N(2)—C(15)	1.342 (3)	C(13)—C(14)	1.389 (3)
C(1)—C(2)	1.376 (3)		
C(8)—O(1)—C(9)	118.3 (2)	C(9)—C(10)—C(11)	118.0 (2)
C(15)—O(3)—C(16)	115.8 (2)	C(10)—C(11)—C(12)	120.6 (2)
C(5)—N(1)—C(8)	127.7 (2)	C(11)—C(12)—C(13)	120.2 (2)
C(13)—N(2)—C(15)	127.4 (2)	N(2)—C(13)—C(12)	117.5 (2)
Cl—C(1)—C(2)	118.8 (2)	N(2)—C(13)—C(14)	122.5 (2)
Cl—C(1)—C(6)	118.1 (2)	C(12)—C(13)—C(14)	120.0 (2)
C(2)—C(1)—C(6)	123.0 (2)	C(9)—C(14)—C(13)	118.0 (2)
C(1)—C(2)—C(3)	117.7 (2)	O(3)—C(15)—O(4)	122.9 (2)
C(2)—C(3)—C(4)	121.3 (2)	O(3)—C(15)—N(2)	109.3 (2)
C(3)—C(4)—C(5)	119.8 (2)	O(4)—C(15)—N(2)	127.8 (2)
N(1)—C(5)—C(4)	116.6 (2)	O(1)—C(8)—N(1)	107.4 (2)
N(1)—C(5)—C(6)	123.4 (2)	O(2)—C(8)—N(1)	127.9 (2)
C(4)—C(5)—C(6)	120.0 (2)	O(1)—C(9)—C(10)	118.3 (2)
C(1)—C(6)—C(5)	118.3 (2)	O(1)—C(9)—C(14)	118.5 (2)
O(1)—C(8)—O(2)	124.6 (2)	C(10)—C(9)—C(14)	123.1 (2)

C(9)—C(10) = 1.366 (4) Å; the angles vary in the range 117.7 (2)—123.1 (2)°.

Bond lengths and angles in both carbamate groups are similar to those found in other compounds involving phenylcarbamate: (*A*) 3-(methoxycarbonylamino)phenyl *N*-(3-methylphenyl)carbamate (Thozet, Ramiliarisoa, Perrin, Bavoux & Meallier, 1991); (*B*) isopropyl *N*-[3-(*N*-ethyl-*N*-phenylcarbamoyloxy)phenyl]carbamate (Kravtsov, Biyushkin,

Malinovskii, Danilin, Ivanov & Yavolovskii, 1988); (*C*) 2,4-hexadiyne-1,6-bis(phenylurethane) (Whuler, Spinat & Brouty, 1984); and (*D*) 2,4-hexadiyne-1,5-bis(*m*-tolylurethane) (Patel, Duesler, Curtin & Paul, 1980).

As described in other derivatives, four least-squares planes can be defined: plane I, through atoms C(1) to C(6) (first benzene ring); plane II, through atoms C(9) to C(14) (second benzene ring); plane III, through atoms N(1), C(8), O(2) and O(1) (first carbamate group); plane IV, through atoms N(2), C(15), O(4) and O(3) (second carbamate group). Angles between planes I and III, II and IV are 9.8 (4) and 13.6 (3)° respectively; in (*A*), they were 42.3 (2) and 40.5 (2)°. The dihedral angle between the benzene ring (plane II) and the carbamate group linked *via* an O atom (plane III) is 70.3 (1)°; it can be compared with the value of 71° found in (*B*). We observe that this angle is much smaller when the connection is *via* an N atom: 13.6 (1)° in the title compound and 14.6° in (*B*). The angles between the two benzene rings and the two carbamate groups are 65.56 (8) and 74.27 (8)° respectively.

The C=O and C—Cl bonds are in the same direction. This is different from (*A*) where the C=O and C—CH<sub>3</sub> bonds are in opposite directions.

The conformation of the molecule produces an intramolecular C—H...O interaction. The bond distance C(6)—H(61) is 0.93 (2) Å, the C(6)...O(2) distance is 2.920 (4) Å and the angle C(6)—H(61)...O(2) is 120.0(2.0)°. Therefore, the substitution of a methyl group by a Cl atom changes the molecular conformation.

N—H...O interactions are found between two molecules I and I'(-*x*, -*y*, -*z*) giving a dimer: N(2)—H(201) = 0.89 (2), H(201)'<sup>1</sup>...O(2)'<sup>1</sup> = 2.14 (3), N(2)'<sup>1</sup>...O(2)'<sup>1</sup> = 3.01 (3) Å and angle N(2)'<sup>1</sup>—H(201)'<sup>1</sup>...O(2)'<sup>1</sup> = 165 (2)°. These dimers have their benzene ring plane II very near without overlapping; the shortest C...C distance is 3.271 (3) Å, and the N(2) atom of one molecule is nearly above the centre of the benzene ring of the second molecule. These dimers are interconnected by the formation of a herringbone pattern along [011] *via* N—H...O intermolecular H bonds. The N(1)...O(4)(*x*, -*y* +  $\frac{1}{2}$ , *z* +  $\frac{1}{2}$ ) and H(101)'<sup>1</sup>...O(4)(*x*, -*y* +  $\frac{1}{2}$ , *z* +  $\frac{1}{2}$ ) distances are 2.900 (2) and 1.99 (2) Å respectively with an N—H...O angle of 160.2 (2)°. Between herringbone arrangements there are only van der Waals contacts.

## References

- FRENZ, B. A. (1980). *Enraf-Nonius Structure Determination Package*. Version 17. College Station, Texas, USA.  
 KRAVTSOV, V. KH., BIYUSHKIN, V. N., MALINOVSKII, T. I., DANILIN, V. V., IVANOV, E. I. & YAVOLOVSKII, A. A. (1988). *Kristallografiya*, **33**, 370–373.

- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1982). *MULTAN11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO78*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
- PATEL, G. N., DUESLER, E. N., CURTIN, D. Y. & PAUL, I. C. (1980). *J. Am. Chem. Soc.* **102**, 461–466.
- SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- THOZET, A., RAMILARISOA, H., PERRIN, M., BAVOUX, C. & MEALLIER, P. (1991). *Acta Cryst.* **C47**, 121–123.
- WHULER, A., SPINAT, P. & BROUTY, C. (1984). *Acta Cryst.* **C40**, 693–696.

*Acta Cryst.* (1991). **C47**, 126–129

## Structure of a Highly Crowded Linear Trisilane

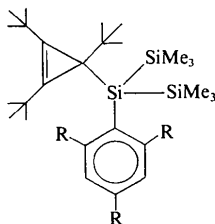
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(Received 29 July 1989; accepted 6 April 1990)

**Abstract.** Hexamethyl-2-(1,2,3-tri-*tert*-butylcyclopropenyl)-2-(2,4,6-triisopropylphenyl)trisilane, C<sub>36</sub>H<sub>68</sub>Si<sub>3</sub>, *M<sub>r</sub>* = 585.2, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 15.907 (2), *b* = 11.537 (3), *c* = 20.928 (3) Å, β = 94.31 (1)°, *V* = 3830 (1) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.02 g cm<sup>-3</sup>, λ(Mo *K*α) = 0.71069 Å, μ = 1.40 cm<sup>-1</sup>, *F*(000) = 1304, *T* = 298 K, *R* = 0.043 for 2115 unique reflections [*I* ≥ 3σ(*I*)]. The molecular geometry of this compound is distinguished by extreme crowding resulting in long Si—Si [2.441 (2) and 2.464 (2) Å] and Si—C [1.973 (4) and 1.988 (4) Å] bonds about the central Si atom. The Si—Si—Si angle is 92.60 (7)°, significantly compressed from a tetrahedral value. A number of short non-bonding contacts between peripheral groups (≤ 3.5 Å) are observed.

**Introduction.** Hexamethyl-2-(1,2,3-tri-*tert*-butylcyclopropenyl)-2-(2,4,6-triisopropylphenyl)trisilane (*R* = isopropyl, shown below), is a photochemical source of highly hindered silylenes and silacyclobutadienes (Puranik & Fink, 1989). This highly crowded molecule is unusual because of the juxtaposition of extremely bulky groups at the central Si atom. An X-ray structure determination was undertaken in order to explore the structural consequences of the steric crowding in this molecule, and to present comparisons with the structures of two closely similar compounds where *R* = H and Me (Puranik, Johnson & Fink, 1989).



**Experimental.** A colorless plate-shaped crystal, 0.40 × 0.40 × 0.17 mm, was obtained from ethanol–hexane; intensity data collected on an Enraf–Nonius CAD-4 diffractometer at 298 K, Mo *K*α radiation (graphite monochromator), lattice parameters from setting of 25 reflections with 4 < θ < 13°; ω–2θ scans, with 1 ≤ 2θ ≤ 50°; scan width (0.8 + 0.2tanθ)°; 0 ≤ *h* ≤ 18, 0 ≤ *k* ≤ 13, –24 ≤ *l* ≤ 24; 6975 total reflections, 6457 unique, 2115 observed with *I* ≥ 3σ(*I*); 2.2% variation in three standard reflections measured every 7200 s; Lorentz–polarization corrections made; absorption corrections based on ψ scans of five reflections near χ = 90 (min. and max. transmission factors are 0.97 and 0.99, respectively); linear decay correction applied to data; *R*<sub>int</sub> = 0.026. The structure was solved by direct methods using *MULTAN11/82* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) in the *Structure Determination Package* (Frenz, 1985); refined on *F* by full-matrix least squares with minimization [Σ(|*F<sub>o</sub>*| – |*F<sub>c</sub>*|)<sup>2</sup>/Σ*w*(*F<sub>o</sub>*)<sup>2</sup>]<sup>1/2</sup>, *w* = 1/σ<sup>2</sup>*F*<sup>2</sup> using the same program. All non-H atoms were refined anisotropically; H atoms were located in a difference map and included as fixed contributions riding on attached C atoms with isotropic thermal parameters 1.3 times those of respective C atoms; the remainder of the H atoms were placed in calculated positions and treated as above. The refinement is not based on a model which includes disorder. The non-H atoms with high thermal parameters, C(15), C(16), C(17), C(29), C(29*A*), C(29*B*), and associated H atoms were removed after final refinement, followed by a reexamination of the difference Fourier map. The Δ*F* map revealed no additional electron density which could be attributed to the presence of disorder of the associated *tert*-butyl or *para*-isopropyl groups in question. Reassignment of the C atoms followed by