Preparation, Structure, and Properties of 3,3,5,5-Tetrakis(trifluoromethyl)-4*H*-1λ⁴,2,4,6-thiatriazine

David J. Brauer**, Alois Haas*, Keith E. Peterman***, and Matthias Rieland**

Abstract: Condensation of $(CF_3)_2C=NLi$ with $Cl_3S_3N_3$ in boiling CCl_4 gives presumably the intermediate $(CF_3)_2C=N-SN$, which forms with excess $(CF_3)_2C=NLi$ in the presence of moisture by a [2 + 4]-cycloaddition the isolated thiatriazine. A X-ray structure determination of the new compound as well as IR, NMR, and mass spectra are provided.

Compounds containing a $=N-S\equiv N$ group seem to be only stable if the amino-ligand has strong element-nitrogen bonds unsuitable for rearrangements. The first example 1-thiazyl-2,3,4,5-tetrakis(trifluoromethylthio)pyrrole was made from the corresponding tetrasubstituted pyrrole and $Cl_3S_3N_3$ in boiling CCl_4 in the presence of pyridine[1]. Another imine suitable for such a substitution is $(CF_3)_2C=NH$. Its lithium salt reacts with $Cl_3S_3N_3$ according to the following procedure to yield 3,3,5,5-tetrakis(trifluoromethyl)-4*H*-1λ⁴,2,4,6-thiatriazine (1).

According to literature method[2] $LiN=C(CF_3)_2$ was prepared in a rigorously flame-dried pyrex reaction vessel. The solvent was removed under dynamic vacuum leaving a brown amorphous solid. A dry argon atmosphere was introduced into the vessel containing 1.2 g (7 mmol) $LiN=C(CF_3)_2$ after which it was attached as a side-arm to a second vessel containing 0.42 g (5.1 mmol) $N_3S_3Cl_3$ in 3 mL CCl_4. The trimeric thiazyl chloride was pyrolized to the monomer NSCl by heating the solution in an oil bath at 70°C until complete

dissolution of the solid trimer occurred with concomitant appearance of a green color characteristic of the monomer. The $NSCl/CCl_4$ solution was then poured directly into the side-arm flask containing the $LiN=C(CF_3)_2$ which had been preheated by a heat-gun.

The reaction mixture was agitated and allowed to cool to ambient temperature. Vacuum fractional distillation provided a deep-green liquid in a −35/−65°C trap which turned brown on standing at room temperature. Refractionation converted the liquid from brown back to the original green color. Upon standing in a glass vessel under a static vacuum for several weeks the liquid slowly volatilized and condensed nearly quantitatively as clear, colorless crystals on the side walls of the storage vessel, $C_6HF_{12}N_3S$ ($M_r = 375.14$), m.p. 44°C.

Crystals of $S[NC(CF_3)_2]_2NH$ (1) were grown by sublimation and sealed in glass capillaries under argon. They belong to the triclinic space group $P\bar{1}$ with $a = 6.821(1)$, $b = 9.240(2)$, $c = 10.871(2)$ Å, $\alpha = 68.830(6)$, $\beta = 75.093(8)$, $\gamma = 68.821(8)°$, $Z = 2$, and $\rho_{calc} = 2.11$ g/cm³. The structure was solved by direct methods using the 2058 unique reflections ($4° \leq 2\theta \leq 50°$) obtained in the $\omega-2\theta$ scan mode with a Siemens AED-1 diffractometer employing Zr-filtered $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The H-atom was located with a ΔF synthesis and refined isotropically while the other atoms were assigned anisotropic thermal parameters. Convergence was obtained with $R = \Sigma\Delta/\Sigma|F_o| = 0.041$ and $R_w = [\Sigma w\Delta^2/\Sigma w|F_o|^2]^{1/2} = 0.053$, where $\Delta = \|F_o| - |F_c\|$ and $w^{-1} = \sigma^2(F_o) + 0.0001|F_o|^2$, for the 1634 reflections obeying $|F_o| \geq 4\sigma(F_o)$[3]. Computations were made with SHELX-76[4], and Fig. 1 was prepared with ORTEP-II[5].

With a six-membered ring which is planar to within 0.016 Å, the symmetry of **1** approaches C_{2v}. Average values of the C−NH and C−NS bond lengths, 1.436(4) and 1.445(3) Å respectively, correspond to single bond lengths while the S−N distances, average 1.517(4) Å, fall close to the previous estimate of 1.52 Å for the $S^{IV}=N$ linkage[6]. The mean of the F−C−F bond angles and librationally-corrected C−F distances are 107.6(5°) and 1.342(9) Å, respectively. The C−C bond lengths (average 1.541(5) Å) are normal, and each CF_3 group is exactly staggered with respect to the corresponding C−NS bond.

Considerable steric congestion occurs with two short $F\cdots F$ contacts (2.584(4)–2.744(4) Å) between CF_3 groups on the same ring atom. While the cross-ring distances $F(3)\cdots F(9)$ (2.900(4) Å) and $F(6)\cdots F(12)$ (2.872(4) Å) are somewhat longer, they are also less than the van der Waals diameter of fluorine, 2.94 Å[7].

The stereochemistry of N(1) is unusual. Although this amine is not engaged in π-bonding, its three valencies are coplanar to within experimental error, and the C(1)-N(1)-C(2) angle is very wide, 128.3(2)°. Both of these features may be results of steric crowding. While enlarging the C(1)-N(1)-C(2) angle relaxes cross-ring $F\cdots F$ interactions, sp^2 hybridization of N(1) allows the N(1)−H bond to pertrud symmetrically through an opening in the van der Waals surface of the fluorine atoms.

The IR-spectrum (Bruker IFS 85 FT) of **1** in the gas phase shows the following absorptions: 3460 (m), 1490 (m), 1285 (ms), 1250 (vs), 1233 (vs), 1180 (ms), 1016 (m), 953 (ms), 721 (ms), 705 (ms), 541 (m); weak bands are not given. The ¹⁹F-NMR-spectrum (Bruker WM 250 FT, lock $CDCl_3$, internal standard $CFCl_3$) consists of a single line appearing at $\delta = -79.95$ proving that all twelve fluorine atoms are equivalent. ¹H- and ¹³C-NMR spectra (Bruker AM 400 FT, $CDCl_3$ as solvent and $Si(CH_3)_4$ as internal standard) show $\delta(NH) = 3.45$; $\delta(CF_3) = 120.5$(q); $\delta(C_{ring}) = 69.8$ (sept.); $^1J(^{13}C-F) = 290$ Hz, $^2J(^{13}C_{ring}-F) \approx 32.5$ Hz. Mass spectral data are consistent with the determined structure. The spectrum was registered with a Varian MAT CH 5 instrument at 70 eV
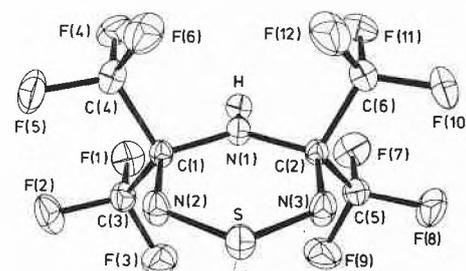
*Fig. 1.   A perspective drawing of $S[NC(CF_3)_2]_2NH$ (**1**) with 20% probability thermal ellipsoids.*

and 100 µA showing the following fragmentation: m/z 356 (4) $M^+ - F$, 306 (100) $M^+ - CF_3$, 287 (1.7) $M^+ - CF_4$, 261 (1.7) $M^+ - (CF_3 + FCN)$, 237 (39) $M^+ - 2CF_3$, 226 (2.5) $(CF_3)_2CNCCF_2^+$, 211 (9.2) $(CF_3)_2C(NH)NS^+$, 196 (9.2) $(CF_3)_2CNS^+$, 191 (4) $CF_3(CF_2)CN_2S^+$, 164 (4) $(CF_3)_2CN^+$, 116 (12.5) CF_3NSH^+, 97 (1.7) F_2CNSH^+, 96 (35) CF_3CNH^+, 76 F_2CCN^+, 69 (64.2) CF_3^+, 50 (4) CF_2^+, 47 (40) HNS^+, 46 (70.8) SN^+.

In order to understand the overall reaction leading to the thiatriazine one has to assume the formation of $(CF_3)_2C=NSN$ as a reactive intermediate which undergoes a [4 + 2]-cycloaddition with the starting imine according to

On standing the lithium salt hydrolyzes to the isolated product **1**.

[1] A. Haas, C. Klare, *Chem. Ber. 118* (1985) 4588.
[2] R.F. Swindell, D.P. Babb, T.J. Oulette, J.M. Shreeve, *Inorg. Chem. 11* (1972) 242.
[3] Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Energie Physik Mathematik, D–7514 Eggenstein-Leopoldshafen 2, by quoting the deposit number CSD 51827, the authors, and the reference.
[4] G.M. Sheldrick, *SHELX 76, Program for Crystal Structure Determination*, University Chemical Laboratory, Cambridge, England (1976).
[5] C.K. Johnson, *ORTEP-II, Report ORNL-5138*, Oak Ridge National Laboratory, Tennessee (1976).
[6] G. Leandri, V. Busetti, G. Valle, M. Mammi, *J. Chem. Soc. D* (1970) 413.
[7] A. Bondi, *J. Phys. Chem. 68* (1964) 441.