

Crystal Structure of a New Dimethyl Carbonate/2,4,6-Tris(trifluoromethyl)-1,3,5-triazine 1:1 Adduct

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Z. Naturforsch. **58b**, 356–358 (2003);
received November 4, 2002

The crystal structure of a new 1:1 complex of dimethyl carbonate and 2,4,6-tris(trifluoromethyl)-1,3,5-triazine is reported. A high tendency of sublimation was observed by differential thermal analysis (DTA) and thermogravimetry (TG). Donor-acceptor interactions between dimethyl carbonate and 2,4,6-tris(trifluoro-methyl)-1,3,5-triazine are assumed to be responsible for the complex formation.

Key words: Dimethyl Carbonate, Fluoroalkyl 1,3,5-triazine Complex, Single Crystal Structure, Thermal Behaviour

Introduction

In the literature, different synthetic pathways are described for the synthesis of fluoroalkyl 1,3,5-triazines. The two principal routes to these 1,3,5-triazines are chlorine/fluorine exchange of chlorinated precursors and the trimerisation of fluorinated nitriles, amidines or imidates [1–3]. Far less is known on the reactivity of the compounds.

A few alkylations of 1,3,5-triazines [4–6] and complexes of 2,4,6-trimethyl-1,3,5-triazine with picric acid (1:1) [7], bromine (1:1) [8] and AgNO₃ (2:3) [9] have been reported.

Results and Discussion

To the best of our knowledge no complexes of 2,4,6-tris(trifluoromethyl)-1,3,5-triazine with organic carbonates have been described. Surprisingly, we found that this triazine forms a 1:1 complex with dimethyl carbonate.

Several linear and cyclic organic carbonates were tested by us for their ability to form complexes with

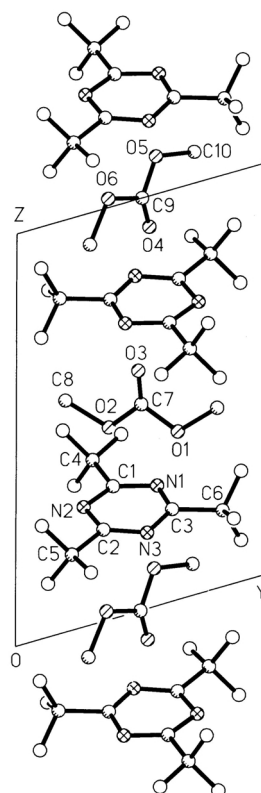


Fig. 1. Crystal structure of the dimethyl carbonate/2,4,6-tris(trifluoromethyl)-1,3,5-triazine adduct. For each disordered CF₃-group and dimethyl carbonate molecule only one position is shown for clarity.

2,4,6-tris(trifluoromethyl)-1,3,5-triazine, but the complex formation was found to be specific to dimethyl carbonate. Diethyl carbonate and propylene carbonate gave no products.

The title complex was found to be soluble in various organic solvents. The ¹H and ¹³C NMR data of the complex in CDCl₃ showed the unchanged shifts of both starting compounds. From this data we concluded that no chemical reaction occurs between the two components. Even heating of the complex in a stainless steel autoclave for 8 h at 100 °C did not cause a chemical reaction.

The X-ray crystallographic study revealed the presence of the 2,4,6-tris(trifluoromethyl)-1,3,5-triazine and dimethyl carbonate molecules (ratio 1:1) separated by long distances (Fig. 1). In the triazine moiety, all CF₃-groups are rotationally disordered. The hexagonal ring is planar within standard deviations with C–N bond distances in a narrow range of 1.320–1.327(3) Å (average 1.324 Å). As a comparison, C–N distances of 1.315–1.319 Å were found in the unsubstituted

triazine [10], whereas slightly longer C–N distances, 1.318–1.334(6) Å, were determined for the trisubstituted carbonitrile triazine [11]. Two crystallographically dependent dimethyl carbonate molecules are disordered around centres of inversion. The average distances for C=O of 1.125 Å and for C–O of 1.365 Å correspond well to the lengths of double and single C–O bonds, respectively.

The packing in the crystal is characterized by alternation of 2,4,6-tris(trifluoromethyl)-1,3,5-triazine and dimethyl carbonate molecules (Fig. 1). The shortest intermolecular contacts, 2.957–3.098 Å, are between ether oxygen atoms of dimethyl carbonate and F atoms (2.92–3.09 Å) or N atoms (2.94 Å). Carbonyl oxygen atoms of dimethyl carbonate also have some short contacts (2.96–3.10 Å) to all three N atoms of the triazine ring.

Thus, a weak donor-acceptor interaction is assumed to be responsible for the structure of the complex, where the three oxygen atoms of dimethyl carbonate might act as donor atom. The nitrogen and fluorine atoms are expected to be the acceptor sites in the 2,4,6-tris(trifluoromethyl)-1,3,5-triazine.

The DTA/TG study showed that sublimation of the complex starts already at room temperature, well below the boiling points of the individual components (98 °C for the triazine and 90 °C for the carbonate).

Experimental Section

Dimethyl carbonate/2,4,6-tris(trifluoromethyl)-1,3,5-triazine complex

2,4,6-Tris(trifluoromethyl)-1,3,5-triazine (28.5 g; 0.1 mol) was placed in a 100 ml three-necked flask equipped with a stirrer, dropping funnel and thermometer and kept at 10 °C with stirring. Spontaneous crystallisation occurred on slow addition of dimethyl carbonate (9.0 g; 0.1 mol).

The product was obtained as white needles and plates (yield: 36.2 g, 96.5%).

DTA/TG

The DTA/TG study was performed at a Mettler Toledo Star system with a heating rate of 12.5 grd min^{−1} on atmo-

spheric conditions. The sublimation of the 1:1 adduct was found to start already at room temperature. Hence, a distinct determination of the onset temperature is impossible. However, these measurements clearly show that the decomposition is complete at around 72 °C well below the boiling points of the individual compounds.

X-ray structure determination

Separation of crystals for X-ray diffraction experiments was complicated due to a low sublimation (decomposition) temperature of the complex. Larger crystals had to be separated (they become much smaller during the observation time with the polarization microscope) and transferred to the low temperature nitrogen flow at the diffractometer. Data collection for the crystal with dimensions 0.9 × 0.5 × 0.5 mm³ was carried out at 180 K on a STADI4 four circle diffractometer (Stoe) using graphite monochromated Mo-K α radiation (λ = 0.71073 Å). The crystals are triclinic with a = 7.901(2), b = 8.295(2), c = 12.409(3) Å, α = 71.85(3), β = 81.62(3), γ = 68.38(3)°, V = 718.0(3) Å³, Z = 2, space group $P\bar{1}$. 3601 reflections were collected, 2836 were independent and 2062 were with $I \geq 2\sigma(I)$. Absorption correction was not applied (μ = 2.03 cm^{−1}).

Structure solution and refinement were performed with SHELXS-97 and SHELXL-93, respectively. In the 2,4,6-tris(trimethyl)-1,3,5-triazine molecule, all CF₃ groups were found to be disordered between two positions with occupancies ranging from 0.14 to 0.86. The central carbon atoms (C(7) and C(9)) of the two crystallographically independent dimethyl carbonate molecules are situated in inversion centres and, therefore, the molecules (each with a half occupancy) are equally disordered between two positions. Due to a high degree of disorder, hydrogen atoms of methyl groups were neither found nor calculated. The final anisotropic refinement for all non-hydrogen atoms with 2543 reflections and 338 parameters converged to R_1 = 0.054 and wR_2 = 0.139.

The supplementary material has been sent to the Cambridge Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK as supplementary material with deposition number 195657 and can be obtained by contacting the CCDC and quoting the article details and the corresponding SUP numbers.

- [1] T. R. Norton, J. Am. Chem. Soc. **72**, 3527 (1950).
- [2] E. R. Bissell, R. E. Spenger, J. Org. Chem. **24**, 1147 (1959).
- [3] G. A. Grindahl, W. X. Bajzer, O. R. Pierce, J. Org. Chem. **32**, 603 (1967).

- [4] R. Hirt, H. Nidecker, R. Berchtold, Helv. Chim. Acta **33**, 1365 (1950).
- [5] H. Bader, E. A. Ruckel, F. X. Markley, C. G. Santangelo, P. Schickedantz, J. Org. Chem. **30**, 702 (1965).

- [6] G. Ostrogovich, T. Simonescu. Studii Cercetari Sti. Chim. (Baza Cercetari Sti Timosvara) **7**, 69 (1960); C.A. **55**, 14477g (1961).
- [7] Ch. Grundmann, G. Weisse, Chem. Ber. **84**, 684 (1951).
- [8] Ch. Grundmann, A. Kreutzberger, J. Am. Chem. Soc. **77**, 44 (1955).
- [9] K. Yanagiya, Bull. Chem. Soc. Jpn. **46**, 2809 (1973).
- [10] P. Coppens, Science, **158**, 1577 (1967).
- [11] E. Kroke, M. Schwarz, R. Riedel, I. Svoboda, H. Fuess, Z. Krist. New. Cryst. Struct, **214**, 111 (1999).