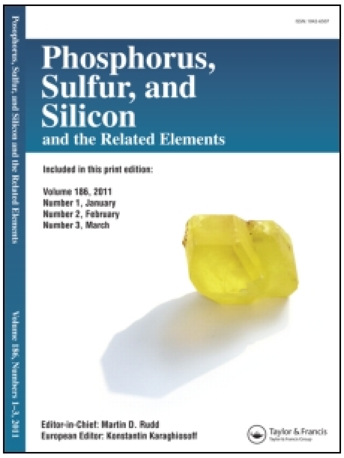

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On the Reactivity of the 1,3,5-Triazine Ring Systems Substituted with Pseudo Halogens – Characterization of Triazine Isocyanates

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We have recently been studying the nucleophilic substitution reactions of cyanuric chloride $(CNCl)_3$ with MX (M = K, Na, x = NNN, OCN, SCN and SeCN). 2,4-Dichloro-6-isocyanato-1,3,5-triazine and 2-chloro-4,6-diisocyanato-1,3,5-triazine can only be obtained by the reaction of the amino compounds with phosgene or oxalyl chloride.[1]Both compounds have been characterized by X-ray, ^{13}C NMR, Raman and IR spectroscopy. 2,4-Dichloro-6-isocyanato-1,3,5-triazine: Space group *Pbca*, Z = 8, lattice dimensions at 293 K: $a = 7.4363(11)$, $b = 9.6019(11)$, $c = 20.078(5)$ Å, $V = 1433.6(4)$ Å^3; 2-Chloro-4,6-diisocyanato-1,3,5-triazine: Space group $P2_1/n$, Z = 4, lattice dimensions at 293 K: $a = 7.4370(7)$, $b = 9.158(2)$, $c = 11.571(2)$ Å, $\beta = 105.033(11)$, $V = 761.1(2)$ Å^3.

Keywords: Crystallography; Triazine; Isocyanate; Raman spectroscopy

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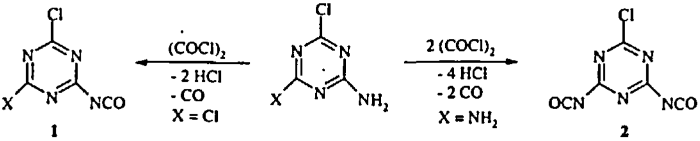
* X-ray structure analysis

INTRODUCTION

Triazine chemistry has been extensively studied and well established in the past century. Due to the big range of applications they represent a very interesting compound class, e. g. the use of the azide as explosive or the isocyanates in polymer chemistry.[2b] We report here the results of our studies on the nucleophilic substitution reactions of cyanuric chloride $(CNCl)_3$ with MX (M = K, Na, X = NNN, OCN, SCN and SeCN), the X-Ray structures, Raman, IR, and ^{13}C NMR spectra of 2,4–dichloro–6–isocyanato–1,3,5–triazine (**1**) and 2–chloro–4,6–diiso-cyanato–1,3,5–triazine (**2**).

Only the azide and thiocyanate substituted products could be isolated by nucleophilic substitution of chloride. Formation of the analogue OCN and SeCN products could not be observed. The mono- and disubstituted cyanuric isocyanates can be obtained from reaction of 2–Amino–4,6–dichloro–1,3,5–triazine and 2,4–diamino–6–chloro–1,3,5–triazine with oxalyl chloride (Scheme 1).[1]



SCHEME 1

Staudinger reaction was investigated for 2,4,6–triazido–1,3,5–triazine, 2,4–dichloro–6–isocyanato–1,3,5–triazine and 2–chloro–4,6–diiso cyanato–1,3,5–triazine. In the latter two cases no reaction occurred. For the reaction of cyanuric azide with triphenyl phosphane it has been shown that the final products and their distribution very much depend on the reaction conditions, the stoichiometry and temperature leading to different exactly defined products. As the generated azido group is attached to a C atom adjacent to an annular nitrogen it may spontaneously cyclize to give a tetrazole ring or an equilibrium mixture of both forms. This azido-tetrazole isomerisation has been the subject of our study by means of ^{31}P NMR spectroscopy.[2a] The novel 2–triphenylphosphanimino–4–azidotetrazolo[5,1-*a*]–[1,3,5]triazine, 2,4–bis(triphenylphosphanimino)tetrazolo[5,1-*a*]–[1,3,5]triazine and 2,4,6–Tris(triphenylphosphanimino)–1,3,5–triazine could be isolated and have been characterised by X-ray, ^{31}P NMR, Raman and IR spectroscopy.[2]

X-RAY SPECTROSCOPY

Suitable single crystals of **1** and **2** were obtained by sublimation. **1** crystallizes in the orthorombic space group *Pbca* with eight molecules in the unit cell and **2** crystallizes in the monoclinic space group $P2_1/n$ with four molecules in the unit cell. Selected bond lengths [Å] and angles [°] are given in Table 1. The crystallographic data for **1** and **2** is summarized in the experimental section. Figure 1 shows the crystal structures of **1** and **2**.

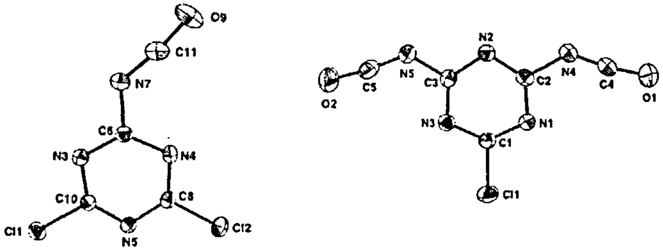


FIGURE 1 The ORTEP drawings of **1** and **2**. Thermal ellipsoids with 25% probability at 293 K

1		**2**	
C(11)-O(9)	1.145	C(5)-O(2)	1.163
N(7)-C(11)	1.204	C(4)-O(1)	1.156
C(6)-N(7)	1.381	N(5)-C(5)	1.189
C(10)-Cl(1)	1.716	N(4)-C(4)	1.168
N(7)-C(11)-O(9)	172.50	C(3)-N(5)	1.390
C(6)-N(7)-C(11)	126.07	N(5)-C(5)-O(2)	171.91
		N(4)-C(4)-O(1)	172.43
		C(3)-N(5)-C(5)	126.65

TABLE 1 Selected bond lengths [Å] and angles [°] for **1** and **2**

EXPERIMENTAL SECTION

Used solvents were freshly distilled, dried and stored under nitrogen. – NMR: Jeol EX400 Delta (^{13}C, chemical shifts refer to $\delta_{TMS} = 0.00$ – IR: Nicolet 520 FT-IR. – Raman: Perkin Elmer Spectrum 2000R NIR FT. – CHN analyses: Analysator Elementar Vario EL. **1** and **2** were prepared according to the procedure given in the literature.[1]

1: $C_4Cl_2N_4O$ (190.98) sensitive to a humidity atmosphere – **HCN** calcd: C: 25.16%, N: 29.34% found: C: 25.26%, N: 29.22%. – **Raman** (50 scans, 300 mW, 180°, 20 °C): $\tilde{\nu} = 2266\ cm^{-1}$ (0.5, ν_{as} (NCO)), 1536 (2, ν ((CN)$_3$)), 1491 (3, ν ((CN)$_3$)), 1289 (1, νs (NCO)), 985 (10, ν ((CN)$_3$)). – **^{13}C NMR** ($CDCl_3$, 68 MHz, 25 °C): δ = 131.4 (s, N$\underline{C}$O), 165.2 (s, $\underline{C}$–NCO) 172.7 (s, $\underline{C}$–Cl). – **X-ray**: Crystal system: orthorombic; Space group: P*bca*; *a* = 7.4363Å; *b* = 9.6019 Å; *c* = 20.078 Å; Z = 8; *V* = 1433.6 Å^3; d_{calcd} = 1.770 Mg/m^3; Mo-*K*α λ = 0.71073 Å; Final R indices [I>2sigma(I)] R1 = 0.0293, wR2 = 0.0741; R indices (all data) R1 = 0.0385, wR2 = 0.0799.

2: $C_5ClN_5O_2$ (197.55); sublimation temperature: 84-85 °C (0.2 Torr, 2.67 * 10^{-4} bar); sensitive to a humidity atmosphere – **HCN** calcd: C: 30.40%, N: 35.45% found: C: 30.24%, N: 35.28%. – **IR** (in Nujol on CsJ): $\tilde{\nu}$ = 2246 cm−1 (s, ν_{as} (NCO)), 1288 (m, ν_s (NCO)). – **Raman** (50 scans, 500 mW, 180°, 20 °C): $\tilde{\nu} = 2247\ cm^{-1}$ (4, ν_{as} (NCO)), 1530 (60, ν ((CN)$_3$)), 1500 (45, ν ((CN)$_3$)), 1299 (10, νs (NCO)), 985 (100, ν ((CN)$_3$)). – **^{14}N NMR** (27.38 MHz, C_6D_6): −124.5 ($N_{triazine}$), −135.3 ($N_{triazine}$), −307.9 ($\underline{N}$CO). – **^{13}C NMR** (67.94 MHz, C_6D_6): 173.2 ($\underline{C}$-Cl), 166.0 ($\underline{C}$-NCO), 131.5 (N$\underline{C}$O). – **X-ray**: Crystal system: monoclinic; Space group: P2$_1$/n; *a* = 7.4370Å; *b* = 9.158 Å; *c* = 11.571 Å; β = 105.033°; Z = 4; *V* = 761.1 Å^3; d_{calcd} = 1.724 Mg/m^3; Mo-*K*α λ = 0.71073 Å; Final R indices [I>2sigma(I)] R1 = 0.0562, wR2 = 0.1172; R indices (all data) R1 = 0.0914, wR2 = 0.1373.

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