Characterization, Crystal Structure of 2,4-Bis(triphenylphosphanimino)tetrazolo[5,1-*a*]-[1,3,5]triazine, and Improved Crystal Structure of 2,4,6-Triazido-1,3,5-triazine

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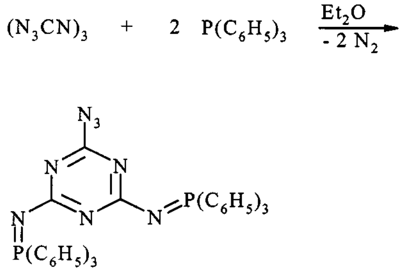
2,4-Bis(triphenylphosphanimino)tetrazolo[5,1-*a*][1,3,5]triazine (**1**) was synthesized by reaction of cyanuric azide with triphenylphosphane. **1** is characterized by X-ray structural analysis, IR, Raman, and NMR spectroscopy. The obtained spectra showed that the remaining azide group in **1** reacts with the N4 atom of the triazine ring and forms a tetrazole. An improved crystal structure for 2,4,6-triazido-1,3,5-triazine (**2**) was determined and for the first time a ^{14}N-NMR spectrum was obtained. CAUTION: **2** (Cyanuric azide) is explosive! The explosive nature increases with greater purity and crystal size.

Introduction

Since the discovery of cyanuric azide by H. Finger[1] in 1907 and the development of an improved method in 1921 by E. Ott and E. Ohse[2], there has been considerable interest in the reactivity and the explosive character of cyanuric azide[1]-[11]. In this present study we determined an improved structure[4] of cyanuric azide and investigated the reaction of cyanuric azide with triphenylphosphane, first attempted by W. Kesting in 1923[10].

According to Staudinger and Meyer[12], phenylazide reacts with triphenylphosphane in anhydrous ether to form a phosphazide. The intermediate cannot be isolated at room temperature and spontaneously emits nitrogen to form triphenylphosphanophenylimine. This can be isolated in almost quantitative yield.

In Kesting's application of the Staudinger-Meyer reaction, substituting **2** for phenyl azide[10], the proposed reaction path is given in Equation 1.



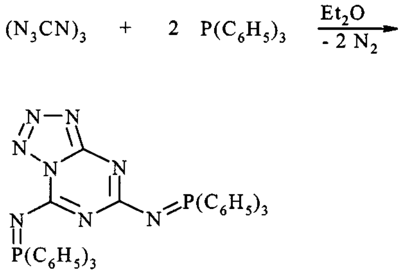
(1)

The product was, however, only characterized by elemental analyses and melting point. The compound 2,4-bis(triphenylphosphanimino)-6-azido-1,3,5-triazine that W. Kesting described showed no shock or heat sensitivity, in spite of the remaining azide group. In this paper, we report our studies on the synthesis, characterisation, and crystal structure of $C_{39}H_{30}N_8P_2$ (**1**).

Results and Discussion

In the reaction of **2** at room temperature with two equivalents of triphenylphosphane the color changed from colorless to yellow-green. This is thought to be due to the formation of $R-NNN-P(C_6H_5)_3$ (R = residue)[12]. This adduct has only fleeting existence and decomposes by giving off N_2, while the solution again becomes colorless. The end product is shown below (**1**). Raman- and ^{31}P-NMR spectroscopy indicates that **1** is not an azide, due to the absence of the asymmetric and symmetric vibrations of the azide group in the Raman spectrum and two ^{31}P-NMR signals found at δ = 21.7 (s) and δ = 17.2 (s). The single crystal X-ray structure analysis for **1** further confirms that there is no azide group in the molecule.

The azide group reacts with the N4 atom of the triazine ring and forms a tetrazole (Equation 2).



(2)

1

[+] X-ray structure analysis.

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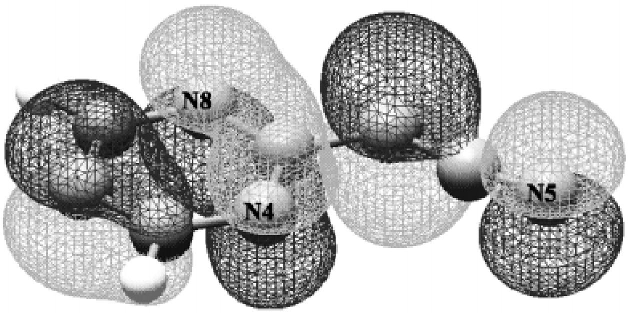
Looking at the calculated (Mulliken) partial charges[13] (N4: −0.38 e; N5: −0.36 e; PM3 level) of the azide, it can be seen, that the ring closure could not take place from the electrostatic point of view. Even the tetrazole has an "unusual" charge distribution with N4: −0.03 e and N5: −0.19 e (assignment see Figure 2).

The driving force for the ring-closure in reaction (2) can only be explained in terms of a π-stabilization of the tetrazole-triazine ring-system. This reaction is therefore orbital controlled. This is confirmed by the symmetry of the molecular orbital shown in Figure 1. Here, only the N5−N4 or N5−N8 interaction is symmetry allowed.

Figure 1. HOMO[a]

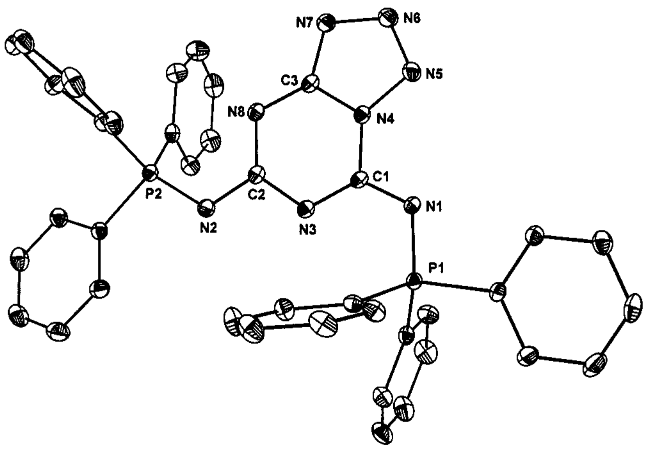


[a] Calcd. for hydrogen derivative.

Crystal Structure of 1

The crystallographic data and refinement details for compound **1** are summarized in the experimental section. **1** crystallizes from chloroform in the monoclinic space group $P2_1/n$ with four molecules and two solvent molecules per tetrazole molecule in the unit cell. Figure 2 shows the crystal structure of compound **1**.

Figure 2. Molecular Structure of **1**



The P−N distance in **1** is 1.614 Å and 1.608 Å. This corresponds to a bond order between one and two. In comparison, the sum of the covalent radius (PN) is 1.8 Å and a typical P−N bond length is found in $R_3-P=N-R$ compounds to be 1.602 Å[15]. The bond lengths and angles of the tetrazole ring (N5−N6: 1.292 Å, N6−N7: 1.364 Å, N5−N6−N7: 112.7°) also correspond to the literature[16]. The C1−N1 and C2−N2 bond lengths in **1** are 1.323 Å and 1.349 Å, respectively their bond order is also between one and two. The sum of the covalent radii (CN) is 1.47 Å for a single bond and 1.27 Å for a double bond[14]. Selected bond lengths [Å] and angles [°] for **1** are given in Table 1.

Table 1. Selected bond lengths [Å] and angles [°] for **1**

P(1)−N(1)	1.614(2)	P(2)−N(2)	1.608(2)
N(1)−C(1)	1.323(3)	N(2)−C(2)	1.349(3)
N(3)−C(1)	1.323(3)	N(3)−C(2)	1.374(3)
N(4)−C(3)	1.359(3)	N(4)−N(5)	1.371(3)
N(4)−C(1)	1.397(3)	N(5)−N(6)	1.292(3)
N(6)−N(7)	1.364(3)	N(7)−C(3)	1.337(3)
N(8)−C(3)	1.334(3)	N(8)−C(2)	1.354(3)
C(1)−N(1)−P(1)	121.50(18)	C(2)−N(2)−P(2)	118.45(18)
C(1)−N(3)−C(2)	119.5(2)	C(3)−N(4)−N(5)	109.3(2)
C(3)−N(4)−C(1)	121.2(2)	N(5)−N(4)−C(1)	129.3(2)
N(6)−N(5)−N(4)	104.9(2)	N(5)−N(6)−N(7)	112.7(2)
C(3)−N(7)−N(6)	105.7(2)	C(3)−N(8)−C(2)	114.0(2)
N(1)−C(1)−N(3)	127.5(2)	N(1)−C(1)−N(4)	115.9(2)
N(3)−C(1)−N(4)	116.5(2)	N(2)−C(2)−N(8)	119.6(2)
N(2)−C(2)−N(3)	115.0(2)	N(8)−C(2)−N(3)	125.4(2)
N(8)−C(3)−N(7)	129.7(2)	N(8)−C(3)−N(4)	122.9(2)
N(7)−C(3)−N(4)	107.4(2)		

The difference in the bond lengths of the triazine (C1−N4 = 1.397 Å, C1−N3 = 1.323 Å) can be explained by different donor-acceptor interactions of the free p-orbital (p-LP) of N1 or N2 with the unoccupied antibonding σ* orbital of the C1−N4 and C2−N3 bond respectively in the ring. From a steric point of view there is more electron density in the antibonding σ* orbital of the C1−N4 bond. This bond therefore is weaker than the C1−N3 bond. This hyperconjugation destabilizes the C−N bond and also explains the π-character of the N1−C1 bond.

Crystal Structure of 2

Cyanuric azide crystallizes from acetone in the hexagonal space group $P\bar{3}$ with two molecules in the unit cell (Figure 3). The C−N−C angle in the triazine ring is 113.09(14)° and the N−C−N angle is 126.91(14)°. The molecule is planar and the distance between the layers is 2.947 Å.

Figure 3. Molecular Structure of **2**

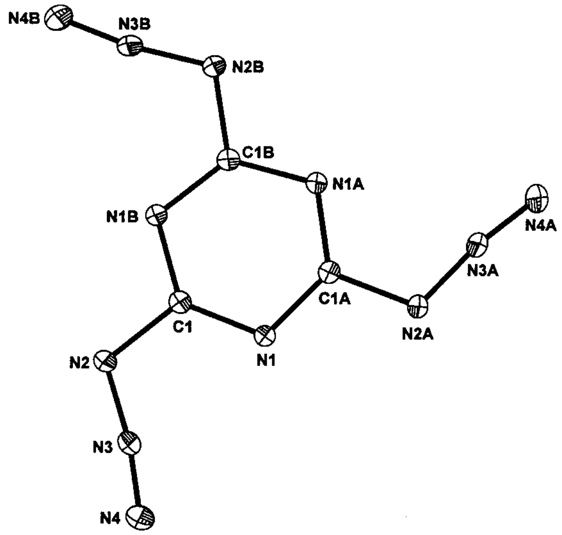


Table 2. ^{14}N- and ^{15}N-NMR shifts for **2**

compound	chemical shift δ [ppm] rel. nitromethane (= 0 ppm) N2	N3	N4	N_{ring}	coupling constant ^1J [Hz] N2−N3	N3−N4	solvent
$(CNN_3)_3$	−271	−146	−137	−162			acetone
$(CN^{15}N)_3$[9]	−258	−142	−131		16.1	6.1	CD_2Cl_2

The N2−N3 bond length is 1.2658(17) Å, respectively the bond order is between one and two. The covalent radius[14] for single bonded nitrogen atom is r_{cov} = 0.7 Å, 0.6 Å for a double bonded nitrogen atom and 0.55 Å for a triple bonded nitrogen atom. The bond order for N3−N4 [1.1156(19) Å] is between two and three. The angle of the azide group (N2−N3−N4) is 172.00(15)°. With the results of the X-ray structure analysis and the calculated (Mulliken) partial charges[13] (C1: 0.22 e; N1: −0.29 e; N2: −0.42 e; N3: 0.75 e; N4: −0.27 e; PM3 level) the ^{14}N-NMR signals are assigned as shown in Table 2.

The assignment further confirms to the results J. Müller[9] obtained for the ^{15}N-NMR shifts of the azide group.

The crystallographic data and refinement details for **2** are shown in the Experimental Section.

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Experimental Section

General Remarks: CAUTION: **2** is explosive! The explosive nature increases with greater purity and crystal size. Only PE equipment should be used during the preparation and handling of cyanuric azide and safety equipment like leather gloves and face-shield is recommended.

Used solvents were freshly distilled, dried and stored under nitrogen. − NMR: Jeol EX400 Delta (^{1}H, ^{13}C, chemical shifts refer to δ_{TMS} = 0.00 according to the chemical shifts of residual solvent signals; ^{14}N, external standard: $\delta(CH_3NO_2)$ = 0.00; ^{31}P, external standard $\delta(H_3PO_4$, 85%) = 0.00. − IR: Nicolet 520 FT-IR (as KBr pellets or in Nujol on KBr). − Raman: Perkin Elmer Spectrum 2000R NIR FT. − CHN analyses: Analysator Elementar Vario EL. − MS: Finnigan MAT 90. − Melting points are uncorrected (Büchi B540).

2 was prepared according to the procedure given in the literature[2], but the solution was cooled to 5°C for recrystallization from acetone and the crystals were dried in vacuo.

2,4-Bis(triphenylphosphanimino)tetrazolo[5,1-a][1,3,5]triazine (**1**): To a solution of 0.5 g ($2.45 \cdot 10^{-3}$ mol) of **2** in anhydrous ether, a solution of 1.4 g ($5.3 \cdot 10^{-3}$ mol) of PPh_3 was added in two hours at room temperature. The solution was refluxed for 12 h. **1** can be purified by recrystallization from chloroform. $C_{39}H_{30}N_8P_2$ (672.3) Yield: quantitative, colorless crystals; m.p. 239°C (dec.), ref.[10]: 243°C. − IR (KBr): $\tilde{\nu}$ = 3078 cm^{-1} (CH) (w), 1597 (C=C) (s). − Raman (460 scans, 400 mW, 180°, 20°C): $\tilde{\nu}$ = 3064 cm^{-1} (4.5) (CH), 1592 (6.0) (CC), 1576 (1.5) (CC), 1522 (0.5), 1484−1455 (0.5), 1440 (0.7), 1340 (0.5), 1296 (4.0), 1223 (0.6), 1186 (1.0), 1164 (2.0), 1112 (2.0), 1088 (0.5), 1032 (3.5), 1004 (10) (CH), 966 (1.0), 900−854 (0.5), 691 (1.0), 648 (0.7), 620 (1.5), 583 (2.0), 261 (2.5). − ^{1}H NMR ($CDCl_3$, 400 MHz, 25°C): δ = 7.35−7.98 (m, 30 H, aromatic H). − ^{13}C NMR ($CDCl_3$, 101 MHz, 25°C): δ = 127−134 (m, 36 C, aromatic C), 152 (dd, J_{CP} = 6.9 Hz / 3.1 Hz, $C_{triazine}$), 159 (d, J_{CP} = 1.5 Hz, $C_{triazine}$), 167 (s, $C_{triazine}$). − ^{31}P NMR ($CDCl_3$, 162 MHz, 25°C) δ = 17.3 (s, P), 21.7 (s; P). − MS (EI, 70 eV); *m/z* (%): 672.1 (11) [M^+], 645 (3) [$M^+ - N_2$], 386 (100), 262.0 (44) [PPh_3^+], 185 (37) [PPh_2^+], 77 (9) [Ph^+]. − $C_{39}H_{30}N_8P_2 \cdot 2\,CHCl_3$ (911.39): calcd. C 53.99, H 3.54, N 12.29; found C 54.53, H 3.58, N 12.40.

2,4,6-Triazido-1,3,5-triazine (**2**): 3.1 g (16.8 mmol) cyanuric chloride in 30 ml of acetone; 5 g (77 mmol) of sodium azide. − C_3N_{12} (204.15) Yield: 3.29 g (96%), colorless needles, very sensitive to shock or heat, m.p. 94°C, ref.[2]: 94°C. − IR (in Nujol on KBr): $\tilde{\nu}$ = 2192.1 (s), 2157.6 [$\nu_{as}(N_3)$] (s), 2114.8 (s), 1571.5 (s), 1532.4 [$\delta((CN)_3)$] (s), 1480.1 (sh), 1350.4 [$\delta((CN)_3)$] (s), 1197.7 [$\nu_s(N_3)$] (s), 984.3 (w), 809.4 [$\delta((CN)_3)$] (m), 775.8 (vw), 706.8 [$\gamma((CN)_3)$] (m), 550.2 [$\delta(N_3)$] (w), 501.1 (vw), 331.2 (vw). − Raman (300 scans, 200 mW, 180°, 20°C): $\tilde{\nu}$ = 2475 [$\nu_{as}(N_3) + \gamma(N_3)$] (0.5), 2206 [$\nu_s(N_3) + \nu(C-N_3)$] (1), 2158 [$\nu_{as}(N_3)$] (2), 2144 [$\nu_{as}(N_3)$] (3), 2177 (1), 1571 (1), 1533 [$\delta((CN)_3)$] (3), 1426 [$\nu_s((CN)_3)$] (6), 1337 (9), 1238 (1), 1194 [$\nu_s(N_3)$] (7), 1150 [$\nu_s(N_3)$] (4), 982 [$\nu(C-N_3)$] (10), 709 (2), 562 (4), 471 (1), 330 (7), 237 (2). − ^{13}C NMR ([D_6]acetone, 68 MHz, 25°C): δ = 171.9 (s). − ^{14}N NMR (acetone, 29 MHz, 25°C): δ = −137 (s, N4), −146 (s, N3), −162 (s, N_{ring}), −271 (s, N2). − C_3N_{12} (204.11): calcd. C 17.65, N 82.35; found C 17.45, N 82.19.

Crystal Structure Analysis of **1**: $C_{39}H_{30}N_8P_2 \cdot 2\,CHCl_3$, *M* = 911.39, crystal size: 0.35 × 0.3 × 0.25 mm, colorless prism, monoclinic, space group $P2_1/n$, *a* = 11.013(2), *b* = 23.182(5), *c* = 17.195(3) Å, α = 90.00, β = 101.580(9), γ = 90.00°, *V* = 4300.7(15) Å^3, *Z* = 4, $d_{calcd.}$ = 1.408 Mg/m^3, μ = 0.515 mm^{-1}, *F*(000) = 1864. Siemens SMART Area detector, scan type = Hemisphere, Mo-K_α, λ = 0.71073 Å, *T* = 173(2) K, 2θ range = 2.98 to 58.54° in $-14 \le h \le 14$, $-28 \le k \le 28$, $-18 \le l \le 23$, reflections collected: 24656, independent reflections: 7509 (R_{int} = 0.0292), observed reflections: 6006 [$F > 4\sigma(F)$]. Structure solution program: SHELXS-97 (G. M. Sheldrick, University of Göttingen, Germany, 1997), direct methods, data-to-parameter ratio: 14.6:1 {11.7:1 [$F > 4\sigma(F)$]}, final *R* indices [$F > 4\sigma(F)$]: *R*1 = 0.0481, *wR*2 = 0.0976, *R*1 = 0.0664, *wR*2 = 0.1069 (all data), GOF on F^2 = 1.109, largest and mean Δ/σ: 0.002, 0.000, largest difference peak/hole: 0.404, −0.425 e Å^{-3}, program used: SHELXL-97 (G. M. Sheldrick, University of Göttingen, Germany, 1997).

Crystal Structure Analysis of **2**: C_3N_{12}, *M* = 204.11, crystal size: 0.2 × 0.2 × 0.15 mm, colorless prism, hexagonal, space group $P\bar{3}$, *a* = 8.7456(2), *b* = 8.7456(2), *c* = 5.8945(3) Å, *V* = 390.44(2) Å^3, *Z* = 2, $d_{calcd.}$ = 1.736 Mg/m^3, μ = 0.138 mm^{-1}, *F*(000) = 204. Siemens SMART Area detector, Mo-K_α, λ = 0.71073 Å, scan type = hemisphere, *T* = 183(2) K, 2θ range = 5.38 to 55.84° in $-8 \le h \le 11$, $-11 \le k \le 10$, $-7 \le l \le 7$, reflections collected: 2306, independent reflections: 582 (R_{int} = 0.0284), observed reflections: 531 [$F > 4\sigma(F)$]. Structure solution program: SHELXS-97 (G. M. Sheldrick, University of Göttingen, Germany, 1997), direct methods, data-to-parameter ratio: 12.4:1 {11.3 :1 $[F>4\sigma(F)]$},final R indices $[F>4\sigma(F)]$: $R1 = 0.0342$, $wR2 = 0.0894$, $R1 = 0.0384$, $wR2 = 0.0912$ (all data), GOF on $F^2 = 1.411$, largest and mean Δ/σ: 0.013, 0.002, largest difference peak/hole: 0.182, −0.164 e Å^{-3}, program used: SHELXL-97 (G. M. Sheldrick, University of Göttingen, Germany, 1997).

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[17] Further details of the crystal structure determination are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, United Kingdom, on quoting the depository number 102718 (**1**), 102717 (**2**), the names of the authors, and the journal citation.

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