2,4,6-Tripiperidino-1,3,5-triazine

Arif Ali Khan, Cathleen Wismach, Peter G. Jones* and Rainer Streubel†

Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany

† Current address: Institut für Anorganische Chemie, Universität Bonn, Gerhard-Domagk-Straße 1, 53121 Bonn, Germany

Correspondence e-mail: p.jones@tu-bs.de

In the title compound, $C_{18}H_{30}N_6$, the central triazine ring is planar, with C—N bond lengths 1.3415 (14)–1.3504 (13) Å, N—C—N angles 125.58 (10)–125.97 (9)° and C—N—C angles 113.82 (9)–114.33 (9)°.

Comment

Cyclotrimerization of organic nitriles is a well known method for the industrial synthesis of 1,3,5-triazines (Martin *et al.*, 1978). These triazines have wide applications in pharmaceutical and other industries and they are also used as monomers for the synthesis of heat-resistant and thermostable polymers. Generally this cyclotrimerization is catalysed by hydrochloric acid (Grundmann *et al.*, 1952) but various other catalysts (Michurin *et al.*, 1969; Zilberman *et al.*, 1969, 1971) can also be used. The formation of 2,4,6-tripiperidino-1,3,5-triazine, (I), has been reported (Shishulina *et al.*, 1999) together with the crystal structure of its 2:2:1 solvated adduct with 2,6-bis(trichloromethyl)-1,4,3,5-oxathiadiazine 4,4-dioxide and benzene. The formation of (I) in this molecular adduct resulted from the reaction of piperidinonitrile with 6-piperidino-2-trichloroacetylimino-4-trichloromethyl-1,2,3,5-oxathiadiazine 2-oxide in benzene. However, (I) could not be isolated as a pure compound from the adduct. We report here the synthesis of (I) by metal-carbonyl-catalysed cyclotrimerization of piperidinonitrile, together with its crystal structure.


(I)
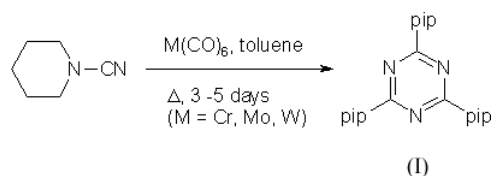
The crystal structure of (I) (Fig. 1) can be compared with that of the triazine in the 2:2:1 adduct solvate (Shishulina *et al.*, 1999) and also with the simplest 1,3,5-triazine, namely $(HCN)_3$ (Smith & Rae, 1978).

The six-membered triazine ring in (I) is essentially planar (0.008 Å mean deviation from the least-squares plane). The piperidine rings are rotated out of this plane, as defined by torsion angles of 14.03 (13) (N1—C2—N6—C18), −5.34 (15) (N3—C1—N4—C8) and −4.87 (15)° (N2—C3—N5—C9). The CN bond distances (see Table 1) are similar to those reported for the same triazine in the solvate complex. The triazine $(HCN)_3$ shows one independent CN bond distance in the same range [1.338 (4) Å; Smith & Rae, 1978]. The exocyclic CN bond distances for the triazine (I) [1.3535 (15)–1.3713 (13) Å] are significantly larger than those in the solvate
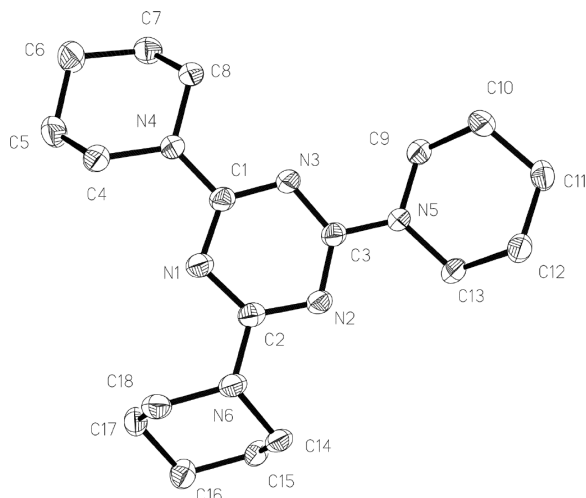
Figure 1
The molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.

complex (1.325–1.333 Å). The narrow CNC angles (*ca* 114°) and the wide NCN angles (*ca* 126°) are similar to the CNC [114.8 (10)°] and the NCN [125.2 (10)°] angles of (HCN)$_3$.

Experimental

Metal carbonyls $M(CO)_6$ (M = Cr, Mo, W) effectively catalyse the cyclotrimerization of *N*-cyanopiperidine to (I), in good to excellent yields, in toluene under heating conditions. The best results are obtained in the reaction catalysed by $W(CO)_6$. Metal carbonyls are recovered in almost quantitative yield in all reactions, and the triazine is obtained in pure form and in good to excellent yields. A solution of piperidinonitrile (1.10 g, 10 mmol) and $W(CO)_6$ (5% mol) in toluene (5 ml) was heated for 3–5 d. All reactions were monitored by thin-layer chromatography. The resulting pale-brown solution was concentrated and the product was separated by low-temperature column chromatography (SiO$_2$, 271 K, 10% diethyl ether in petroleum ether). Evaporation of the solvents of the second fraction and recrystallization from dichloromethane at 253 K yielded the title compound as colourless crystals. Analysis calculated for C$_{18}$H$_{30}$N$_6$: C 65.42, H 9.15, N 25.43%; found: C 65.40, H 9.20, N 25.39%. M.p. 492 K, *cf.* 423 K for the solvate complex. ^{1}H NMR (CDCl$_3$): δ 1.43–1.49 (*m*, 12H, piperidine ring), 1.52–1.57 (*m*, 12H, piperidine ring), 3.62–3.64 (*m*, 6H, piperidine ring); ^{13}C NMR: δ 25.1 (*s*, piperidine ring), 25.8 (*s*, piperidine ring), 44.1 (*s*, piperidine ring), 165.4 [*s*, triazine ring; *cf.* Tornieporth-Oetting *et al.* (1992)]; MS (70 eV, EI) *m/z* 330 (molecular ion peak; 100%) (M^+); IR (KBr, cm^{-1}): ν (C≡N) 1533 (*cf.* 1725 and 1625 cm^{-1} for the solvate complex; Shishulina *et al.*, 1999).

Crystal data

C$_{18}$H$_{30}$N$_6$	$Z = 2$
$M_r = 330.48$	$D_x = 1.228$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.3527$ (8) Å	Cell parameters from 5270
$b = 9.8192$ (10) Å	reflections
$c = 12.0219$ (12) Å	$\theta = 2$–30°
$\alpha = 98.377$ (3)°	$\mu = 0.08$ mm^{-1}
$\beta = 101.455$ (3)°	$T = 133$ (2) K
$\gamma = 108.361$ (3)°	Cut tablet, colourless
$V = 893.88$ (15) Å^3	$0.38 \times 0.22 \times 0.13$ mm

Data collection

Bruker SMART 1000 CCD diffractometer	$R_{int} = 0.031$
	$\theta_{max} = 28.3°$
ω and φ scans	$h = -11 \rightarrow 11$
12 279 measured reflections	$k = -13 \rightarrow 13$
4407 independent reflections	$l = -16 \rightarrow 16$
3407 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.065P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.040$	$+ 0.0581P]$
$wR(F^2) = 0.117$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} < 0.001$
4407 reflections	$\Delta\rho_{max} = 0.27$ e Å^{-3}
217 parameters	$\Delta\rho_{min} = -0.17$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

C1—N3	1.3422 (14)	C2—N6	1.3713 (13)
C1—N1	1.3504 (13)	C3—N3	1.3465 (13)
C1—N4	1.3614 (13)	C3—N2	1.3482 (13)
C2—N2	1.3415 (14)	C3—N5	1.3535 (15)
C2—N1	1.3480 (13)		
N3—C1—N1	125.97 (9)	C2—N1—C1	113.82 (9)
N2—C2—N1	125.97 (9)	C2—N2—C3	114.33 (9)
N3—C3—N2	125.58 (10)	C1—N3—C3	114.27 (9)
N3—C1—N4—C4	−178.34 (9)	N1—C2—N6—C18	14.03 (13)
N2—C3—N5—C9	176.35 (9)		

H atoms were positioned at calculated positions with C—H = 0.99 Å and U_{iso}(H) = 1.2U_{eq}(C), and refined using a riding model.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL*97.

References

Bruker (1998). *SMART* (Version 5.0) and *SAINT* (Version 4.0). Bruker AXS Inc., Madison, Wisconsin, USA.
Grundmann, C., Weisse, G. & Seide, S. (1952). *Annalen*, **577**, 77–95.
Martin, D., Bauer, M. & Pankratov, V. A. (1978). *Russ. Chem. Rev.* **47**, 975–990.
Michurin, A. A., Sivenkov, A. E. & Zilberman, E. N. (1969). *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* **12**, 1534–1536.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Shishulina, A. V., Michurin, A. A., Utkina, E. N. & Zakharov, L. N. (1999). *Russ. J. Org. Chem.* **35**, 1410–1411.
Siemens (1994). *XP*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Smith, J. H. & Rae, A. I. M. (1978). *J. Phys. C: Solid State Phys.* **11**, 1761–1770.
Tornieporth-Oetting, I. C., Klapötke, T. M., Behrens, U. & White, P. S. (1992). *J. Chem. Soc. Dalton Trans.* pp. 2055–2058.
Zilberman, E. N., Pomerantseva, E. G., Kulikova, A. E. & Michurin, A. A. (1969). *Zh. Org. Khim.* **5**, 2143–2147.
Zilberman, E. N., Kulikova, A. E. & Pomerantseva, E. G. (1971). *Vysokomol. Soedin.* **13**B, 179–184.