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Crystal structure of tetraphenylphosphonium cyanate, $[P(C_6H_5)_4]OCN$

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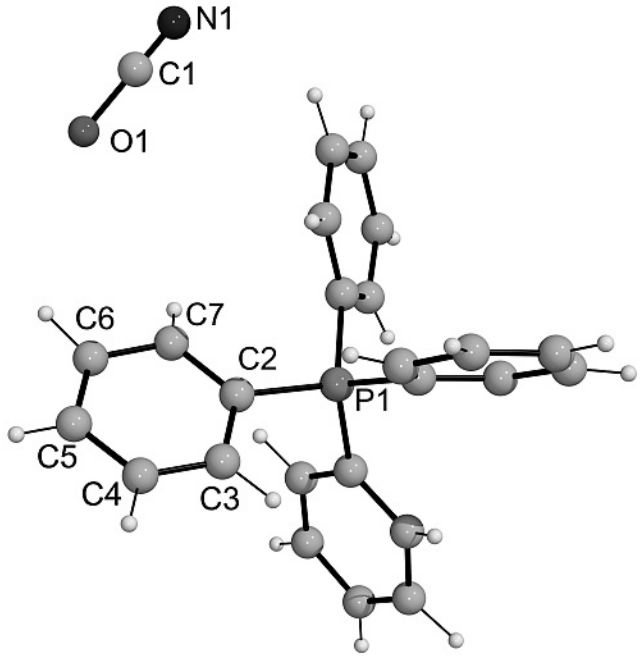

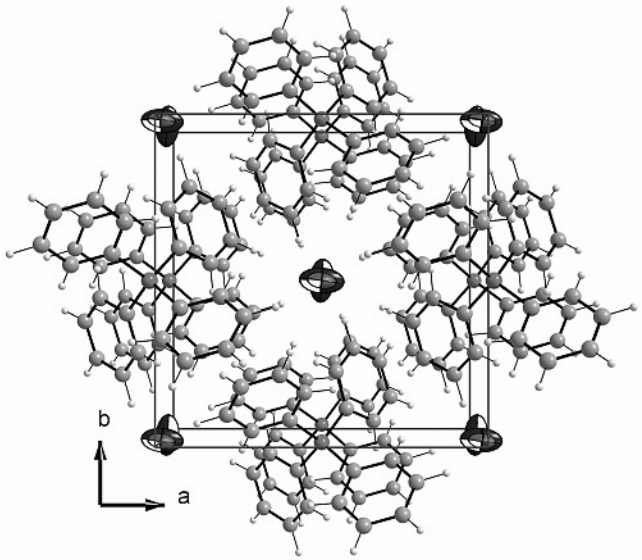

Abstract

$C_{25}H_{20}NOP$, tetragonal, $I\bar{4}$ (no. 82), a = 11.6046(4) Å, c = 7.0938(3) Å, V = 955.3 Å^3, Z = 2, $R_{gt(F)}$ = 0.048, $wR_{ref(F^2)}$ = 0.129, T = 173 K.

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Source of material

Stoichiometric amounts of tetraphenylphosphonium chloride and potassium cyanate were dissolved in acetonitrile. The precipitate of KCl was filtered off. Suitable single crystals were obtained by slow evaporation of the solvent.

Discussion

In the crystal structure of $[Ph_4P]OCN$, the anion is disordered with equal amounts of the two different orientations on a site with twofold rotation symmetry. This distortion is quite similar to the one of the SCN anion in $[Ph_4P]SCN$ [1]. Interatomic distances in the anion compare well with those of $[(CH_3)_4N]OCN$ [2].

The huge U_{22}:U_{11}:U_{33} ratio for N1 can be explained by the structural surrounding of the linear OCN anion. It is located in a tetrahedral hole of four surrounding PPh_4 cations. Because of the linear arrangement of atoms in the anion, the distances of the three atoms of the anion to the surrounding four cations are not the same. Each end atom of the linear anion (the O and the N atom) is closest to two of the four surrounding PPh_4 cations. This means that the vibrational/disorder choices in this direction are less than in the direction perpendicular. Therefore, U_{22} for N is much larger than U_{11} (because in this direction there is much more space), whereas for the atom at the other end of the linear anion, U_{11} is much larger than U_{22} (figure, bottom). The space available for the end atoms of the anion within the tetrahedral environment of cations gives rise to the huge U_{22} value for N and U_{11} value for O. A similar variation of U_{xy} values is found for the isostructural thiocyanate [1].

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.11 × 0.12 × 0.13 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.60 cm^{-1}
Diffractometer, scan mode:	Bruker Apex II CCD, φ/ω
$2\theta_{max}$:	65.1°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	12354, 1752
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1719
$N(param)_{refined}$:	89
Program:	SHELX-97 [3]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(3)	8*g*	0.827(2)	0.533(2)	–0.003(4)	0.015(5)
H(4)	8*g*	0.710(2)	0.407(2)	–0.213(4)	0.023(7)
H(5)	8*g*	0.776(3)	0.214(3)	–0.248(6)	0.042(8)
H(6)	8*g*	0.927(3)	0.130(3)	–0.047(5)	0.044(9)
H(7)	8*g*	1.016(3)	0.258(3)	0.133(5)	0.035(8)

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	4*e*	0.50	½	½	0.186(2)	0.101(7)	0.030(3)	0.021(5)	–0.009(3)	0	0
C(1)	2*b*		½	½	0	0.046(2)	U_{11}	0.069(5)	0	0	0
N(1)	4*e*	0.50	½	½	–0.139(2)	0.078(9)	0.24(2)	0.013(7)	0.01(1)	0	0
P(1)	2*c*		1	½	¼	0.0162(2)	U_{11}	0.0149(3)	0	0	0
C(2)	8*g*		0.9228(2)	0.4032(2)	0.0997(3)	0.0218(8)	0.0225(8)	0.0163(7)	–0.0055(6)	0.0001(6)	0.0023(6)
C(3)	8*g*		0.8351(2)	0.4474(2)	–0.0129(3)	0.037(1)	0.0229(9)	0.0251(9)	–0.0048(8)	–0.0098(8)	0.0042(7)
C(4)	8*g*		0.7782(2)	0.3763(2)	–0.1387(3)	0.039(1)	0.032(1)	0.029(1)	–0.0076(9)	–0.0141(9)	0.0052(8)
C(5)	8*g*		0.8121(2)	0.2623(2)	–0.1578(3)	0.038(1)	0.033(1)	0.025(1)	–0.0149(9)	–0.0009(8)	–0.0038(8)
C(6)	8*g*		0.8995(2)	0.2177(2)	–0.0473(3)	0.0271(9)	0.0268(9)	0.036(1)	–0.0047(7)	0.0025(8)	–0.0095(8)
C(7)	8*g*		0.9548(2)	0.2869(2)	0.0845(3)	0.0195(8)	0.0247(9)	0.031(1)	–0.0009(7)	–0.0001(7)	–0.0055(7)

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