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Refinement of the Structure of 2′, 2′′, 2′′′-Phosphinetriyltriacetonitrile from Neutron Diffraction Data at 95 K

By Sine Larsen

Department of Physical Chemistry, University of Copenhagen, The H. C. Ørsted Institute, Universitetsparken 5, *DK*-2100 *Copenhagen, Denmark*

and Mogens S. Lehmann

Institut Laue–Langevin, BP 156, 38042 *Grenoble CEDEX, France*

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Abstract. $C_6H_6N_3P$, $M_r = 151{\cdot}11$, rhombohedral, $R3c$, hexagonal axes, $a = 11{\cdot}500\,(2)$, $c = 9{\cdot}333\,(1)$ Å, $V = 1068{\cdot}9\,(5)$ Å^3, $Z = 6$, $D_x = 1{\cdot}4085\,(5)$ g cm^{-3}, neutrons, $\lambda = 0{\cdot}896$ Å, $\mu = 1{\cdot}313$ cm^{-1}, $F(000) = 301{\cdot}18$ fm, $T = 95$ K, final $R = 0{\cdot}030$ from 748 reflections. The bond lengths observed are P—C = 1·865 (1), C—C = 1·452 (1) and C—N = 1·155 (1) Å. Compared with a room-temperature X-ray study the C—N bond is significantly longer, although other bond lengths and angles are similar. The thermal parameters satisfy Hirshfeld's rigid-bond test except for the C—H bonds.

Introduction. Cyanoalkylphosphines are exceptional by being air-stable crystalline compounds with a low nucleophilic activity.

To investigate if common features of the crystalline state can account for the low reactivity of these molecules the crystal structures have been determined for the lower members, $P(CH_2CN)_3$ (Dahl & Larsen, 1979) and $P(CH_2CH_2CN)_3$ (Larsen, Vinzents & Dahl, 1983; Cotton, Darensbourgh, Fredrich, Ilsley & Troup, 1981). The conclusion from these structure determinations was that the inertness of the compounds cannot only be rationalized in terms of packing effects but rather in the electronic structure of the molecules. The charge density of $P(CH_2CN)_3$ has been examined by both theoretical (*ab initio*) and experimental (X-ray diffraction) methods (Larsen, Rettrup & Dahl, 1981). The experimental deformation density was based on parameters derived from low-temperature X-ray diffraction data. In the region around the phosphorus atom some ambiguities were observed between the experimental and theoretical deformation densities. As the experimental density is correlated with the thermal parameters it became pertinent to obtain another estimate of the thermal parameters at low temperature by a neutron diffraction measurement.

Experimental. Four-circle diffractometer, D8, at Institut Laue–Langevin high-flux reactor, neutron wavelength 0·896 Å from (220) plane of a Cu monochromator. Crystal prepared as described by Dahl & Larsen (1979). Single crystal, 0·5 × 0·5 × 5 mm, cooled by closed-loop refrigerator (Allibon, Filhol, Lehmann, Mason & Simms, 1981), temperature 95(0·5) K. Space group $R3c$, centering of 12 reflections, $41 < 2\theta < 85°$, data measured by ω–2θ step-scan technique using 35 points, intensities obtained by minimal $\sigma(I)/I$ method (Lehmann & Larsen, 1974) including corrections for known bias. 2680 reflections ($\pm hkl$) with $\sin\theta/\lambda \le 0{\cdot}93$ Å^{-1} recorded, no variations of intensity of one standard reflection. Correction for Lorentz and absorption effects using *DATAP*, transmission factors between 0·944 and 0·957. Symmetry-related reflections averaged, $R_{\rm int} = 0{\cdot}038$, 893 symmetry-independent reflections, programs from Institut Laue–Langevin. Starting coordinates from X-ray study, 748 reflections with $I/\sigma(I) \ge 2{\cdot}0$ used in final refinements with *XRAY*76 system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976), minimizing $\sum w(|F_o| - |F_c|)^2$, $w^{-1} = \sigma^2(F) + 4\times10^{-5}|F|^2$. Anisotropic thermal parameters for all atoms, 48 parameters, $R = 0{\cdot}030$, $wR = 0{\cdot}022$, max. shift $0{\cdot}04\sigma$, final difference Fourier map featureless, peaks between −0·7 and 0·7 fm Å^{-3}. Scattering lengths ($b_{\rm H} = -3{\cdot}742$, $b_{\rm C} = 6{\cdot}648$, $b_{\rm N} = 9{\cdot}21$ and $b_{\rm P} = 5{\cdot}13$ fm) from Koester & Rauch (1981). Final parameters in Table 1.* The data required no correction for extinction.

Discussion. A drawing of the molecule viewed along the threefold axis is shown in Fig. 1. The bond lengths and bond angles are listed in Table 2. The two C—H bonds agree well internally and with the normal value for a C—H bond, 1·09 Å. Compared with the room-temperature investigation (Dahl & Larsen, 1979) the only significant difference is in the C(2)—N bond, which is 0·01 Å shorter at room temperature owing to the effects of thermal vibrations.

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* Lists of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42401 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Positional and anisotropic thermal parameters in units of* 10^{-2} Å^2 *from a low-temperature neutron diffraction study of* $P(CH_2CN)_3$; *e.s.d.'s are in parentheses*

The temperature factors follow the expression $\exp\{-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + \cdots + 2kl\, b^*c^*U_{23})\}$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P	0·00000	0·00000	0·00001 (15)	0·78 (2)	0·78 (2)	0·72 (4)	0·39 (1)	0·00	0·00
C(1)	0·11283 (6)	0·15861 (6)	0·09792 (9)	0·86 (2)	0·78 (2)	0·93 (2)	0·35 (2)	−0·05 (2)	0·04 (2)
C(2)	0·11011 (6)	0·27089 (6)	0·03028 (9)	1·11 (2)	0·80 (2)	1·25 (2)	0·47 (2)	0·39 (2)	0·09 (2)
N	0·10587 (6)	0·35843 (5)	−0·02530	1·92 (2)	1·13 (2)	1·83 (2)	0·89 (2)	0·11 (2)	0·40 (2)
H(1)	0·2155 (2)	0·1764 (2)	0·0923 (2)	1·37 (5)	2·56 (7)	3·79 (8)	0·97 (5)	−0·23 (6)	−0·11 (7)
H(2)	0·0839 (2)	0·1524 (2)	0·2105 (2)	3·36 (8)	2·47 (7)	1·58 (5)	1·18 (7)	0·18 (6)	−0·03 (5)

Table 2. *Bond lengths* (Å) *and bond angles* (°) *for* $P(CH_2CN)_3$

P–C(1)	1·865 (1)	C(1')–P–C(1)	98·06 (7)
C(1)–C(2)	1·452 (1)	P–C(1)–C(2)	110·07 (6)
C(2)–N	1·155 (1)	P–C(1)–H(1)	108·51 (12)
C(1)–H(1)	1·094 (2)	P–C(1)–H(2)	111·49 (9)
C(1)–H(2)	1·094 (2)	H(1)–C(1)–H(2)	108·8 (2)
		C(1)–C(2)–N	178·6 (6)

Table 3. *Root-mean-square displacements for atoms A and B in the direction of the bond A–B*

A	*B*	$10^4 \times Z^2_{A,B}$Å^{-2}	$10^4 \times Z^2_{B,A}$Å^{-2}
P	C(1)	76	83
C(1)	C(2)	82	83
C(2)	N	84	83
C(1)	H(1)	92	133
C(1)	H(2)	97	162

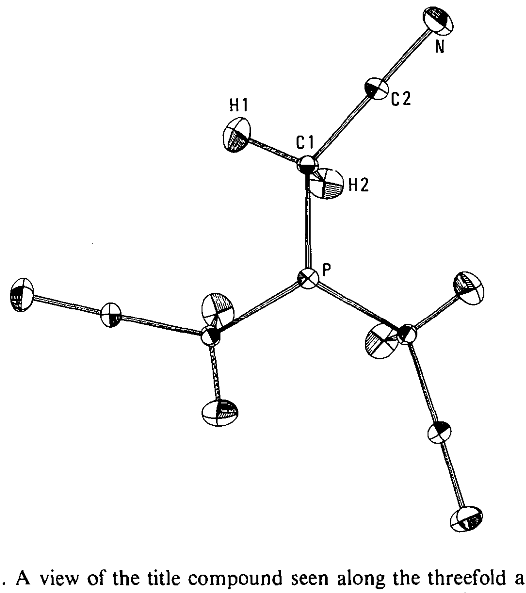

Fig. 1. A view of the title compound seen along the threefold axis. The thermal ellipsoids correspond to 50% probability.

The main purpose of this examination was to obtain accurate and reliable thermal parameters. To prove the correctness of the refined set of thermal parameters Hirshfeld (1976) suggests that one uses the rigid-bond postulate (Harel & Hirshfeld, 1975) as a test of the thermal parameters. The values for a rigid-bond test, *i.e.* the root-mean-square displacements, $Z^2_{A,B}$, along the bond A–B, are listed in Table 3. An inspection of this table reveals that the best agreement with Hirshfeld's rigid-bond requirement is obtained for bonds between similar atoms. For the C–H bonds the vibrational component along the bond for H is 30–60% larger than the vibrational component for C. Hirshfeld's rigid-bond postulate is based on the neglect of bond stretching vibrations and it could be expected that this would be most significant for bonds between light atoms with very different masses. Assuming the observed difference to arise from the stretching mode of C–H, we get a frequency of 3400 cm^{-1}, in good agreement with expectation.

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