All other distances and angles agree well with the expected values.

A crystallographic study on other products of this series has been undertaken in order to evaluate the structure modification by a 4-dialkylaminoalkyl substituent and to confirm the influence of the sp^2-hybridized N atom on the pharmacological activity.

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3′, 3″, 3‴-Phosphinetriyltripropionitrile, $C_9H_{12}N_3P$, at 100 K

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Abstract. $M_r = 193{\cdot}19$, monoclinic, $P2_1/m$, $a = 6{\cdot}597\,(2)$, $b = 12{\cdot}761\,(2)$, $c = 5{\cdot}9276\,(14)$ Å, $\beta = 90{\cdot}95\,(2)°$, $V = 498{\cdot}9\,(2)$ Å^3, $Z = 2$, $D_x = 1{\cdot}286\,(1)$, $D_m(298\text{ K}) = 1{\cdot}18\,(1)$ Mg m^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}214$ mm^{-1}, $F(000) = 204$. Final $R = 0{\cdot}040$ for 2484 observed reflections. This low-temperature study shows that the bond lengths and angles in the two independent PCH_2CH_2CN groups are identical, although the C—P—C angles are different [96·79 (4) and 103·17 (4)°]. The result is at variance with recent data from a room-temperature structure determination.

Introduction. Generally, trialkylphosphines are very reactive compounds which oxidize easily and are strong nucleophiles towards carbon and transition metals. Cyanoalkylphosphines are exceptions, the lower members, $P(CH_2CN)_3$ and $P(CH_2CH_2CN)_3$, being air-stable, crystalline compounds with a low nucleophilic reactivity (Henderson & Buckler, 1960; Dahl, Henriksen & Trebbien, 1983). To elucidate the origins of this low reactivity a determination of the crystal structure of $P(CH_2CN)_3$ (Dahl & Larsen, 1979) and an examination of its charge density by theoretical (*ab initio* and CNDO/2) and experimental (X-ray diffraction, IR and photoelectron spectroscopy) methods was initiated (Borch, Dahl, Klæboe & Nielsen, 1981; Larsen, Rettrup & Dahl, 1981). To investigate if common features of the spatial arrangement of the molecules in the crystal can be related to the unusual properties (high melting points, inertness) of these compounds a structure determination was undertaken of $P(CH_2CH_2CN)_3$. After this work was completed another report of the crystal structure of $P(CH_2CH_2CN)_3$ appeared (Cotton, Darensbourg, Fredrich, Ilsley & Troup, 1981), but since our deter-

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mination is based on low-temperature data (100 K) to a higher resolution, and the results from the two independent structure determinations of $P(CH_2CH_2CN)_3$ are not in complete agreement, we think it of interest to report our results.

Experimental. Compound prepared as described by Sasse (1963), recrystallization from water (m.p. 368–369 K). D_m measured by flotation. Space group and preliminary cell constants from photographs. Prismatic crystals elongated along **c**, 0·40 × 0·25 × 0·10 mm. Picker FACS-1 diffractometer, graphite-monochromated Mo $K\alpha$; modified (Hope, 1979) Nonius gas-flow low-temperature device (100 ± 0·5 K). Setting angles for 15 reflections well distributed over reciprocal lattice with 2θ values between 36 and 48° used in least-squares refinement of cell parameters and orientation matrix. Scan rate 2° min^{-1} in 2θ, scan type ω–2θ, background counts for 20 s, $2\theta < 80°$. Four standards measured after every 100 reflections, isotropic decay of 15% corrected by rescale function linear in exposure time. Lp correction, absorption ignored. 3175 independent ($-11 \le h \le 11$, $0 \le k \le 23$, $0 \le l \le 10$), 2484 with $I \ge 2\sigma(I)$. $R_{\text{int}} = 0{\cdot}0146$. Heavy-atom method (XRAY76, Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976); P-phased electron density, ρ, showed all non-H atoms of a molecule with m symmetry, space group $P2_1/m$ confirmed by successful refinement, anisotropic full-matrix, H (from ρ_{diff}) isotropic, $\sum w(|F_o| - |F_c|)^2$ minimized, $w^{-1} = 5\sigma(F)^2 + 0{\cdot}01\,F + 0{\cdot}001\,F^2$. P anomalous dispersion (Cromer & Liberman, 1970); scattering factors: P, C, N (Cromer & Mann, 1968), H (Stewart, Davidson & Simpson, 1965). Final $R = 0{\cdot}040$, $wR = 0{\cdot}045$. Maximum shifts $0{\cdot}3\sigma$. $\Delta\rho = -0{\cdot}3$–$0{\cdot}3$ e Å^{-3}.

Discussion. The final atomic coordinates are given in Table 1.* The mirror symmetry of the molecule and the atom numbering are illustrated in Fig. 1. Bond lengths and bond angles are listed in Table 2. As it is of obvious interest to compare these results with those obtained from room-temperature data (Cotton *et al.*, 1981), Table 3 lists some of the pertinent experimental differences between the two structure determinations. The comparison reveals some systematic differences in the molecular dimensions obtained at the different temperatures, so a statistical analysis does not seem meaningful. The bond lengths in the chain P–C(1)–C(2)–C(3)–N(1) are slightly longer in the present structure determination than in the room-temperature structure showing the effects of thermal vibrations. The other independent chain P–C(4)–C(5)–C(6)–N(2) betrays more significant differences, most pronounced in the P–C(4) and C(6)–N(2) bond lengths which are 1·853 (1) and 1·148 (2) Å at 100 K compared to 1·818 (5) and 1·111 (6) Å at 298 K. In connection with these apparent differences, it should be mentioned that Cotton *et al.* encountered difficulties localizing and refining the H atoms of this chain. In contrast to the room-temperature study the two crystallographically independent PCH_2CH_2CN groups have virtually identical dimensions at 100 K. The two independent C–P–C angles differ significantly at both temperatures but the C(1)–P–C(4) angle is considerably smaller at 100 K [103·17 (4)°] than at 298 K [106·9 (1)°]. This difference represents the only highly significant change of the molecular structure with temperature. The C(1)–P–C(1)′ angle is 96·79 (4)° at 100 K and 97·1 (2)° at 298 K. The average P–C bond length in $P(CH_2CH_2CN)_3$, 1·852 (1) Å, supports the observation that the presence of the electronegative –CN groups slightly increases the P–C bond length, *cf.* P–C = 1·866 (1) Å in $P(CH_2CN)_3$(Dahl & Larsen, 1979) and 1·841 (3) Å in $P(CH_3)_3$ (Lide & Mann, 1958).

Table 1. *Final positional parameters and isotropic temperature factors*

$U_{\text{eq}} = \frac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j$.

	x	y	z	U_{eq}/U (Å^2 × 100)
P	0·19812 (5)	0·25000	0·20845 (5)	1·137 (7)
C(1)	0·3513 (1)	0·1415 (1)	0·3294 (1)	1·32 (2)
C(2)	0·2686 (1)	0·0324 (1)	0·2700 (1)	1·42 (2)
C(3)	0·2510 (1)	0·0162 (1)	0·0247 (2)	1·42 (2)
C(4)	−0·0314 (2)	0·2500	0·3844 (2)	1·31 (3)
C(5)	0·0003 (2)	0·2500	0·6414 (2)	1·71 (3)
C(6)	−0·1930 (2)	0·2500	0·7608 (2)	1·73 (3)
N(1)	0·2375 (1)	0·0042 (1)	−0·1676 (1)	1·79 (2)
N(2)	−0·3459 (2)	0·2500	0·8506 (2)	2·67 (3)
H(11)	0·3648 (20)	0·1489 (11)	0·4898 (22)	2·0 (3)
H(21)	0·1326 (19)	0·0238 (11)	0·3288 (21)	1·6 (3)
H(4)	−0·1116 (21)	0·3106 (11)	0·3397 (23)	2·7 (4)
H(5)	0·0743 (22)	0·3100 (13)	0·6881 (26)	3·7 (4)
H(12)	0·4835 (20)	0·1497 (10)	0·2672 (21)	1·6 (3)
H(22)	0·3609 (19)	−0·0218 (11)	0·3291 (22)	1·5 (3)

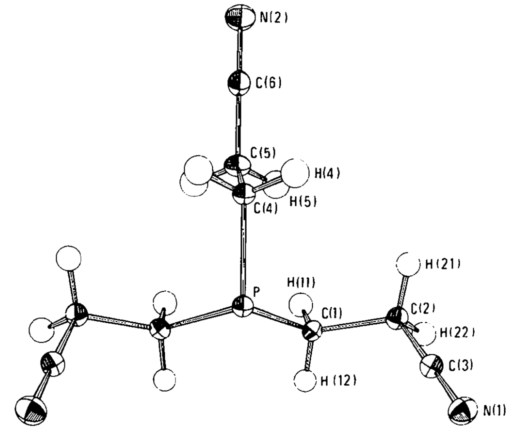

Fig. 1. A view of the title compound showing the mirror symmetry.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38623 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å), *bond angles* (°) *and dihedral angles* (°)

P—C(1)	1·8511 (9)	P—C(4)	1·8525 (13)
C(1)—C(2)	1·5348 (12)	C(4)—C(5)	1·534 (2)
C(2)—C(3)	1·4713 (12)	C(5)—C(6)	1·469 (2)
C(3)—N(1)	1·1522 (12)	C(6)—N(2)	1·148 (2)
C(1)—H(11)	0·959 (13)	C(4)—H(4)	0·972 (14)
C(1)—H(12)	0·959 (13)		
C(2)—H(21)	0·974 (12)	C(5)—H(5)	0·95 (2)
C(2)—H(22)	0·982 (13)		
C(1)—P—C(1)′	96·79 (4)	C(1)—P—C(4)	103·17 (4)
P—C(1)—C(2)	113·61 (6)	P—C(4)—C(5)	117·39 (8)
C(1)—C(2)—C(3)	112·08 (7)	C(4)—C(5)—C(6)	111·0 (1)
C(2)—C(3)—N(1)	180 (1)	C(5)—C(6)—N(2)	178·7 (3)
P—C(1)—C(2)—C(3)	57·04 (8)	C(4)—P—C(1)—C(2)	73·54 (6)
C(1)—P—C(4)—C(5)	50·17 (2)		

Table 3. *Experimental differences between two structure determinations of* $P(CH_2CH_2CN)_3$

	100K[a]	298K[b]
a (Å)	6·597 (2)	6·812 (3)
b (Å)	12·761 (2)	12·988 (7)
c (Å)	5·9276 (14)	5·869 (2)
β (°)	90·95 (2)	91·08 (3)
Radiation	Mo	Cu
2 *θ* range (°)	0–80	0–115
Number of reflections used	2484	650
Number of variables	91	83
R	0·040	0·056
wR	0·045	0·094

(*a*) This work. (*b*) Cotton *et al.* (1981).

There are large differences between the molecular conformations in $P(CH_2CH_2CN)_3$ and $P(CH_2CN)_3$. The latter is a propeller-shaped molecule placed on a crystallographic threefold axis like $OP(CH_2CH_2CN)_3$ (Cotton *et al.*, 1981). It appears that arranging the side chains in $P(CH_2CN)_3$ in a conformation like that in $P(CH_2CH_2CN)_3$ would place two of the cyano groups in the molecule so close that this arrangement would be energetically unfavourable. Although dipole–dipole interactions influence the crystal packing in both $P(CH_2CH_2CN)_3$ and $P(CH_2CN)_3$ they lead to quite different molecular arrangements. In $P(CH_2CN)_3$ the dipoles are placed orthogonally whereas they are almost antiparallel in $P(CH_2CH_2CN)_3$.

Table 3 shows that the unit cell behaves strongly anisotropically on cooling. The remarkable increase of the *c* axis on cooling has been confirmed by our room-temperature photographs.

As no phase transition occurs between 298 K and 100 K we found it likely that the expansion of the *c* axis could have its origin in steric interactions. Inspection of the intermolecular contacts reveals that the interatomic distances are generally longer than the sum of the van der Waals radii. The only exceptions are the distances from N(1) to six surrounding methylene H atoms, which fall in the range 2·63–2·88 Å, compared with the sum of the van der Waals radii, 2·80 Å. A reduction of the *c* axis would diminish some of the N(1)—H distances and could lead to an energetically less favourable crystal packing.

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Structure of *syn*-9-Acetyl-1,6-imino-8,13-methano[14]annulene,* $C_{17}H_{15}NO$

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Abstract. $M_r = 249{\cdot}3$, monoclinic, space group $P2_1/n$, $a = 11{\cdot}242\ (2)$, $b = 6{\cdot}590\ (1)$, $c = 17{\cdot}152\ (2)$ Å, $\beta = 97{\cdot}88\ (1)°$, $V = 1258{\cdot}7\ (6)$ Å^3, $Z = 4$, $D_m = 1{\cdot}30$, $D_x = 1{\cdot}316$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}076$ mm^{-1}, $F(000) = 528$, $T = 298$ K. Final $R = 0{\cdot}069$ for 2550 independent observed reflections. The

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* Alternative nomenclature: 4-acetyl-15-azatricyclo[8.4.1.1^{3,8}]-hexadeca-1,3,5,7,9,11,13-heptaene.

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