C2—C3	1.493 (11)	C9—C10	1.574 (9)
C3—C4	1.536 (12)	C10—C20	1.553 (10)
C4—C5	1.541 (10)	C11—C12	1.512 (11)
C4—C19	1.543 (13)	C12—C13	1.509 (11)
C4—C18	1.550 (13)	C13—C14	1.527 (11)
C5—C6	1.534 (10)	C13—C16	1.545 (11)
C5—C10	1.550 (10)	C15—C16	1.543 (13)
C6—C7	1.528 (11)	C16—C17	1.543 (14)
C7—C8	1.508 (12)	O1—C2	1.224 (10)
C8—C15	1.537 (10)	O2—C12	1.224 (10)
C8—C14	1.548 (11)		

C2—C1—C10	109.7 (6)	C11—C9—C8	110.9 (6)
O1—C2—C3	124.0 (7)	C11—C9—C10	113.4 (5)
O1—C2—C1	121.0 (7)	C8—C9—C10	115.8 (5)
C3—C2—C1	115.0 (7)	C1—C10—C5	107.7 (5)
C2—C3—C4	112.1 (6)	C1—C10—C20	107.3 (5)
C3—C4—C5	109.9 (6)	C1—C10—C9	108.0 (5)
C3—C4—C19	106.5 (7)	C5—C10—C20	113.9 (6)
C3—C4—C18	109.1 (7)	C5—C10—C9	107.7 (5)
C5—C4—C19	110.6 (7)	C20—C10—C9	112.0 (5)
C5—C4—C18	113.9 (6)	C12—C11—C9	115.0 (6)
C19—C4—C18	106.5 (8)	O2—C12—C13	122.4 (7)
C6—C5—C4	114.5 (6)	O2—C12—C11	122.5 (7)
C6—C5—C10	110.4 (6)	C13—C12—C11	115.0 (6)
C4—C5—C10	116.8 (5)	C12—C13—C14	107.6 (6)
C7—C6—C5	110.6 (6)	C12—C13—C16	110.3 (6)
C8—C7—C6	113.4 (7)	C14—C13—C16	102.9 (6)
C7—C8—C15	110.8 (6)	C13—C14—C8	101.9 (6)
C7—C8—C14	113.4 (6)	C8—C15—C16	107.5 (6)
C7—C8—C9	110.5 (6)	C17—C16—C15	114.2 (8)
C15—C8—C14	99.9 (6)	C17—C16—C13	111.4 (8)
C15—C8—C9	110.1 (6)	C15—C16—C13	104.2 (6)
C14—C8—C9	111.8 (5)		

Initial structure analysis was performed with a continuous process connected to the data collection using the fully automatic procedure *FASE* (Yamaguchi, 1993). Data collection and cell refinement were performed using *AFD* (Rigaku Corporation, 1985*a*); data reduction was by *FASE*. The structure was solved by direct methods, included in *FASE*, and with *SAPI*85 (Yao, Zheng, Qian, Han, Gu & Fan, 1985), and refined using *RCRYSTAN* (Rigaku Corporation, 1985*b*). Molecular graphics were obtained using *ACV* (Stardent Computer Inc., 1990) and the material for publication was prepared with *XPACK* (Yamaguchi, 1987).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71804 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1084]

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Triphenylphosphoranylideneammonium Azide, $[Ph_3P{=}NH_2][N_3]$

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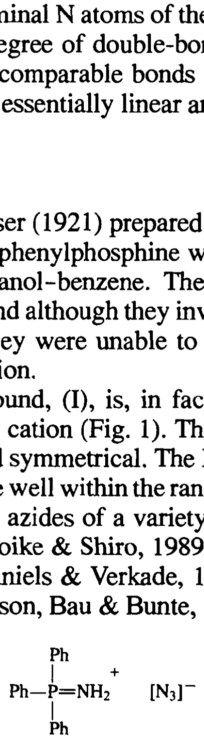
Abstract

The structure consists of $[Ph_3P{=}NH_2]^+$ cations and $[N_3]^-$ anions, which are linked together into polymeric chains by hydrogen bonding between the cationic NH_2 groups and the terminal N atoms of the anions. The P=N bond has a high degree of double-bond character and is shorter than most comparable bonds in other structures. The azide anion is essentially linear and symmetrical.

Comment

Staudinger & Hauser (1921) prepared the title compound by treatment of triphenylphosphine with hydrogen azide in solution in ethanol-benzene. They formulated it as $Ph_3P{=}NH.N_3H$ and although they investigated a number of its reactions, they were unable to deduce the precise chemical constitution.

The title compound, (I), is, in fact, the azide salt of the $[Ph_3P{=}NH_2]^+$ cation (Fig. 1). The azide anion is essentially linear and symmetrical. The N—N bond lengths (mean 1.164 Å) are well within the range (1.136-1.188 Å) reported for linear azides of a variety of organic cations (Kimura, Anan, Koike & Shiro, 1989; Bracuti & Extine, 1990; Woning, Daniels & Verkade, 1990; Lex & Linke, 1976; Christe, Wilson, Bau & Bunte, 1992).



$$\mathrm{Ph}{-}\overset{\overset{\displaystyle\mathrm{Ph}}{|}}{\underset{\underset{\displaystyle\mathrm{Ph}}{|}}{\mathrm{P}}}{=}\mathrm{NH_2}^{+}\quad[\mathrm{N_3}]^-$$

(I)

The cation has a pseudo-tetrahedral P atom and a trigonal planar N atom (at least within the accuracy to which the two H atoms have been placed), consistent with partial P=N double bonding. The $Ph_3P{=}N$ unit is

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known in many crystal structures, but in a high proportion of these it occurs in the $[(Ph_3P)_2N]^+$ cation or is bonded to metal atoms. The P—N bond length in the remaining structures with three-coordinate N atoms ranges from 1.601 to 1.681 Å (Böhm, Dehnicke, Beck, Hiller, Strähle, Maurer & Fenske, 1988; Llamas-Saiz, Foces-Foces, Elguero, Molina, Alajarín & Vidal, 1991*a*,*b*, 1992; Molina, Alajarín, Lopez-Leonardo, Claramunt, Foces-Foces, Cano, Catalán, de Paz & Elguero, 1989; Molina, Alajarín, Lopez-Leonardo, Cano, Llamas-Saiz, Foces-Foces, Claramunt & Elguero, 1992). The length in the present structure lies at the bottom end of this range, representing a higher degree of double bonding than in most related structures. There is a trend towards a longer P—N bond when the N atom carries no H atoms and a shorter bond when one or both of the substituents are H atoms.

Each terminal N atom of the azide anion forms a hydrogen bond with N—H of an adjacent cation, the N—N···H(N) angles being close to 120° [127 (1) and 121 (1)°]. Both H atoms of the cationic NH_2 group are thus hydrogen bonded to azide anions, with N···H distances of 2.02 (4) and 2.03 (4) Å (calculated from the refined coordinates with no correction for the X-ray shortened N—H bond lengths) and N—H···N angles of 176 (3) and 169 (3)°. These hydrogen bonds link the cations and anions into chains along the *a* axis (Fig. 2).

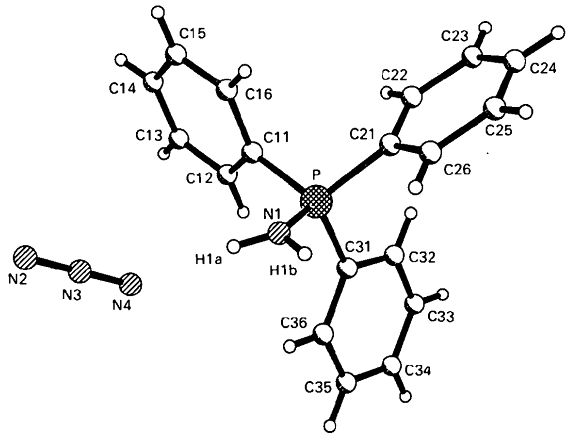

Fig. 1. The structure of one cation-anion pair (the asymmetric unit) with atom labels.

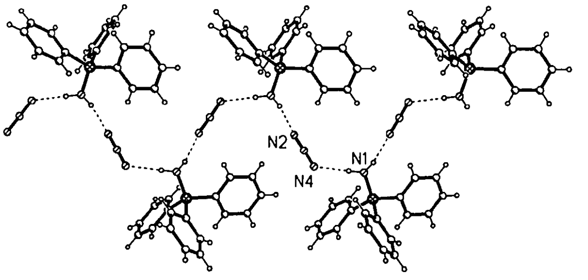

Fig. 2. Part of the hydrogen-bonded polymeric chain of cations and anions.

Experimental

The compound was prepared from triphenylphosphine and hydrogen azide in a 1:2 molar ratio in tetrahydrofuran-benzene solution, and was recrystallized from 2-propanol.

Crystal data

$C_{18}H_{17}NP^+.N_3^-$
$M_r = 320.33$
Orthorhombic
$P2_12_12_1$
$a = 10.6499\ (4)$ Å
$b = 11.7953\ (5)$ Å
$c = 13.3206\ (8)$ Å
$V = 1673.32\ (14)$ Å^3
$Z = 4$
$D_x = 1.272$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 32 reflections
$\theta = 10.57\text{-}12.28°$
$\mu = 0.169$ mm^{-1}
$T = 295\ (2)$ K
Block
0.80 × 0.32 × 0.26 mm
Colourless

Data collection

Stoe Siemens diffractometer
ω/θ scans with on-line profile fitting (Clegg, 1981)
Absorption correction: none
3717 measured reflections
2937 independent reflections
2467 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.030$
$\theta_{\rm max} = 25.02°$
$h = -12 \rightarrow 12$
$k = -14 \rightarrow 14$
$l = -15 \rightarrow 15$
3 standard reflections
frequency: 60 min
intensity variation: none

Refinement

Refinement on F^2
$R(F) = 0.0449$
$wR(F^2) = 0.1085$
$S = 1.079$
2933 reflections
217 parameters
Calculated weights
$w = 1/[\sigma^2(F_o^2) + (0.0322P)^2 + 0.5774P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.157$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.140$ e Å^{-3}

Extinction correction: *SHELXL* (Sheldrick, 1994)
Extinction coefficient: 0.0049 (12)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute structure parameter (Flack, 1983): −0.08 (14)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
P	0.69751 (7)	0.47755 (6)	0.36591 (6)	0.0424 (2)
C11	0.5895 (3)	0.4526 (3)	0.2655 (2)	0.0461 (7)
C12	0.5099 (3)	0.3606 (3)	0.2636 (3)	0.0590 (9)
C13	0.4218 (4)	0.3513 (3)	0.1873 (3)	0.0712 (11)
C14	0.4140 (4)	0.4316 (4)	0.1144 (3)	0.0701 (11)
C15	0.4946 (3)	0.5228 (4)	0.1144 (3)	0.0723 (10)
C16	0.5823 (3)	0.5337 (3)	0.1897 (3)	0.0609 (9)
C21	0.8517 (3)	0.5044 (2)	0.3167 (2)	0.0445 (7)
C22	0.8967 (3)	0.4410 (3)	0.2371 (2)	0.0538 (8)
C23	1.0192 (3)	0.4563 (3)	0.2046 (3)	0.0641 (10)
C24	1.0944 (3)	0.5356 (4)	0.2505 (3)	0.0723 (11)
C25	1.0491 (4)	0.6001 (3)	0.3279 (3)	0.0708 (11)
C26	0.9280 (3)	0.5847 (3)	0.3624 (3)	0.0572 (8)
C31	0.7083 (3)	0.3536 (2)	0.4441 (2)	0.0429 (7)
C32	0.7845 (4)	0.2623 (3)	0.4213 (3)	0.0660 (10)

C33	0.7917 (4)	0.1702 (3)	0.4853 (3)	0.0722 (11)
C34	0.7252 (4)	0.1686 (3)	0.5717 (3)	0.0655 (10)
C35	0.6496 (4)	0.2575 (4)	0.5955 (3)	0.0766 (12)
C36	0.6411 (4)	0.3506 (3)	0.5322 (3)	0.0637 (10)
N1	0.6486 (3)	0.5876 (2)	0.4248 (3)	0.0560 (8)
H1*A*	0.5677 (33)	0.5934 (26)	0.4302 (25)	0.053 (10)
H1*B*	0.6946 (35)	0.6220 (28)	0.4679 (25)	0.060 (11)
N2	0.2748 (3)	0.7763 (3)	0.4269 (3)	0.0711 (9)
N3	0.3287 (2)	0.6920 (3)	0.4404 (2)	0.0543 (7)
N4	0.3808 (3)	0.6062 (3)	0.4532 (3)	0.0901 (12)

Table 2. *Selected geometric parameters* (Å, °)

P—N1	1.603 (3)	C23—C24	1.375 (5)
P—C11	1.788 (3)	C24—C25	1.369 (5)
P—C21	1.796 (3)	C25—C26	1.381 (5)
P—C31	1.798 (3)	C31—C36	1.375 (4)
C11—C12	1.378 (4)	C31—C32	1.383 (4)
C11—C16	1.394 (4)	C32—C33	1.382 (5)
C12—C13	1.388 (5)	C33—C34	1.352 (5)
C13—C14	1.359 (5)	C34—C35	1.361 (5)
C14—C15	1.375 (5)	C35—C36	1.387 (5)
C15—C16	1.376 (5)	N1—H1*A*	0.87 (3)
C21—C22	1.384 (4)	N1—H1*B*	0.86 (4)
C21—C26	1.389 (4)	N2—N3	1.161 (4)
C22—C23	1.387 (5)	N3—N4	1.167 (4)
N1—P—C11	106.9 (2)	C21—C22—C23	119.7 (3)
N1—P—C21	109.5 (2)	C24—C23—C22	119.9 (4)
C11—P—C21	110.12 (14)	C25—C24—C23	120.5 (3)
N1—P—C31	113.3 (2)	C24—C25—C26	120.4 (4)
C11—P—C31	109.90 (14)	C25—C26—C21	119.4 (4)
C21—P—C31	107.21 (14)	C36—C31—C32	118.2 (3)
C12—C11—C16	119.5 (3)	C36—C31—P	118.8 (2)
C12—C11—P	122.6 (3)	C32—C31—P	122.9 (2)
C16—C11—P	117.7 (2)	C33—C32—C31	120.6 (3)
C11—C12—C13	119.4 (3)	C34—C33—C32	120.5 (4)
C14—C13—C12	120.6 (3)	C33—C34—C35	119.8 (3)
C13—C14—C15	120.5 (3)	C34—C35—C36	120.5 (3)
C14—C15—C16	119.8 (4)	C31—C36—C35	120.4 (3)
C15—C16—C11	120.1 (3)	P—N1—H1*A*	115 (2)
C22—C21—C26	120.1 (3)	P—N1—H1*B*	122 (2)
C22—C21—P	120.1 (2)	H1*A*—N1—H1*B*	118 (3)
C26—C21—P	119.7 (2)	N2—N3—N4	178.6 (4)

H atoms were placed at expected positions, riding, with $U = 1.2U_{\rm eq}(\rm C)$, except for those attached to N which were refined freely. Data collection: *DIF*4 (Stoe & Cie, 1988). Cell refinement: *DIF*4. Data reduction: local programs. Program(s) used to solve structure: *SHELXTL*/*PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL* (Sheldrick, 1994). Molecular graphics: *SHELXTL*/*PC*. Software used to prepare material for publication: *SHELXL*; local programs.

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Low-Temperature Structure of Bicyclohexylidene, $C_{12}H_{20}$

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Abstract

The two apical C_{sp^3}—C_{sp^3} bonds [mean 1.521 (2) Å] in bicyclohexylidene are significantly shorter than the other two C_{sp^3}—C_{sp^3} bonds [mean 1.530 (2) Å]. The molecule exhibits approximate C_{2h} symmetry in the solid.

Comment

Well defined oligomers of [1.1.1]propellane (Murthy, Hassenrück, Lynch & Michl, 1989; Friedli, Lynch,