Inorganica Chimica Acta, *105* (1985) 89–97

Cyano and Isocyano Derivatives of the Octahydrotriborate Anion; Molecular and Crystal Structures of the $[(Ph_3P)_2N]^+$ Salts of $[B_3H_7NCBH_3]^-$, $[(B_3H_7)_2CN]^-$ and $[Ag(CNB_3H_7)_2]^-$

STEVEN J. ANDREWS and ALAN J. WELCH*

Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ, U.K.

Received February 22, 1985

Abstract

$[(Ph_3P)_2N][B_3H_7NCBH_3]$ is triclinic, $P\bar{1}$, with 2 ion pairs in a cell of dimensions $a = 9.832(3)$, $b = 11.490(3)$, and $c = 16.889(2)$ Å, $\alpha = 105.66(2)$, $\beta = 92.43(2)$, and $\gamma = 101.59(2)°$ at 185 K. Using 5255 amplitudes the structure has been refined to $R = 0.059$. There are 4 ion pairs of $[(Ph_3P)_2N][(B_3H_7)_2CN]$ in a monoclinic unit cell, $a = 17.003(4)$, $b = 11.823(9)$, and $c = 19.519(8)$ Å, $\beta = 108.78(3)°$, space group $P2_1/a$. $R = 0.066$ for 4840 reflections, again measured at 185 K. For $[(Ph_3P)_2N][Ag(CNB_3H_7)_2]$ the unit cell is $a = 17.976(6)$, $b = 11.559(3)$, and $c = 19.20(3)$ Å, $\beta = 94.30(6)°$, space group $P2_1/c$, and $Z = 4$. 3742 reflections measured at 185 K have been used to refine to $R = 0.074$. The arrangement of hydrogen atoms in four of the five B_3H_7 moieties contained within these three crystal structures is common, there being one bridging-H across the B–B connectivity not involving the substituted atom.

Introduction

Crystallographic studies of derivatives $[B_3H_7X]^{-n}$ of the octahydrotriborate anion have now revealed three structural types, characterised by the number and nature of the bridging hydrogen atoms. When X = CO, n = 0 there is a single μ_2-H opposite the substituted boron atom [1]. For X = H, n = 1, however, peaks assigned to two, somewhat asymmetric μ_2-H atoms were observed in an early structural study [2], later corroboration for this bonding mode coming from *ab initio* molecular orbital (MO) calculations on $[B_3H_8]^-$ itself [3], and from a crystallographic study of $[B_3H_6Cl_2]^-$ [4]. Finally, an intermediate arrangement in which one fully edge bridging-H lies opposite the substituted boron, and one semi-μ_2-H involves that atom (and is more strongly bound to it), has been noted when X = NH_3, n = 0 [5] and, more recently in these laboratories, when X = NCS or NCSe [6], or CH_2PPh_3 [7], n = 1.

Early attempts [1, 8] to establish a correlation between the structure type observed and the electronic properties of the substituent have suggested that the differing σ-donor characters of the latter are important. As a preliminary to our own MO study of the (now considerably expanded) series, we wished to structurally characterise at least one further member of the family with just one bridging hydrogen atom. The isoelectronic-isolobal relationship between CO and CN^- implied that $[B_3H_7CN]^-$ would be a suitable species and, indeed, the synthesis of this derivative has already been reported by Jacobsen and Morris [9]. Unfortunately, however, attempts to obtain diffraction-quality crystals of salts of this anion have so far failed.

Nevertheless, three cyano and isocyano derivatives of $[B_3H_8]^-$ that should be equally appropriate have also recently been prepared [4, 9] and were found to yield good quality crystals as $[(Ph_3P)_2N]^+$ salts. Accordingly, this paper reports structural studies of $[(Ph_3P)_2N][B_3H_7NCBH_3]$, **1**, $[(Ph_3P)_2N][(B_3H_7)_2CN]$, **2**, and $[(Ph_3P)_2N][Ag(CNB_3H_7)_2]$, **3**.

Experimental

Compounds **1** and **2** were recrystallised from dichloromethane, whilst crystals of **3** were obtained by solvent diffusion using dichloromethane/n-hexane. Single crystals were glued to thin glass fibres using a low temperature epoxy resin adhesive, and were screened for singularity and diffraction quality by preliminary Weissenberg photography. On the diffractometer each sample was carefully cooled [6] to 185 ± 1 K, and accurate unit cell parameters were obtained by the automatic centering of 25 high-angle strong general reflections. Cell dimensions and other relevant crystallographic data are listed in Table I. In no case was significant crystal movement or decomposition detected during the experiment, although the (colourless) crystal of **3** used for data

---

*Author to whom correspondence should be addressed.

0020-1693/85/$3.30

TABLE I. Crystallographic Data and Data Collection Parameters.

Diffractometer	Enraf Nonius CAD4 with ULT1 attachment		
Radiation	Mo Kα ($\bar{\lambda}$ = 0.71069 Å), graphite monochromated		
Formula	$C_{37}H_{40}N_2P_2B_4$, **1**	$C_{37}H_{44}N_2P_2B_6$, **2**	$C_{38}H_{44}N_3P_2AgB_6$, **3**
Temperature (K)	185	185	185
M	617.93	643.60	777.47
F(000)	652	1360	1600
Space group	$P\bar{1}$	$P2_1/a$	$P2_1/c$
a (Å)	9.832(3)	17.003(4)	17.976(6)
b	11.490(3)	11.823(9)	11.559(3)
c	16.889(2)	19.519(8)	19.20(3)
α (deg)	105.66(2)	90	90
β	92.43(2)	108.78(3)	94.30(6)
γ	101.59(2)	90	90
V (Å^3)	1791	3715	3977
Z	2	4	4
ρ_c (g cm^{-3})	1.15	1.15	1.30
μ (cm^{-1})	1.13	1.76	5.98
Crystal size (mm)	0.5 × 0.3 × 0.02	0.03 × 0.05 × 0.1	0.5 × 0.5 × 0.05
Collection range	$+h \pm k \pm l$, $2\theta \leqslant 54°$	$+h + k \pm l$, $2\theta \leqslant 50°$	$+h + k \pm l$, $2\theta \leqslant 50°$
Scan type	ω–2θ	ω–2θ	ω–2θ
Scan width	$0.8 + 0.35 \tan\theta$	$0.8 + 0.35 \tan\theta$	$0.8 + 0.35 \tan\theta$
Max. counting time (s)	90	90	90
X-ray exposure time (h)	164	157	180
No. unique data	7806	6514	6989
No. data with $F_o \geqslant 2\sigma(F_o)$	5255	4840	3742
No. parameters	364	394	421
R	0.059	0.066	0.074
R_w	0.064	0.100	0.097
[a]Largest shift	0.02	0.08	0.01
[b]Largest peak (eÅ^{-3})	0.34	0.48	0.43

[a]Largest parameter shift in final refinement cycle. [b]Largest peak in final ΔF synthesis.

collection was found to have decomposed to a black non-diffracting solid following *ca.* 6 weeks storage at room temperature after the experiment was complete. Data were corrected for Lorentz and polarisation effects and, for **3** only, empirically for X-ray absorption (psi-scan method). Only reflections with $F_o \geqslant 2.0\sigma(F_o)$ were retained to solve and refine the structures.

Solution and Refinement

1 and **2** were initially solved by automatic centrosymmetric direct methods [10, 11] (P atoms) whilst the Ag atom in **3** was located via a Patterson synthesis [10]. Work-up of all three structures by an iterative combination of full-matrix least-squares refinement and ΔF syntheses yielded the positions of the B, C and N atoms. Carbons of the phenyl groups were refined as regular planar hexagons, C–C = 1.395 Å, but were allowed independent thermal parameters. Phenyl-H atoms were allowed to ride on their respective carbon, C–H = 1.08 Å with U_H[†] = 0.05 Å^2. All borane-H atoms were successfully located from ΔF maps and positionally refined, U_H = 0.05 Å^2.

Due to initial ambiguity over the identities of the bridging atoms within the anion of **2**, a ΔF synthesis was computed using a $[(B_3H_7)_2]^-$ model whereupon the two residual bridging peaks were found to possess electron density in the ratio 6:7, and were thus assigned C and N scattering factors respectively. Refinement of this model afforded R = 0.067 and R_w = 0.101. However, this scheme produced a higher isotropic temperature factor for N(2) compared to that for C(1) (U values of 0.061 and 0.042 Å^2, respectively) suggesting [12] a statistical C/N disorder within the crystal to which there is no *a priori* obstacle. Restarting the refinement with a 50:50 C:N occupancy at each site improved the discrepancy indices and also the positional e.s.d.'s. Such a model is also justified when one considers the internuclear distances within the anion (see later).

Structure factors were weighted according to $w^{-1} = [\sigma^2(F_o) + x(F_o)^2]$ with $x = 0.00264$ (**1**) and 0.18150 (**2**). No improvement over unit weights was found for **3**. In the final stage of refinement all non-H atoms were allowed anisotropic thermal motion, leading to the discrepancy indices at con-

---

[†] The isotropic temperature factor is defined as $\exp[-8\pi^2 U(\sin^2\theta)/\lambda^2]$.

vergence of Table I, where $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$, and $R_w = [\Sigma w(|F_o| - |F_o|)^2/\Sigma w(|F_o|)^2]$. For **1**, **2**, and **3** respectively, refined coordinates are given in Tables II, III, and IV. Tables of final anisotropic temperature factors (Tables V, VI, and VII) and phenyl-H coordinates (Tables VIII, IX, and X, are available as supplementary material, and comparisons of 10 F_o *vs.* 10 F_c at the termination of refinement for all three determinations may be obtained upon request. Crystallographic calculations employed the SHELX76 [10], SHELX84 [11] XRAY76 [13], XANADU [14], and ORTEPII [15] programs or packages implemented on the University of Edinburgh ICL 2972 computer, using inlaid neutral scattering factors [10], except for Ag where coefficients for an analytical approximation were taken from 'International Tables for X-Ray Crystallography' [16].

TABLE II. Fractional Coordinates of Refined Atoms for 1.

	x	*y*	*z*
P(1)	1.00806(8)	−0.04148(7)	0.22097(5)
N(1)	0.8835(3)	0.02271(23)	0.25124(17)
P(2)	0.84703(8)	0.15442(7)	0.26948(5)
C(12)[a]	1.08783(24)[b]	−0.01686(17)	0.38483(11)
C(13)	1.14612	−0.05253	0.44884
C(14)	1.20278	−0.15759	0.43100
C(15)	1.20115	−0.22698	0.34915
C(16)	1.14286	−0.19130	0.28514
C(11)	1.08620	−0.08624	0.30298
C(22)	1.27337(22)	0.10611(23)	0.22554(12)
C(23)	1.36941	0.18783	0.19659
C(24)	1.33376	0.21639	0.12434
C(25)	1.20206	0.16321	0.08103
C(26)	1.10601	0.08149	0.10999
C(21)	1.14166	0.05293	0.18224
C(32)	0.80351(19)	−0.24073(18)	0.13019(12)
C(33)	0.75359	−0.35082	0.06756
C(34)	0.84336	−0.39982	0.01255
C(35)	0.98306	−0.33873	0.02017
C(36)	1.03298	−0.22864	0.08280
C(31)	0.94320	−0.17964	0.13781
C(42)	0.73042(25)	0.08249(15)	0.10674(13)
C(43)	0.67127	0.10222	0.03626
C(44)	0.65864	0.22108	0.03655
C(45)	0.70516	0.32021	0.10731
C(46)	0.76431	0.30046	0.17778
C(41)	0.77694	0.18162	0.17750
C(52)	0.63756(22)	0.04449(14)	0.34681(13)
C(53)	0.52433	0.04326	0.39385
C(54)	0.48396	0.15347	0.43070
C(55)	0.55681	0.26490	0.42050
C(56)	0.67004	0.26613	0.37346
C(51)	0.71041	0.15592	0.33661
C(62)	1.07467(24)	0.33871(20)	0.26684(11)
C(63)	1.19326	0.43087	0.30251
C(64)	1.22686	0.46773	0.38797
C(65)	1.14187	0.41243	0.43776
C(66)	1.02327	0.32027	0.40209

TABLE II *(continued)*

	x	*y*	*z*
C(61)	0.98967	0.28341	0.31663
B(1)	0.6252(5)	0.6028(4)	0.3471(3)
B(2)	0.7678(6)	0.7378(4)	0.3953(3)
B(3)	0.8087(5)	0.6106(4)	0.3286(3)
B(4)	0.3992(6)	0.6709(7)	0.1496(4)
C(1)	0.4809(4)	0.6437(4)	0.2225(3)
N(2)	0.5416(4)	0.6255(3)	0.27503(21)
HB(11)	0.630(4)	0.502(4)	0.330(2)
HB(12)	0.571(4)	0.643(4)	0.410(3)
HB(21)	0.798(4)	0.760(4)	0.462(3)
HB(22)	0.733(4)	0.822(4)	0.378(2)
HB(31)	0.857(4)	0.551(4)	0.369(3)
HB(32)	0.814(4)	0.598(4)	0.260(3)
HB(41)	0.286(5)	0.640(4)	0.158(2)
HB(42)	0.418(4)	0.604(4)	0.093(3)
HB(43)	0.441(4)	0.778(4)	0.155(3)
H('23)	0.864(4)	0.707(4)	0.349(2)

[a] Atomic numbering scheme: C(i1)–C(i6) are phenyl carbons, numbered cyclically with C(i1) (i = 1–3) bound to P(1), and C(i1) (i = 4–6) bound to P(2). [b] Phenyl rings refined as rigid bodies, hence errors in fractional coordinates are common.

TABLE III. Fractional Coordinates of Refined Atoms for **2**.

	x	*y*	*z*
P(1)	0.82538(6)	0.22403(8)	0.68167(5)
P(2)	0.93713(6)	0.22277(8)	0.83369(5)
N(1)	0.86068(20)	0.1936(3)	0.76479(17)
C(12)	0.93659(15)	0.34953(17)	0.63470(13)
C(13)	0.99915	0.36182	0.60335
C(14)	1.02686	0.26794	0.57435
C(15)	0.99202	0.16177	0.57670
C(16)	0.92947	0.14948	0.60806
C(11)	0.90176	0.24336	0.63706
C(22)	0.74161(18)	0.39634(24)	0.72315(11)
C(23)	0.69371	0.49457	0.71235
C(24)	0.66775	0.54638	0.64453
C(25)	0.68969	0.49996	0.58752
C(26)	0.73759	0.40172	0.59832
C(21)	0.76355	0.34991	0.66614
C(32)	0.75308(15)	0.01334(19)	0.67789(9)
C(33)	0.70360	−0.07748	0.64361
C(34)	0.66241	−0.07404	0.56922
C(35)	0.67069	0.02022	0.52910
C(36)	0.72018	0.11104	0.56338
C(31)	0.76137	0.10760	0.63777
C(42)	1.04525(19)	0.08992(23)	0.93922(13)
C(43)	1.09717	−0.00327	0.96314
C(44)	1.10186	−0.08689	0.91418
C(45)	1.05463	−0.07731	0.84130
C(46)	1.00270	0.01588	0.81738
C(41)	0.99802	0.09950	0.86634
C(52)	0.81816(14)	0.2574(3)	0.89970(13)
C(53)	0.78725	0.3051	0.95122
C(54)	0.83867	0.3717	1.00669

(continued overleaf)

TABLE III *(continued)*

	x	*y*	*z*
C(55)	0.92100	0.3905	1.01064
C(56)	0.95192	0.3428	0.95912
C(51)	0.90050	0.2763	0.90364
C(62)	1.07579(15)	0.29472(16)	0.80023(15)
C(63)	1.12541	0.37638	0.78274
C(64)	1.10485	0.49063	0.78255
C(65)	1.03465	0.52322	0.79984
C(66)	0.98503	0.44156	0.81732
C(61)	1.00559	0.32730	0.81752
N(2)	0.1233(3)	0.2664(4)	0.27771(25)
C(1)	0.1306(3)	0.2441(4)	0.22385(23)
B(11)	0.1159(4)	0.2958(5)	0.3536(3)
B(12)	0.0866(4)	0.1718(5)	0.3944(4)
B(13)	0.0136(4)	0.2744(7)	0.3604(4)
B(21)	0.1421(5)	0.2099(7)	0.1502(4)
B(22)	0.2488(5)	0.2453(6)	0.1551(4)
B(23)	0.1695(4)	0.3306(6)	0.1051(3)
H(111)	0.087(3)	0.383(4)	0.3517(23)
H(112)	0.171(3)	0.299(4)	0.3862(25)
H(121)	0.093(3)	0.106(4)	0.3553(24)
H(122)	0.110(3)	0.162(4)	0.4521(25)
H(131)	−0.028(3)	0.218(4)	0.3017(25)
H(132)	−0.002(3)	0.332(4)	0.4000(23)
H(1B)	0.015(3)	0.153(4)	0.3824(22)
H(211)	0.089(3)	0.224(4)	0.104(3)
H(212)	0.175(3)	0.116(4)	0.1477(23)
H(221)	0.291(3)	0.255(4)	0.2190(24)
H(222)	0.276(3)	0.194(4)	0.1184(23)
H(231)	0.157(3)	0.410(4)	0.1316(23)
H(232)	0.151(3)	0.319(4)	0.0453(24)
H(2B)	0.249(3)	0.347(4)	0.1273(23)

TABLE IV. Fractional Coordinates of Refined Atoms for 3.

	x	*y*	*z*
P(1)	0.25931(16)	1.39048(24)	1.03711(14)
P(2)	0.20442(16)	1.16972(25)	0.96863(14)
N(1)	0.2258(6)	1.2988(9)	0.9838(5)
C(12)	0.3681(4)	1.2684(6)	1.1165(3)
C(13)	0.3972	1.2117	1.1767
C(14)	0.3595	1.2161	1.2376
C(15)	0.2927	1.2772	1.2383
C(16)	0.2635	1.3340	1.1782
C(11)	0.3012	1.3296	1.1173
C(22)	0.2112(3)	1.6030(6)	1.0831(4)
C(23)	0.1573	1.6798	1.1041
C(24)	0.0829	1.6454	1.1029
C(25)	0.0622	1.5343	1.0807
C(26)	0.1161	1.4576	1.0597
C(21)	0.1906	1.4919	1.0609
C(32)	0.3203(4)	1.4781(7)	0.9231(3)
C(33)	0.3702	1.5437	0.8873
C(34)	0.4285	1.6023	0.9242
C(35)	0.4368	1.5952	0.9969
C(36)	0.3869	1.5295	1.0328
C(31)	0.3286	1.4710	0.9958
C(42)	0.1421(4)	1.0630(4)	0.8480(3)
C(43)	0.1033	0.0628	0.7823
C(44)	0.0728	1.1654	0.7545
C(45)	0.0812	1.2681	0.7925
C(46)	0.1201	1.2682	0.8581
C(41)	0.1506	1.1657	0.8859
C(52)	0.2784(3)	0.9592(6)	0.9645(3)
C(53)	0.3403	0.8898	0.9550
C(54)	0.4079	0.9404	0.9408
C(55)	0.4137	1.0604	0.9359
C(56)	0.3518	1.1299	0.9454
C(51)	0.2841	1.0792	0.9597
C(62)	0.0748(3)	1.1115(6)	1.0298(3)
C(63)	0.0353	1.0674	1.0837
C(64)	0.0736	1.0201	1.1429
C(65)	0.1514	1.0170	1.1482
C(66)	0.1909	1.0611	1.0943
C(61)	0.1526	1.1084	1.0351
Ag(1)	0.35361(6)	0.58380(10)	1.26363(5)
C(2′)	0.2538(7)	0.6649(12)	1.2790(6)
N(2′)	0.2001(6)	0.7107(9)	1.2897(5)
B(1′)	0.1228(8)	0.7652(13)	1.3029(7)
B(2′)	0.1318(9)	0.9114(13)	1.3347(8)
B(3′)	0.1151(13)	0.8020(15)	1.3948(9)
C(2″)	0.4487(7)	0.4872(11)	1.2638(6)
N(2″)	0.5035(6)	0.4345(8)	1.2689(4)
B(1″)	0.5764(9)	0.3613(13)	1.2794(7)
B(2″)	0.5733(11)	0.2589(14)	1.3504(8)
B(3″)	0.6267(10)	0.3777(15)	1.3644(9)
H(11′)	0.109(5)	0.788(6)	1.268(5)
H(12′)	0.084(5)	0.692(6)	1.326(5)
H(21′)	0.193(5)	0.933(6)	1.327(5)
H(22′)	0.091(5)	0.988(6)	1.328(5)
H(31′)	0.164(5)	0.751(6)	1.413(5)
H(32′)	0.059(5)	0.822(6)	1.414(5)
H(1B)	0.138(5)	0.909(6)	1.390(5)
H(11″)	0.560(5)	0.290(6)	1.227(5)
H(12″)	0.625(5)	0.418(6)	1.278(5)
H(21″)	0.510(5)	0.238(6)	1.358(5)
H(22″)	0.592(5)	0.199(6)	1.342(5)
H(31″)	0.595(5)	0.459(6)	1.385(5)
H(32″)	0.690(5)	0.343(6)	1.369(5)
H(2B)	0.588(5)	0.311(6)	1.408(5)

Results and Discussion

In Figures 1–3 are presented views of the anions of **1**–**3** respectively, demonstrating in each case the atomic numbering scheme adopted. Tables XI–XIII respectively list the derived molecular parameters.

Between the three crystal structures are determined the stereochemistries of five boron triangles. For **1**, **2** and the B(1′)B(2′)B(3′) unit of **3**, the triangle is characterised by the presence of a single bridging hydrogen atom opposite the substituted boron. There is no evidence of any additional semi-

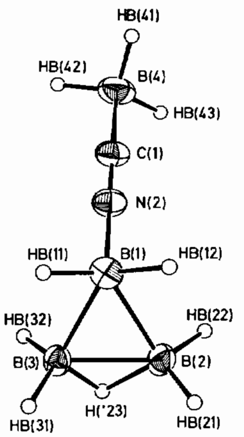

Fig. 1. The anion $[B_3H_7NCBH_3]^-$, **1**, with thermal ellipsoids of non-hydrogen atoms drawn at the 30% probability level.

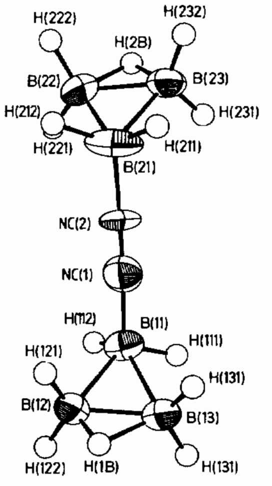

Fig. 2. The anion $[(B_3H_7)_2CN]^-$, **2**. NC(1) and NC(2) are 50:50 disordered N and C atoms.

bridging H atom, since all distances between H's bound to the unique boron and any other are >1.82 Å; indeed, the disposition of functions terminal to the substituted boron atom maintains the local C_s symmetry of the triangle in each case. For the second triangle of **3**, B(1″)B(2″)B(3″), an additional semi-bridging H is implied by the measured H(12″)···B(3″) distance of 1.70(9) Å, but the relatively high error on this measurement, coupled with the non-observation of a consequent shortening [7] of B(1″)–B(3″) c.f. B(1″)–B(2″) casts some doubt on the validity of this result.

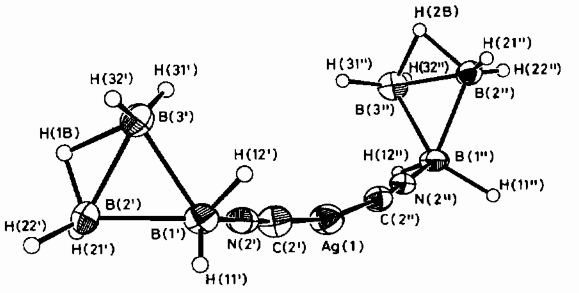

Fig. 3. Perspective view of the anion $[Ag(CNB_3H_7)_2]^-$, **3**.

Thus compounds **1**–**3** are broadly similar in type to B_3H_7CO [1], as might have been expected for these cyano/isocyano derivatives. Consistent with the carbonyl derivative, the bridged B–B connectivities in **1**–**3** are in all cases appreciably shorter that unbridged ones; in the case of the more accurately determined compounds **1** and **2** the difference is statistically significant, 1.710(10)–1.718(7) Å *vs.* 1.804(10)–1.840(7) Å.

No ion has crystallographically imposed symmetry. However, the overall anion in **1** has approximate C_s symmetry, whilst in **2** the C/N disorder in the bridge and the transoidal disposition of the two boron triangles increases the effective symmetry of the anion to D_{2h}. Measured B–NC distances in **2**, both 1.566(9) Å, reflect the even nature of the disorder since the mean value of the B–C and B–N bond lengths in **1** is 1.563 Å.

In **3** the approximate symmetry of the anion is C_2, the species being both bent at Ag, 169.8(5)°, and twisted about the linking NCAgCN unit, the torsion angle H(1B)···B(1′)···B(1″)···H(2B) being 54.2°. Although the B–N distances in **3**, 1.56 Å, might also seem to imply C/N disorder, and, indeed, this cannot be unequivocally excluded, we favour an ordered –NCAgCN– linkage for the following reasons; firstly, refinement of this model produced sensible and approximately equal U_{ii} values for the C and N atoms, unlike the situation encountered with **2**; secondly, whilst solid AgCN is strictly both a cyanide and an isocyanide being composed of –Ag–C≡N–Ag–C≡N– chains, it presumably reacts [4, 9] to afford **3** as $[Ag(CN)_2]^-$. This latter supposition is consistent both with the greater strength of the Ag–C *vs.* Ag–N bond in solid AgCN [17], and with the fact that $[Ag(CN)_2]^-$ is a known (C-coordinated) species [18].

Figures 4, 5 and 6, unit cell packing diagrams for **1**, **2**, and **3** respectively, are all available as supplementary material, as are lists of closest intermolecular contacts (Table XIV) and details of quasi-graphitic interactions between phenyl rings in the $[(Ph_3P)_2N]$ cations (Table XV). Of particular interest is the presence in the crystal of two weak intermolecular Ag···H interactions in **3**, involving Ag(1) at x, y, z (Table IV) and the phenyl H atoms H(22″) and H(11″) at $1-x$, $0.5+y$, $2.5-z$. These contacts, 2.68(9) and 2.84(9) Å respectively, deform the linear coordination geometry at Ag(1) somewhat towards tetrahedral in a manner not dissimilar to that caused by an adjacent, weakly bidentate PF_6^- anion in the crystal structure of $[(2,4,6\text{-}^tBu_3C_6H_2\text{-}NC)_2Ag]PF_6$ recently described by Yamamoto and co-workers [19].

TABLE XI. Molecular Dimensions for **1**.

A. Internuclear Distances (Å)			
P(1)–N(1)	1.586(3)	B(2)–B(3)	1.718(7)
P(1)–C(11)	1.7960(22)	B(3)–HB(31)	1.22(4)
P(1)–C(21)	1.7937(24)	B(3)–HB(32)	1.13(4)
P(1)–C(31)	1.7934(21)	B(3)–H('23)	1.08(4)
N(1)–P(2)	1.578(3)	B(2)–HB(21)	1.10(4)
P(2)–C(41)	1.8010(23)	B(2)–HB(22)	1.19(4)
P(2)–C(51)	1.7942(22)	B(2)–H('23)	1.29(4)
P(2)–C(61)	1.7985(23)	B(4)–C(1)	1.577(8)
B(1)–B(3)	1.833(7)	B(4)–HB(41)	1.13(4)
B(1)–B(2)	1.840(7)	B(4)–HB(42)	1.10(4)
B(1)–N(2)	1.549(6)	B(4)–HB(43)	1.20(5)
B(1)–HB(11)	1.12(4)	C(1)–N(2)	1.137(6)
B(1)–HB(12)	1.23(4)		
B. Interbond Angles (deg)			
N(1)–P(1)–C(11)	110.54(13)	B(1)–B(3)–H('23)	108.3(23)
N(1)–P(1)–C(21)	113.90(13)	B(2)–B(3)–HB(31)	109.2(20)
N(1)–P(1)–C(31)	109.83(13)	B(2)–B(3)–HB(32)	123.8(22)
C(11)–P(1)–C(21)	108.84(11)	B(2)–B(3)–H('23)	48.6(23)
C(11)–P(1)–C(31)	107.31(10)	HB(31)–B(3)–HB(32)	125.5(30)
C(21)–P(1)–C(31)	106.14(11)	HB(31)–B(3)–H('23)	109.9(31)
P(1)–N(1)–P(2)	139.07(19)	HB(32)–B(3)–H('23)	96.9(32)
N(1)–P(2)–C(41)	112.04(13)	B(1)–B(2)–B(3)	61.9(3)
N(1)–P(2)–C(51)	107.16(13)	B(1)–B(2)–HB(21)	118.4(23)
N(1)–P(2)–C(61)	115.32(13)	B(1)–B(2)–HB(22)	105.0(21)
C(41)–P(2)–C(51)	105.98(10)	B(1)–B(2)–H('23)	98.7(20)
C(41)–P(2)–C(61)	107.10(11)	B(3)–B(2)–HB(21)	119.7(23)
C(51)–P(2)–C(61)	108.82(10)	B(3)–B(2)–HB(22)	127.5(21)
B(2)–B(1)–B(3)	55.8(3)	B(3)–B(2)–H('23)	39.0(20)
B(2)–B(1)–N(2)	111.1(3)	HB(21)–B(2)–HB(22)	111.1(31)
B(3)–B(1)–HB(11)	78.2(22)	HB(21)–B(2)–H('23)	114.2(30)
B(3)–B(1)–HB(12)	131.2(20)	HB(22)–B(2)–H('23)	108.2(29)
B(2)–B(1)–N(2)	110.5(4)	C(1)–B(4)–HB(41)	104.2(23)
B(2)–B(1)–HB(11)	127.7(22)	C(1)–B(4)–HB(42)	104.9(23)
B(2)–B(1)–HB(12)	82.8(20)	C(1)–B(4)–HB(43)	107.1(22)
N(2)–B(1)–HB(11)	108.1(22)	HB(41)–B(4)–HB(42)	105.8(32)
N(2)–B(1)–HB(12)	106.7(20)	HB(41)–B(4)–HB(43)	117.0(31)
HB(11)–B(1)–HB(12)	117.6(30)	HB(42)–B(4)–HB(43)	116.5(32)
B(1)–B(3)–B(2)	62.3(3)	B(4)–C(1)–N(2)	178.9(5)
B(1)–B(3)–HB(31)	108.3(20)	B(1)–N(2)–C(1)	179.1(4)
B(1)–B(3)–HB(32)	106.7(22)	B(2)–H('23)–B(3)	92.4(31)

TABLE XII. Molecular Dimensions for **2**.

A. Internuclear Distances (Å)			
P(1)–N(1)	1.580(4)	B(12)–H(122)	1.07(5)
P(1)–C(11)	1.796(3)	B(12)–H(1B)	1.19(5)
P(1)–C(21)	1.791(3)	B(13)–H(131)	1.32(5)
P(1)–C(31)	1.7925(24)	B(13)–H(132)	1.13(5)
P(2)–N(1)	1.578(4)	B(13)–H(1B)	1.50(5)
P(2)–C(41)	1.783(3)	B(21)–B(22)	1.833(11)
P(2)–C(51)	1.789(3)	B(21)–B(23)	1.815(10)
P(2)–C(61)	1.794(3)	B(21)–H(211)	1.07(5)
N(2)–C(1)	1.129(7)	B(21)–H(212)	1.26(5)
N(2)–B(11)	1.566(8)	B(22)–B(23)	1.715(10)
C(1)–B(21)	1.565(9)	B(22)–H(221)	1.23(5)

(continued on facing page)

TABLE XII *(continued)*

B(11)–B(12)	1.813(9)	B(22)–H(222)	1.14(5)
B(11)–B(13)	1.804(10)	B(22)–H(2B)	1.32(5)
B(11)–H(111)	1.13(5)	B(23)–H(231)	1.13(5)
B(11)–H(112)	0.95(5)	B(23)–H(232)	1.11(5)
B(12)–B(13)	1.710(10)	B(23)–H(2B)	1.30(5)
B(12)–H(121)	1.11(5)		

B. Interbond Angles (deg)

N(1)–P(1)–C(11)	115.59(15)	B(12)–B(13)–H(131)	95.6(21)
N(1)–P(1)–C(21)	111.79(16)	B(12)–B(13)–H(132)	117.7(24)
N(1)–P(1)–C(31)	106.73(15)	B(12)–B(13)–H(1B)	42.8(18)
C(11)–P(1)–C(21)	106.79(13)	H(131)–B(13)–H(132)	136.3(31)
C(11)–P(1)–C(31)	106.77(12)	H(131)–B(13)–H(1B)	73.5(27)
C(21)–P(1)–C(31)	108.92(12)	H(132)–B(13)–H(1B)	111.6(29)
N(1)–P(2)–C(41)	110.51(16)	C(1)–B(21)–B(22)	107.9(5)
N(1)–P(2)–C(51)	109.51(16)	C(1)–B(21)–B(23)	111.7(5)
N(1)–P(2)–C(61)	113.80(16)	C(1)–B(21)–H(211)	114.8(27)
C(41)–P(2)–C(51)	108.73(14)	C(1)–B(21)–H(212)	117.1(22)
C(41)–P(2)–C(61)	106.92(13)	B(22)–B(21)–B(23)	56.1(4)
C(51)–P(2)–C(61)	107.20(13)	B(22)–B(21)–H(211)	124.2(27)
P(1)–N(1)–P(2)	139.63(24)	B(22)–B(21)–H(212)	76.0(21)
C(1)–N(2)–B(11)	178.2(5)	B(23)–B(21)–H(211)	75.3(26)
N(2)–C(1)–B(21)	178.3(6)	B(23)–B(21)–H(212)	119.5(21)
N(2)–B(11)–B(12)	110.7(4)	H(211)–B(21)–H(212)	111.6(34)
N(2)–B(11)–B(13)	114.2(5)	B(21)–B(22)–B(23)	61.4(4)
N(2)–B(11)–H(111)	109.6(24)	B(21)–B(22)–H(221)	108.4(22)
N(2)–B(11)–H(112)	106.3(30)	B(21)–B(22)–H(222)	116.0(23)
B(12)–B(11)–B(13)	56.4(4)	B(21)–B(22)–H(2B)	108.9(20)
B(12)–B(11)–H(111)	124.7(24)	B(23)–B(22)–H(221)	128.4(22)
B(12)–B(11)–H(112)	94.9(30)	B(23)–B(22)–H(222)	110.8(23)
B(13)–B(11)–H(111)	73.2(24)	B(23)–B(22)–H(2B)	48.7(20)
B(13)–B(11)–H(112)	136.3(30)	H(221)–B(22)–H(222)	117.7(32)
H(111)–B(11)–H(112)	108.3(38)	H(221)–B(22)–H(2B)	104.8(30)
B(11)–B(12)–B(13)	61.5(4)	H(222)–B(22)–H(2B)	99.6(30)
B(11)–B(12)–H(121)	99.1(24)	B(21)–B(23)–B(22)	62.5(4)
B(11)–B(12)–H(122)	119.3(25)	B(21)–B(23)–H(231)	108.5(24)
B(11)–B(12)–H(1B)	118.4(23)	B(21)–B(23)–H(232)	112.5(24)
B(13)–B(12)–H(121)	116.3(24)	B(21)–B(23)–H(2B)	111.1(20)
B(13)–B(12)–H(122)	117.3(25)	B(22)–B(23)–H(231)	117.5(24)
B(13)–B(12)–H(18)	59.0(22)	B(22)–B(23)–H(232)	115.5(24)
H(121)–B(12)–H(122)	124.1(34)	B(22)–B(23)–H(2B)	49.8(20)
H(121)–B(12)–H(1B)	93.0(33)	H(231)–B(23)–H(232)	123.3(33)
H(122)–B(12)–H(1B)	101.0(33)	H(231)–B(23)–H(2B)	93.1(31)
B(11)–B(13)–B(12)	62.0(4)	H(232)–B(23)–H(2B)	106.4(31)
B(11)–B(13)–H(131)	105.7(21)	B(12)–H(1B)–B(13)	78.2(25)
B(11)–B(13)–H(132)	114.4(24)	B(22)–H(2B)–B(23)	81.6(26)
B(11)–B(13)–H(1B)	103.3(18)		

TABLE XIII. Molecular Dimensions for 3.

A. Internuclear Distances (Å)

P(1)–N(1)	1.562(10)	B(2′)–H(22′)	1.15(9)
P(1)–C(11)	1.805(7)	B(2′)–H(1B)	1.06(9)
P(1)–C(21)	1.788(7)	B(3′)–H(31′)	1.10(9)
P(1)–C(31)	1.788(8)	B(3′)–H(32′)	1.13(9)
P(2)–N(1)	1.563(10)	B(3′)–H(1B)	1.31(9)
P(2)–C(41)	1.797(7)	C(2″)–N(2″)	1.155(16)
P(2)–C(51)	1.792(7)	N(2″)–B(1″)	1.561(18)

(Continued overleaf)

TABLE XIII *(continued)*

P(2)-C(61)	1.781(7)	B(1")-B(2")	1.809(22)
Ag(1)-C(2')	2.064(12)	B(1")-B(3")	1.815(23)
Ag(1)-C(2")	2.042(12)	B(1")-H(11")	1.31(9)
C(2')-N(2')	1.135(16)	B(1")-H(12")	1.09(9)
N(2')-B(1')	1.563(17)	B(2")-B(3")	1.687(24)
B(1')-B(2')	1.801(21)	B(2")-H(21")	1.19(9)
B(1')-B(3')	1.829(24)	B(2")-H(22")	0.78(9)
B(1')-H(11')	0.74(9)	B(2")-H(2B)	1.26(9)
B(1')-H(12')	1.20(9)	B(3")-H(31")	1.19(9)
B(2')-B(3')	1.75(3)	B(3")-H(32")	1.20(9)
B(2')-H(21')	1.14(9)	B(3")-H(2B)	1.37(9)
B. Interbond Angles (deg)			
N(1)-P(1)-C(11)	114.2(5)	B(2')-B(3')-H(31')	115.2(47)
N(1)-P(1)-C(21)	111.9(5)	B(2')-B(3')-H(32')	106.0(45)
N(1)-P(1)-C(31)	108.1(5)	B(2')-B(3')-H(1B)	37.2(38)
C(11)-P(1)-C(21)	106.9(3)	H(31')-B(3')-H(32')	136.3(65)
C(11)-P(1)-C(31)	108.7(3)	H(31')-B(3')-H(1B)	106.5(60)
C(21)-P(1)-C(31)	106.8(3)	H(32')-B(3')-H(1B)	97.1(59)
N(1)-P(2)-C(41)	107.4(4)	Ag(1)-C(2")-N(2")	175.1(11)
N(1)-P(2)-C(51)	112.8(5)	C(2")-N(2")-B(1")	177.2(12)
N(1)-P(2)-C(61)	112.4(4)	N(2")-B(1")-B(2")	112.3(11)
C(41)-P(2)-C(51)	106.4(3)	N(2")-B(1")-B(3")	114.6(11)
C(41)-P(2)-C(61)	110.2(3)	N(2")-B(1")-H(11")	95.9(38)
C(51)-P(2)-C(61)	107.5(3)	N(2")-B(1")-H(12")	109.9(46)
P(1)-N(1)-P(2)	147.9(7)	B(2")-B(1")-B(3")	55.5(9)
C(2')-Ag(1)-C(2")	169.8(5)	B(2")-B(1")-H(11")	98.5(38)
Ag(1)-C(2')-N(2')	177.6(11)	B(2")-B(1")-H(12")	117.7(46)
C(2')-N(2')-B(1')	175.7(12)	B(3")-B(1")-H(11")	145.1(39)
N(2')-B(1')-B(2')	112.0(10)	B(3")-B(1")-H(12")	66.1(45)
N(2')-B(1')-B(3')	112.4(11)	H(11")-B(1")-H(12")	120.3(59)
N(2')-B(1')-H(11')	104.2(70)	B(1")-B(2")-B(3")	62.4(9)
N(2')-B(1')-H(12')	108.8(42)	B(1")-B(2")-H(21")	107.8(43)
B(2')-B(1')-B(3')	57.7(9)	B(1")-B(2")-H(22")	112.8(66)
B(2')-B(1')-H(11')	89.4(70)	B(1")-B(2")-H(2B)	109.1(40)
B(2')-B(1')-H(12')	125.3(42)	B(3")-B(2")-H(21")	133.7(43)
B(3')-B(1')-H(11')	137.6(70)	B(3")-B(2")-H(22")	120.1(66)
B(3')-B(1')-H(12')	74.1(42)	B(3")-B(2")-H(2B)	52.8(39)
H(11')-B(1')-H(12')	113.9(81)	H(21")-B(2")-H(22")	105.6(78)
B(1')-B(2')-B(3')	62.0(9)	H(21")-B(2")-H(2B)	97.8(58)
B(1')-B(2')-H(21')	103.0(44)	H(22")-B(2")-H(2B)	121.8(77)
B(1')-B(2')-H(22')	130.1(44)	B(1")-B(3")-B(2")	62.1(9)
B(1')-B(2')-H(1B)	108.3(47)	B(1")-B(3")-H(31")	99.4(42)
B(3')-B(2')-H(21')	117.0(44)	B(1")-B(3")-H(32")	115.7(42)
B(3')-B(2')-H(22')	119.6(44)	B(1")-B(3")-H(2B)	104.1(37)
B(3')-B(2')-H(1B)	48.0(47)	B(2")-B(3")-H(31")	114.4(43)
H(21')-B(2')-H(22')	115.0(61)	B(2")-B(3")-H(32")	105.3(42)
H(21')-B(2')-H(1B)	96.0(63)	B(2")-B(3")-H(2B)	47.5(36)
H(22')-B(2')-H(1B)	98.9(64)	H(31")-B(3")-H(32")	136.1(59)
B(1')-B(3')-B(2')	60.3(9)	H(31")-B(3")-H(2B)	87.6(55)
B(1')-B(3')-H(31')	93.6(46)	H(32")-B(3")-H(2B)	107.1(55)
B(1')-B(3')-H(32')	120.2(45)	B(2')-H(1B)-B(3')	94.8(63)
B(1')-B(3')-H(1B)	96.3(39)	B(2")-H(2B)-B(3")	79.7(49)

Acknowledgements

We are grateful to Dr. J. H. Morris and his colleagues at the University of Strathclyde for preparing the crystalline compounds, Borax Research Ltd. and the SERC for a CASE studentship (S.J.A.), and the SERC for funds with which to purchase the diffractometer.

Supplementary Material Available

Tables V, VI and VII: thermal parameters for **1**, **2** and **3**; Tables VIII, IX and X: phenyl hydrogen atom coordinates for **1**, **2** and **3**; Table XIV: intermolecular contacts; Table XV: phenyl ring interactions; Tables of 10 F_o *vs.* 10 F_c for **1**, **2** and **3**; Figures 4, 5 and 6: packing diagrams for **1**, **2** and **3**. This material is available from A.J.W. on request.

References

1 J. D. Glore, J. W. Rathke and R. Schaeffer, *Inorg. Chem., 12*, 2175 (1973).
2 C. R. Peters and C. E. Nordman, *J. Am. Chem. Soc., 82*, 5758 (1960).
3 M. L. McKee and W. N. Lipscomb, *Inorg. Chem., 21*, 2846 (1982).
4 M. Arunchaiya, J. H. Morris, S. J. Andrews, D. A. Welch and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 2525 (1984).
5 C. E. Nordman and C. Reimann, *J. Am. Chem. Soc., 81*, 3538 (1959).
6 S. J. Andrews and A. J. Welch, *Inorg. Chim. Acta, 88*, 153 (1984).
7 S. J. Andrews and A. J. Welch, *Acta Crystallogr., Sect. C:*, submitted.
8 L. D. Brown and W. N. Lipscomb, *Inorg. Chem., 16*, 1 (1977).
9 G. B. Jacobsen and J. H. Morris, *Inorg. Chim. Acta, 59*, 207 (1982).
10 G. M. Sheldrick, 'SHELX76', University of Cambridge, U.K., 1976.
11 G. M. Sheldrick, 'SHELX84', University of Göttingen, F. R. G., 1984.
12 G. H. Stout and L. H. Jensen, 'X-Ray Structure Determination', Macmillan, London, 1968, p. 384.
13 'X-RAY76', Technical Report TR-446, Computer Science Centre, University of Maryland, U.S.A., 1967.
14 G. M. Sheldrick and P. Roberts, 'XANADU', University of Cambridge, U.K., 1976.
15 C. K. Johnson, 'ORTEPII', Report ORNL-5138, Oak Ridge National Laboratory, Tenn., U.S.A., 1976.
16 'International Tables for X-Ray Crystallography, Vol. 4', Kynoch Press, Birmingham, U.K., 1974.
17 J. C. Bailar, H. J. Emeléus, R. Nyholm and A. F. Trotman-Dickenson (eds.), 'Comprehensive Inorganic Chemistry, Vol. 3', Pergamon, Oxford, 1973, p. 96.
18 J. L. Hoard, *Z. Kristallogr., 84*, 231 (1933).
19 Y. Yamamoto, K. Aoki and H. Yamazaki, *Inorg. Chim. Acta, 68*, 75 (1982).