Crystal and Molecular Structure of the Complex Isothiocyanato-{*NN*-bis-[2-(diethylamino)ethyl]-2-(diphenylarsino)ethylamine-*NNN*}-nickel(II) Tetraphenylborate and Study of the Conformational Energy of the Tetraphenylborate Ion

By **M. Di Vaira** * and **A. Bianchi Orlandini,** Istituto di Chimica Generale dell'Università di Firenze, Laboratorio del C.N.R., 41 via Jacopo Nardi, 50132 Firenze, Italy

The structure of the title compound has been determined by Patterson and Fourier methods from photographic X-ray data, and refined by least-squares techniques to R 0·080 for 4097 observations. Crystals are triclinic, space group P$\bar{1}$, and $Z = 2$ in a unit cell of dimensions: $a = 12\cdot529(1)$, $b = 13\cdot589(1)$, $c = 14\cdot120(1)$ Å, $\alpha = 95\cdot12(1)$, $\beta = 103\cdot68(1)$, $\gamma = 99\cdot38(1)°$. The co-ordination about nickel is square planar and Ni–N bond lengths are compared with those in a related five-co-ordinate complex. Non-bonding to the metal by the arsenic atom is discussed in terms of simple MO models. Calculation of the conformational energy of the isolated tetraphenylborate ion, as a function of independent rotations of the four phenyl groups, indicates that the bulky counterion does not possess a considerable degree of flexibility.

A SERIES of nickel(II) complexes of general formula [Ni(nas)X]BPh$_4$, where nas is the tripod ligand NN-bis-[2-(diethylamino)ethyl]-2-(diphenylarsino)ethylamine, $(Et_2N\cdot[CH_2]_2)_2N([CH_2]_2\cdot AsPh_2)$, X is Cl, Br, I, or NCS, has been recently prepared [1] as a part of an investigation on the geometry and spin-state multiplicity of five-co-ordinate nickel(II) complexes with ' hybrid ' ligands.[2]

The iodo-derivative is high-spin and may be assigned a five-co-ordinate structure, on the basis of its visible spectrum. On the other hand, spectra of the other complexes, which are diamagnetic, may indicate square planar or square pyramidal co-ordination.[1] Although the former assignment seems favoured, the latter cannot be safely excluded, especially in the case of the iso-thiocyanate, because of the appearance of a shoulder at 13·8 kK in the spectrum of that complex. Five-co-ordination would not be expected for the low-spin complexes, from the value of the overall nucleophilic reactivity constant.[2]

In order to resolve this point, the study of the structure of the complex [Ni(nas)(NCS)]BPh$_4$ was undertaken

by X-ray analysis. We were also interested in drawing possible comparisons with the high-spin complex Ni(nas)(NCS)$_2$ of known structure.[3]

After the structural investigation was completed, revealing some unexpected features of the geometry of the BPh$_4^-$ anion, it was decided to devote closer study to the properties of the anion. There were indications that rotations of the phenyl groups about their axis may be somewhat hindered, for geometrical reasons. This may reduce the flexibility of the bulky anion so that its effectiveness as a precipitating agent may be determined solely by its size, rather than by its size and flexibility. As a particular instance, we wished to determine whether the high-spin state of the Co(np)I chromophore, [where np = tris-[(2-diphenyl-phosphino)ethyl]amine), which is stabilized only by BPh$_4^-$ in the solid,[4] owes its existence to a bulky and flexible matrix or, conversely, to a bulky and essentially rigid matrix. Therefore, we have undertaken the study of the conformation of the tetraphenylborate ion.

[1] L. Sacconi and R. Morassi, *J. Chem. Soc. (A)*, 1969, 2904.
[2] L. Sacconi, *J. Chem. Soc. (A)*, 1970 248.
[3] M. Di Vaira, *J. Chem. Soc. (A)*, 1971, 148.

[4] L. Sacconi and I. Bertini, *J. Amer. Chem. Soc.*, 1968, **90**, 5443; C. Mealli, P. L. Orioli, and L. Sacconi, *J. Chem. Soc. (A)*, 1971, 2691; L. Sacconi, M. Di Vaira, and A. Bianchi, *J. Amer. Chem. Soc.*, 1970, **92**, 4465.

EXPERIMENTAL

Crystal Data.—$C_{51}H_{62}AsBN_4NiS$, $M = 907.52$, Triclinic $a = 12.529(1)$, $b = 13.589(1)$, $c = 14.120(1)$ Å, $\alpha = 95.12(1)$, $\beta = 103.68(1)$, $\gamma = 99.38(1)°$, $U = 2284.2$ Å^3, $D_m = 1.32$ (by flotation), $Z = 2$, $D_c = 1.327$, $F(000) = 956$. Space group, $P\bar{1}$. Cu-K_α radiation, $\lambda = 1.5418$ Å; $\mu(Cu-K_\alpha) = 22.0$ cm^{-1}.

Data Collection.—Cell constants were obtained from least-squares refinement of forty-four 2θ values, collected with a Hilger four-circle automatic diffractometer using Mo-K_α radiation ($\lambda = 0.70926$ Å). Three different crystals (needles with [001] axis of elongation and 0.10—0.15 mm cross-section) were used for data collection, owing to their decomposition in the X-ray beam. The reciprocal lattice levels $hk0$—10 were collected on a Nonius integrating Weissenberg camera with nickel-filtered Cu-K_α radiation, by use of the multiple-film equi-inclination technique. The intensities of a total observed 4097 reflections were measured on a Nonius microdensitometer. No correction for absorption was applied, because values of the transmission factor vary by few units % for reflections from a given level of the reciprocal lattice. The various levels were put on a common scale by means of two Weissenberg photographs, which contained 30° samples from each level, one sample being common to the two photographs. The two parts into which each level was split during data collection, because of the triclinic space group, were scaled with the use of a few common reflections. No correction for extinction was applied. The atomic scattering factors for all atoms except hydrogen were taken from ref. 5, those of arsenic and nickel being corrected for the real part of the anomalous dispersion according to ref. 6, and that of hydrogen was taken from ref. 7a.

Structure Determination.—The structure was solved by the heavy-atom technique. A Patterson synthesis provided the positions of the arsenic, nickel, and sulphur atoms. The aspect of the map was consistent with the assumption of a centrosymmetric space group, which has been confirmed by the final refinement. A series of Fourier syntheses, followed by a difference-Fourier yielded the positions of all atoms except hydrogen; R was then 0.25. A series of full-matrix least-squares cycles was then performed, with individual isotropic temperature factors. Owing to the large number of parameters refined, the least-squares matrix was reduced to four blocks, by allowing about one-fourth of the parameters to refine at one time, and the assignment of the atoms to the blocks was varied, through the cycles performed. In the final set of three cycles, anisotropic temperature factors were used for the arsenic, nickel, and sulphur atoms and each cycle of refinement was followed by one on the lighter atoms. The function minimized in the least-squares calculation was $\Sigma w(|F_o| - |F_c|)^2$ and the weighting scheme was: $w = 1$ for reflections with $F_o \leqslant 25$ and $\sqrt{w} = 25/F_o$ for reflections with $F_o > 25$. Scale factors were allowed to refine during the isotropic cycles and not during the anisotropic cycles. The positions of the 62 hydrogen atoms were determined from a difference Fourier performed before the last cycle, making use in few cases of calculated hydrogen positions in order to resolve ambiguities encountered with the assignment of peaks. The difference Fourier showed few more

peaks of height comparable to that of the hydrogen atoms (<0.5 e Å^{-2}) and two diffuse positive areas (~2 e Å^{-2}) on the two sides of the arsenic position, along the axis of data collection. The hydrogen atoms were introduced in the

TABLE 1

Final positional ($\times 10^4$) and isotropic thermal * parameters of non-hydrogen atoms with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	$B/Å^2$
As	5557(1)	1618(1)	3476(1)	*
Ni	1321(1)	2670(1)	1507(1)	*
S	−1835(3)	2286(3)	−1033(3)	*
N(1)	2672(6)	2944(5)	2535(6)	3.3(0.2)
N(2)	1948(6)	3786(5)	893(6)	3.7(0.2)
N(3)	659(6)	1768(5)	2305(6)	3.6(0.2)
N(4)	31(6)	2359(6)	475(6)	4.0(0.2)
C(1)	3130(8)	4035(7)	2567(7)	4.0(0.2)
C(2)	3085(8)	4247(7)	1552(8)	4.5(0.2)
C(3)	2340(8)	2706(7)	3448(7)	4.2(0.2)
C(4)	1539(8)	1743(7)	3229(7)	4.2(0.2)
C(5)	3511(7)	2302(6)	2332(7)	3.7(0.2)
C(6)	4678(8)	2648(7)	3028(7)	4.4(0.2)
C(7)	−758(7)	2326(6)	−149(7)	3.6(0.2)
C(8)	2023(9)	3476(8)	−143(8)	5.0(0.3)
C(9)	2575(10)	2586(9)	−262(9)	6.4(0.3)
C(10)	1201(8)	4553(7)	776(8)	4.2(0.2)
C(11)	969(9)	4975(8)	1694(8)	4.8(0.2)
C(12)	124(9)	726(8)	1783(8)	4.9(0.2)
C(13)	897(10)	267(9)	1267(9)	6.0(0.3)
C(14)	−234(9)	2273(8)	2582(8)	4.9(0.2)
C(15)	−896(11)	1738(10)	3245(10)	7.3(0.3)
C(16)	4354(8)	713(7)	3799(7)	3.9(0.2)
C(17)	4173(9)	951(8)	4693(8)	5.1(0.2)
C(18)	3363(9)	368(9)	5017(9)	5.8(0.3)
C(19)	2743(9)	−491(8)	4429(9)	5.6(0.3)
C(20)	2892(9)	−743(8)	3521(9)	5.2(0.3)
C(21)	3689(8)	−157(7)	3176(8)	4.5(0.2)
C(22)	5728(10)	975(9)	2283(9)	5.2(0.3)
C(23)	5874(11)	−26(10)	2222(10)	6.9(0.3)
C(24)	6274(13)	−427(12)	1441(12)	8.8(0.4)
C(25)	6452(14)	100(14)	692(13)	10.1(0.5)
C(26)	6314(15)	1108(14)	773(14)	9.6(0.3)
C(27)	5905(11)	1515(10)	1545(10)	6.7(0.3)
C(28)	7834(7)	5362(6)	4166(7)	3.2(0.2)
C(29)	8735(7)	5805(7)	4956(7)	4.0(0.2)
C(30)	9219(9)	5287(8)	5700(8)	4.9(0.3)
C(31)	8784(8)	4302(7)	5710(7)	4.5(0.2)
C(32)	7876(8)	3806(7)	4936(8)	4.7(0.2)
C(33)	7433(7)	4354(7)	4211(7)	4.2(0.2)
C(34)	8166(7)	6998(6)	3277(7)	3.3(0.2)
C(35)	9010(9)	7058(8)	2781(8)	5.3(0.3)
C(36)	9772(10)	7970(9)	2876(9)	5.6(0.3)
C(37)	9749(10)	8779(9)	3489(9)	5.8(0.3)
C(38)	8936(9)	8740(8)	3993(9)	5.2(0.3)
C(39)	8153(8)	7858(7)	3887(8)	4.7(0.2)
C(40)	6104(6)	6246(6)	3363(6)	3.1(0.2)
C(41)	5571(7)	6853(7)	2713(7)	4.0(0.2)
C(42)	4569(8)	7109(8)	2754(8)	4.6(0.2)
C(43)	4047(8)	6783(7)	3467(8)	4.2(0.2)
C(44)	4530(8)	6208(7)	4104(7)	3.9(0.2)
C(45)	5552(7)	5947(6)	4058(6)	3.3(0.2)
C(46)	7065(7)	5164(6)	2238(7)	3.2(0.2)
C(47)	7908(7)	4658(7)	2040(7)	4.0(0.2)
C(48)	7771(8)	3993(7)	1206(7)	4.3(0.2)
C(49)	6761(8)	3796(7)	488(8)	4.4(0.2)
C(50)	5913(8)	4261(7)	663(8)	4.3(0.2)
C(51)	6078(7)	4927(6)	1494(7)	3.7(0.2)
B	7286(8)	5952(7)	3253(8)	3.3(0.2)

* These atoms were refined anisotropically.

last cycle with $B = 5.0$ Å^2 and not refined. The final R is 0.080 and R' is 0.110 on observed reflections only.†

† R′ = $(\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$.

5 D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.
6 D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.
7 ' International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, (*a*) vol. III, 1962, p. 202; (*b*) vol. II, 1952, p. 89.

The Fourier summations were performed on an IBM 1620 with programs written by Albano, Bellon, Pompa, and Scatturin.[8] The full-matrix least-squares and other calculations were performed on the IBM 7090 of C.N.U.C.E. in Pisa, with programs written by Stewart.[9]

Final values of the parameters for atoms heavier than hydrogen and their estimated standard deviations are reported in Tables 1 and 2. Standard deviations of the

TABLE 2

Thermal parameters ($\times 10^4$) for the atoms refined anisotropically,* with estimated standard deviations in parentheses

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
As	62(1)	57(1)	78(1)	15(1)	−6(1)	9(1)
Ni	57(1)	39(1)	32(1)	7(1)	1(1)	5(1)
S	83(3)	120(3)	47(3)	42(2)	−9(2)	−13(2)

* Anisotropic thermal factors are of the form:

$$\exp(-^3\textstyle\sum_{i=1}^3\sum_{j=1}^3 h_i h_j \beta_{ij}).$$

parameters were calculated by the least-squares program according to the expression: $\sigma_j = [\Sigma w \Delta F^2 a^{jj}/(m-n)]^{\frac{1}{2}}$, where m is the number of reflections, n the number of parameters and a^{jj} is the jj^{th} element of the inverse least-squares matrix. The values reported have been multiplied by a suitable correction factor, accounting for the factorization of the least-squares matrix.

TABLE 3

Positional parameters ($\times 10^3$) of hydrogen atoms *

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
H(11)	278	420	300	H(153)	−118	112	290
H(12)	400	432	288	H(17)	460	166	514
H(21)	330	500	158	H(18)	314	48	570
H(22)	358	404	126	H(19)	220	−103	467
H(31)	300	280	370	H(20)	230	−140	308
H(32)	200	328	384	H(21)	390	−32	250
H(41)	120	140	360	H(23)	570	−50	285
H(42)	190	130	304	H(24)	610	−130	140
H(51)	306	148	240	H(25)	680	−20	0
H(52)	348	238	160	H(26)	640	190	37
H(61)	454	282	360	H(27)	575	245	170
H(62)	504	300	268	H(29)	916	640	498
H(81)	130	340	−32	H(30)	988	570	630
H(82)	250	408	−46	H(31)	898	380	620
H(91)	240	230	−110	H(32)	765	310	485
H(92)	224	198	0	H(33)	690	400	360
H(93)	330	280	−8	H(35)	908	635	235
H(101)	60	430	30	H(36)	38	805	230
H(102)	160	518	48	H(37)	20	952	330
H(111)	34	544	154	H(38)	884	920	436
H(112)	72	440	212	H(39)	760	782	427
H(113)	156	536	206	H(41)	600	710	220
H(121)	−2	26	240	H(42)	430	748	208
H(122)	−34	98	128	H(43)	315	688	335
H(131)	26	−42	92	H(44)	418	585	463
H(132)	156	33	160	H(45)	586	553	445
H(133)	134	60	70	H(47)	870	473	270
H(141)	0	280	292	H(48)	846	370	114
H(142)	−70	226	190	H(49)	672	328	−15
H(151)	−120	224	335	H(50)	517	415	−5
H(152)	−50	160	390	H(51)	552	534	155

* The last figure in parenthesis in each atom label, up to H(153), identifies hydrogen atoms attached to the same carbon atom.

Table 3 lists the positional parameters of the hydrogen atoms. A list of observed and calculated structure factors

† See note about Supplementary Publications in Notice to Authors, No. 7, in *J. Chem. Soc. (A)*, 1970, Issue No. 20 (items less than 10 pp. are supplied as full size copies).

is published in Supplementary Publication No. SUP 20394 (7 pp., 1 microfiche).†

DISCUSSION

Description of the Structure.—The structure consists of [Ni(nas)(NCS)]$^+$ cations and of BPh$_4^-$ anions arranged
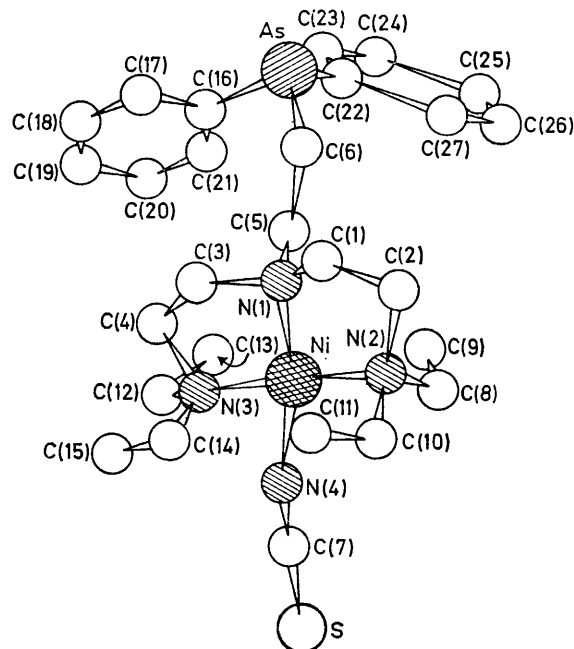
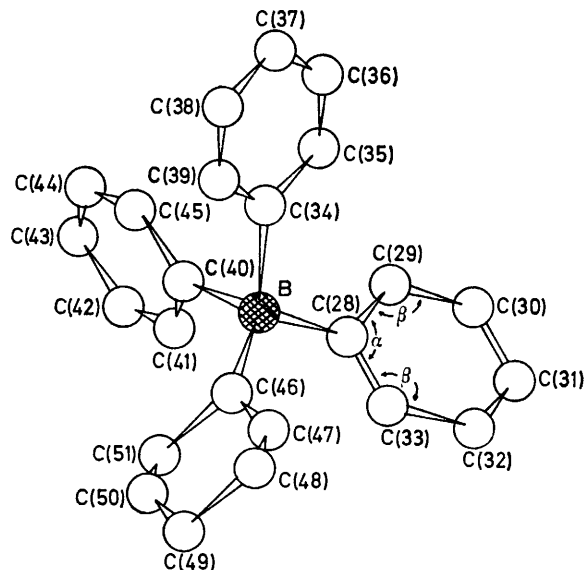

FIGURE 1 A perspective view of the cation

FIGURE 2 A perspective view of the anion

in a distorted sodium chloride type lattice. Figures 1 and 2 show perspective views of the ions, with the labelling of the atoms. Bond distances within each

[8] V. Albano, P. L. Bellon, and F. Pompa, *Ricerca sci. Suppl.*, 1963, **33**, 285; V. Albano, P. L. Bellon, F. Pompa, and V. Scatturin, *ibid.*, p. 1067.

[9] ' *X-Ray '63*,' J. M. Stewart, Technical Report TR-64-6, University of Maryland, 1964.

ion are reported in Table 4 and bond angles in Table 5. The metal atom is four-co-ordinated, with approximate square planar geometry, by the three nitrogens of the ligand molecule and by the NCS nitrogen. The arsenic

TABLE 4

Intramolecular distances (Å)

Ni–N(1)	1·909(7)	C(24)–C(25)	1·37(3)
Ni–N(2)	1·958(7)	C(25)–C(26)	1·41(3)
Ni–N(3)	1·953(7)	C(26)–C(27)	1·42(3)
Ni–N(4)	1·862(8)	C(27)–C(22)	1·37(2)
As–C(6)	1·97(1)	B–C(28)	1·65(2)
As–C(16)	1·95(1)	B–C(34)	1·64(2)
As–C(22)	1·90(2)	B–C(40)	1·63(2)
N(1)–C(1)	1·49(2)	B–C(46)	1·65(2)
N(1)–C(3)	1·49(2)	C(28)–C(29)	1·39(2)
N(1)–C(5)	1·53(2)	C(29)–C(30)	1·39(2)
N(2)–C(2)	1·50(2)	C(30)–C(31)	1·36(2)
N(2)–C(8)	1·52(2)	C(31)–C(32)	1·40(2)
N(2)–C(10)	1·50(2)	C(32)–C(33)	1·38(2)
N(3)–C(4)	1·50(2)	C(33)–C(28)	1·39(2)
N(3)–C(12)	1·51(2)	C(34)–C(35)	1·40(2)
N(3)–C(14)	1·51(2)	C(35)–C(36)	1·41(2)
N(4)–C(7)	1·15(2)	C(36)–C(37)	1·35(2)
S–C(7)	1·60(1)	C(37)–C(38)	1·37(2)
C(1)–C(2)	1·48(2)	C(38)–C(39)	1·39(2)
C(3)–C(4)	1·47(2)	C(39)–C(34)	1·39(2)
C(5)–C(6)	1·53(2)	C(40)–C(41)	1·41(2)
C(8)–C(9)	1·50(2)	C(41)–C(42)	1·37(2)
C(10)–C(11)	1·48(2)	C(42)–C(43)	1·39(2)
C(12)–C(13)	1·52(2)	C(43)–C(44)	1·34(2)
C(14)–C(15)	1·54(2)	C(44)–C(45)	1·40(2)
C(16)–C(17)	1·35(2)	C(45)–C(40)	1·38(2)
C(16)–C(21)	1·42(2)	C(46)–C(47)	1·42(2)
C(17)–C(18)	1·37(2)	C(47)–C(48)	1·38(2)
C(18)–C(19)	1·37(2)	C(48)–C(49)	1·39(2)
C(19)–C(20)	1·36(2)	C(49)–C(50)	1·38(2)
C(20)–C(21)	1·38(2)	C(50)–C(51)	1·37(2)
C(22)–C(23)	1·40(2)	C(51)–C(46)	1·39(2)
C(23)–C(24)	1·42(3)		

atom is not co-ordinated to and lies 5·84 Å from the nickel atom. The positions above and below the co-ordination plane are partially shielded by methyl groups, which exhibit short contacts to the metal [C(11) · · · Ni 3·23; C(13) · · · Ni 3·18 Å]. No intermolecular approach to the nickel atom <4·0 Å is found.

The mean nickel–tertiary-nitrogen distance (1·94 Å) is considerably shorter than the corresponding mean (2·15 Å) in the five-co-ordinate Ni(nas)(NCS)$_2$,[3] which has two NCS groups N-bonded to the metal in addition to the nitrogen atoms of the ligand molecule. The four- and five-co-ordinate complexes will be referred to as complex (I) and (II), respectively, in the rest of the discussion. The 1·862(8) Å value of the Ni–N(4) bond length in complex (I) is lower than the mean Ni–N(NCS) (1·95 Å) in complex (II). These differences should be ascribed to: (a) the lower repulsions exerted between four rather than five ligand atoms, and (b) the lower electron density in the square planar case, occupying antibonding orbitals in the region between the metal and the ligands.

The ligand atoms are not strictly coplanar with the metal. The deviations from the planes are reported in Table 6 with data for other least-squares planes.

Bond distances and angles in the two ions are generally

[10] Chem. Soc. Special Publ., No. 18, 1965.
[11] P. Dapporto and M. Di Vaira, J. Chem. Soc. (A), 1971, 1891.

in agreement with the expected values [10] with some exceptions discussed hereafter. The large values of the N–C–C angles and the short C–C distances in the ethyl groups (mean 114·7° and 1·51 Å) are probably due to uncorrected thermal motion. A similar situation was found in complex (II).[3] Another feature common to the two structures is presented by the short C–C bond lengths in the chelating ethylenediamine rings. The large values of the angles at the carbon atoms of the

TABLE 5

Bond angles (°)

N(1)–Ni–N(2)	88·8(0·3)	As–C(22)–C(23)	119·5(0·9)
N(1)–Ni–N(3)	88·2(0·3)	As–C(22)–C(27)	121·0(0·9)
N(1)–Ni–N(4)	177·3(0·4)	C(23)–C(22)–C(27)	118·4(1·2)
N(2)–Ni–N(3)	168·6(0·3)	C(22)–C(23)–C(24)	119·5(1·2)
N(2)–Ni–N(4)	91·4(0·4)	C(23)–C(24)–C(25)	122·8(1·5)
N(3)–Ni–N(4)	92·2(0·4)	C(24)–C(25)–C(26)	116·7(1·6)
C(6)–As–C(16)	96·9(0·4)	C(25)–C(26)–C(27)	120·8(1·6)
C(6)–As–C(22)	103·0(0·5)	C(22)–C(27)–C(26)	121·4(1·3)
C(16)–As–C(22)	105·0(0·5)	C(28)–B–C(34)	108·4(0·7)
Ni–N(1)–C(1)	105·0(0·5)	C(28)–B–C(40)	111·4(0·7)
Ni–N(1)–C(3)	106·0(0·5)	C(28)–B–C(46)	106·2(0·7)
Ni–N(1)–C(5)	111·9(0·5)	C(34)–B–C(40)	108·2(0·7)
C(1)–N(1)–C(3)	113·0(0·7)	C(34)–B–C(46)	113·0(0·7)
C(1)–N(1)–C(5)	110·7(0·7)	C(40)–B–C(46)	109·7(0·7)
C(3)–N(1)–C(5)	110·1(0·7)	B–C(28)–C(29)	124·2(0·7)
Ni–N(2)–C(2)	107·3(0·6)	B–C(28)–C(33)	122·3(0·8)
Ni–N(2)–C(8)	113·6(0·6)	C(29)–C(28)–C(33)	113·4(0·8)
Ni–N(2)–C(10)	110·4(0·6)	C(28)–C(29)–C(30)	123·6(0·8)
C(2)–N(2)–C(8)	110·9(0·7)	C(29)–C(30)–C(31)	120·3(1·0)
C(2)–N(2)–C(10)	110·6(0·7)	C(30)–C(31)–C(32)	119·2(0·9)
C(8)–N(2)–C(10)	104·1(0·7)	C(31)–C(32)–C(33)	118·1(0·9)
Ni–N(3)–C(4)	108·3(0·5)	C(28)–C(33)–C(32)	125·3(0·9)
Ni–N(3)–C(12)	114·7(0·6)	B–C(34)–C(35)	123·3(0·8)
Ni–N(3)–C(14)	104·6(0·6)	B–C(34)–C(39)	119·6(0·8)
C(4)–N(3)–C(12)	111·8(0·7)	C(35)–C(34)–C(39)	116·8(0·8)
C(4)–N(3)–C(14)	108·3(0·7)	C(34)–C(35)–C(36)	120·2(1·0)
C(12)–N(3)–C(14)	108·7(0·7)	C(35)–C(36)–C(37)	121·2(1·1)
Ni–N(4)–C(7)	169·3(0·7)	C(36)–C(37)–C(38)	119·8(1·1)
N(1)–C(1)–C(2)	108·5(0·8)	C(37)–C(38)–C(39)	120·0(1·0)
N(2)–C(2)–C(1)	109·5(0·8)	C(34)–C(39)–C(38)	121·9(0·9)
N(1)–C(3)–C(4)	109·1(0·8)	B–C(40)–C(41)	119·7(0·8)
N(3)–C(4)–C(3)	108·3(0·8)	B–C(40)–C(45)	125·2(0·7)
N(1)–C(5)–C(6)	113·1(0·7)	C(41)–C(40)–C(45)	115·1(0·7)
As–C(6)–C(5)	118·6(0·6)	C(40)–C(41)–C(42)	122·6(0·9)
S–C(7)–N(4)	178·6(0·9)	C(41)–C(42)–C(43)	119·0(0·9)
N(2)–C(8)–C(9)	115·1(0·9)	C(42)–C(43)–C(44)	119·4(0·9)
N(2)–C(10)–C(11)	115·4(0·8)	C(43)–C(44)–C(45)	120·5(0·9)
N(3)–C(12)–C(13)	111·8(0·8)	C(40)–C(45)–C(44)	122·6(0·8)
N(3)–C(14)–C(15)	116·7(0·9)	B–C(46)–C(47)	121·6(0·7)
As–C(16)–C(17)	115·9(0·7)	B–C(46)–C(51)	125·5(0·7)
As–C(16)–C(21)	124·7(0·7)	C(47)–C(46)–C(51)	112·9(0·8)
C(17)–C(16)–C(21)	119·4(0·9)	C(46)–C(47)–C(48)	124·1(0·8)
C(16)–C(17)–C(18)	121·8(1·0)	C(47)–C(48)–C(49)	119·9(0·9)
C(17)–C(18)–C(19)	118·9(1·1)	C(48)–C(49)–C(50)	117·6(0·9)
C(18)–C(19)–C(20)	120·8(1·0)	C(49)–C(50)–C(51)	121·1(0·9)
C(19)–C(20)–C(21)	121·1(1·0)	C(46)–C(51)–C(50)	124·3(0·8)
C(16)–C(21)–C(20)	118·1(0·9)		

non-chelating chain in the present complex may be ascribed to thermal motion or may result from strain forces acting on the chain, which joins two large groupings of atoms. The NCS group is linear and its axis deviates by 10° from the Ni–N(4) bond direction. Deviations of varying amounts are found in other cases (refs. 3, 11 and references therein) and are probably imposed by packing in the solid. The shortest contacts to the sulphur atom are listed in Table 7, with other contact distances <3·60 Å and some short non-bonded interactions within the BPh$_4^-$ anion.

The mean of the four B–C distances * in the anion is 1·643(4) Å. The mean C–C distance is 1·383(4) Å, to be compared with the expected 1·394 Å.[10] The mean C–H is 1·06 Å. Values of the C–C–C angles in the

TABLE 6

Equations of the least-squares planes in the form $Ax + By + Cz = D$ (in triclinic fractional co-ordinates) with deviations (Å) of atoms from the planes in square brackets

	A	B	C	D
Plane (1): N(1)—(4)	−7·763	9·932	7·110	2·769

[N(1) 0·12, N(2) −0·11, N(3) −0·11, N(4) 0·11, Ni 0·07]

| Plane (2): C(16)—(21) | −8·729 | 9·505 | −4·230 | −4·721 |

[C(16) 0·01, C(17) 0·00, C(18) −0·01, C(19) 0·01, C(20) 0·00, C(21) −0·01, As 0·06]

| Plane (3): C(22)—(27) | 10·172 | 1·523 | 4·024 | 6·879 |

[C(22) −0·01, C(23) 0·01, C(24) −0·02, C(25) 0·02, C(26) −0·02, C(27) 0·02, As −0·42]

| Plane (4): C(28)—(33) | 10·378 | −4·448 | −9·551 | 1·760 |

[C(28) −0·01, C(29) 0·01, C(30) −0·01, C(31) 0·01, C(32) −0·01, C(33) 0·00, B −0·05]

| Plane (5): C(34)—(39) | 6·267 | −6·613 | 9·446 | 3·589 |

[C(34) 0·00, C(35) −0·02, C(36) 0·02, C(37) −0·01, C(38) 0·00, C(39) 0·01, B −0·11]

| Plane (6): C(40)—(45) | 2·776 | 9·509 | 6·438 | 9·804 |

[C(40) 0·01, C(41) −0·01, C(42) 0·00, C(43) 0·00, C(44) 0·00, C(45) 0·00, B 0·03]

| Plane (7): C(46)—(51) | 4·118 | 10·332 | −8·860 | 6·263 |

C(46) 0·00, C(47) 0·00, C(48) 0·00, C(49) −0·01, C(50) 0·01, C(51) −0·01, B 0·00]

Dihedral angles (°)

(2)–(3)	50·8	(4)–(7)	69·3	(5)–(7)	58·4
(4)–(5)	84·6	(5)–(6)	73·5	(6)–(7)	66·5
(4)–(6)	73·0				

TABLE 7

Significant intramolecular contacts (Å), intermolecular contacts <3·60 Å, and contacts involving the sulphur atom

C(28)···C(45ᴵ)	3·06	C(16)···C(18ᴵᴵ)	3·56
C(28)···C(47ᴵ)	3·10	C(50)···C(50ᴵᴵᴵ)	3·59
C(34)···C(29ᴵ)	3·00	C(3)···C(29ᴵⱽ)	3·53
C(34)···C(41ᴵ)	3·13	C(32)···C(44ᴵⱽ)	3·58
C(40)···C(39ᴵ)	2·99	S···C(49ⱽ)	3·75
C(40)···C(51ᴵ)	3·04	S···C(13ⱽᴵ)	3·85
C(46)···C(33ᴵ)	3·05	S···C(20ⱽᴵ)	3·75
C(46)···C(35ᴵ)	3·14		

Roman numerals as superscripts refer to the following equivalent positions:

I	x, y, z	II	$1 - x, -y, 1 - z$
III	$1 - x, 1 - y, -z$	IV	$1 - x, 1 - y, 1 - z$
V	$x - 1, y, z$	VI	$-x, -y, -z$

four benzene rings exhibit a rather consistent trend. The angles at the four carbon atoms bonded to boron (denoted by α in Figure 2) are all less than 120°, mean 114·5(8)°. The eight contiguous angles (β) are all larger than 120°, and mean 123·1(6)°. The other angles have expected values [mean 119·7(3)°]. Preliminary re-

ports[4] seem to show that a similar situation exists for the anion in the structure of the complex [Co(np)I]-BPh₄ although no significant trend is found in the other compounds for which there are detailed reports, i.e. [Ni(npe)Br]BPh₄ [12a] {npe = bis-[2-(diethylamino)ethyl]-2-(diphenylphosphino)ethylamine} and [Co(qp)Cl]-BPh₄ [12b] {qp = tris-[o-(diphenylphosphino)phenyl]phosphine}. The analysis is made uncertain in the last three cases by the large standard deviations. However, these do not prevent the following study of the conformation of the anion in each case, by use of least-squares planes through sets of atoms. No distortions of the type mentioned are found in the phenyl groups in tetraphenyl-phosphonium[13] or -arsonium[14] cations. The situation presently found in the anion may originate from crowding about the boron atom, caused by the shorter B–C than the P–C or As–C bond lengths. Some evidence of crowding about boron is provided by the close non-bonded approaches between α- and β-type carbon atoms from different phenyl groups in the anion (Table 7). Values of the angles between the best planes through the phenyl groups in the anion (Table 6) show some scatter about the mean value of 70·9° (mean deviation from the mean, 6·1°). The situation is similar in the complexes [Co(np)I]BPh₄ (ref. 4) and [Ni(npe)Br]BPh₄ [ref. 12(a)], with mean values of the angles 68·4 and 70·7°, and mean deviations of 7·7 and 7·3°, respectively. In the complex [Co(qp)Cl]BPh₄ [ref. 12(b)] a larger scatter (11·4°) is found about a similar average (69·5°). In the extensively studied cation of related geometry, AsPh₄⁺, with which useful comparisons can be drawn, a large scatter of values is often found [e.g. mean deviations from the mean of 12·4 and 11·0° in ref. 14(a) and 14(b), respectively] with individual values of the angles ranging from 36—89° in one instance.[14a] In some cases a regular geometry is found for the cation, but the geometry may differ from case to case: e.g., crystallographic S_4 symmetry in ref. 14(c) and approximate D_{2d} symmetry in ref. 14(d), with mean values of the angles 70·5 and 55·8°, respectively. This versatility of form, evidently due to the release of some hindrance because of the long As–C bond length, is generally considered to determine the effectiveness of the cation as a precipitating agent.[14e,f] In view of the results discussed above it is doubtful whether BPh₄⁻ possesses a similar degree of versatility.

The arsenic atom does not co-ordinate in complexes (I) and (II) although there seem to be no steric factors to prevent this.[3] In an attempt to understand this point, we have undertaken an approximate MO calculation, expecting that qualitative indications would be provided by comparisons between schematic models,

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* Standard deviations on mean values of equivalent distances or angles are calculated by the formula: $[\Sigma_i(p_i - \bar{p})^2/n(n - 1)]^{\frac{1}{2}}$.[7b]

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13 P. Goldstein, K. Seff, and K. N. Trueblood, Acta Cryst., 1968, B24, 778.

14 (a) T. E. Hopkins, A. Zalkin, D. H. Templeton, and M. G. Adamson, Inorg. Chem., 1966, 5, 1428; (b) G. J. Palenik, Acta Cryst., 1966, 20, 471; (c) J. G. Scane, ibid., 1967, 23, 85; (d) R. C. L. Mooney-Slater, ibid., 1959, 12, 187; (e) F. A. Cotton and C. B. Harris, Inorg. Chem., 1968, 7, 2140; (f) B. Zaslow and R. E. Rundle, J. Phys. Chem., 1957, 61, 490.

in view of the large difference between the ligand atoms involved, nitrogen and arsenic. Models (a) and (b) (Figure 3), were used to approximate the situation in complexes (I) and (II), in that order; models (c) and (d) [15,16] refer to the idealized situations that would be respectively attained from (a) and (b) through attachment of the arsenic atom, without major rearrangements in the geometry. The calculation, of the SCCC type [17] in the WH approximation, has made use of STO's for the $3d$, $4s$, and $4p$ orbitals on nickel and for one σ-type tetrahedral hybrid from the valence shell of each ligand. The diagonal Hamiltonian-matrix elements, approximated as the negative of VOIP's [18] were allowed to vary with charge, for the metal; for the ligands, they were fixed at the neutral atom values. The two-atom overlap integrals, required for the evaluation of group
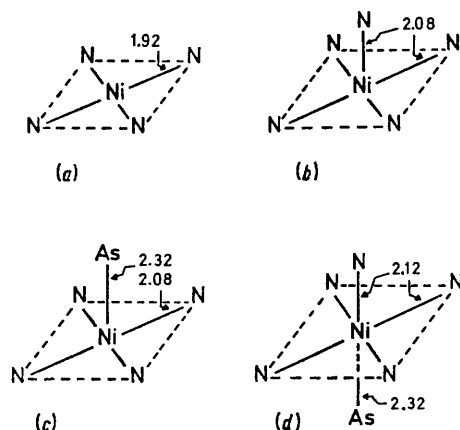
FIGURE 3   Schematic models used in the SCCC–MO calculation. The Ni–N distances (Å) are: (a) mean in complex (I) (see text), (b) and (c) mean in complex (II), and (d) from ref. 15. The Ni–As distance is from ref. 16. The metal atom is in the basal plane of the square pyramids

overlaps (ligand–ligand overlap being included) were calculated with a program kindly supplied to us by Professor Oleari of the Istituto di Chimica Fisica in Parma. The other programs used were written (by M. D. V.) for the IBM 1130.

The calculation has indicated a considerable increase in the energies of the molecular orbitals, caused by bonding of arsenic. Denoting by $E_j = \Sigma_i n_{ij}\varepsilon_{ij}$ the sum for model j of these energies over the occupied ($n_{ij} = 1$ or 2) molecular orbitals and by $E_{\sigma As}$ the energy of a doubly occupied hybrid on neutral arsenic, E_c and E_d are found to exceed $E_a + E_{\sigma As}$ and, respectively, $E_b + E_{\sigma As}$ by $ca.$ 5%. Certainly this is no unequivocal indication of destabilization caused by arsenic, in view of the approximations involved and because the similarity of trends in the sum of orbital energies from extended-Huckel methods on the one hand, and trends in the correct value of the total energy on the other hand, is not firmly stated. The energy increase under

discussion largely stems from the use of charge-dependent VOIP's for the metal and from the considerable metal–arsenic overlap. Another indication is provided by trends in the values of the (positive) gross charge on the metal. This decreases by $ca.$ 0·01 units when one nitrogen is added [$i.e.$ from model (a) to (b), or (c) to (d)], but it decreases as much as 0·16 units if arsenic is attached [(a) to (c), (b) to (d)]. Therefore, metal–ligand bonding with partial ionic character, like Ni–N, is not favoured by the arsenic ligand. In addition, the Ni–N covalent bond strength, as measured by the overlap population n(Ni, N),[19] is considerably decreased by bonding of arsenic: the n(Ni, N) value of the four in-plane bonds decreases by $ca.$ 20% on addition of a fifth nitrogen, but it decreases as much as 38% on addition of arsenic. Assigning no absolute meaning to these figures, one may nevertheless extract from the trends that they present qualitative indications of incompatibility between the arsenic donor and the nitrogen set.

Conformation of the Tetraphenylborate Ion.—The conformational energy of the isolated BPh_4^- ion has been calculated as a function of four parameters, in order to investigate the effects of unsymmetrical environments on the conformation of the anion. A recent calculation of the molecular and crystal structure of CPh_4 and related molecules [20] with geometry similar to that of BPh_4^- has accounted for the rotations of the four phenyl groups with one parameter, in view of the high symmetry of the specific problem considered.[20] The parameters used in the present study were the angles (ϕ_i, $i = 1$—4) for rotations of the four phenyl groups about their B–C axes. The arrangement of the four bonds about boron, assumed tetrahedral, was referred to a set of orthogonal axes (Figure 4).

The four parameters were systematically varied (ϕ_i faster than ϕ_j, with $i < j$) in order to consider all possible combinations of their values. Only the range 0—180° needs to be considered for each angle, owing to the geometry of phenyl groups. Moreover, if one out of four parameters is restricted to the range 0—60°, the set of conformations so considered can be used to generate all the others through rotations of the reference system. If the narrower range 0—30° is covered by one parameter, then a set of mirror-related arrangements is also excluded and the ones considered constitute the group of symmetry-independent arrangements. The parameters were varied in steps of 10° in a first coarse scan and in steps of 5 or 2° in successive scans through the intervals of interest. Calculations were performed on two models assuming: (a) regular phenyl rings, (b) distorted rings, with the mean experimental values of 114·5 and 123·1° for

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angles α and β respectively (Figures 2 and 4). In model (b) the directions of the C–H bonds were assumed to bisect the respective C–C–C angles. Bond distances C–C 1·394, C–H 1·060, and B–C 1·643 Å were assumed in both cases. Where not specified differently, the expression used for the interaction potential between
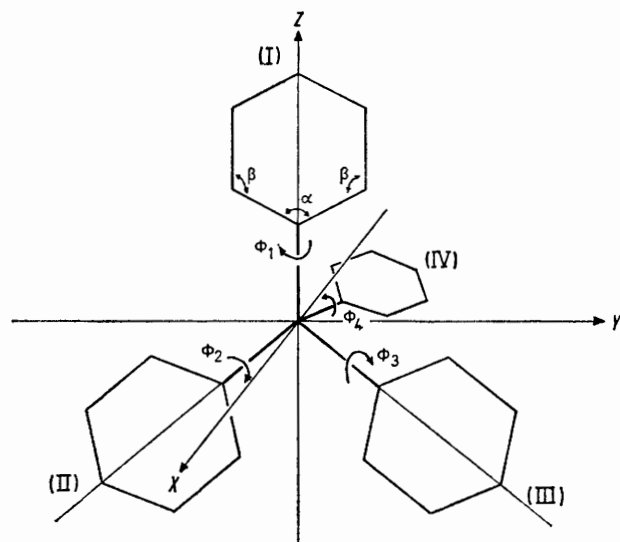

FIGURE 4 Geometry and parameters of model tetraphenyl-borate. The orientation with respect to the orthogonal reference system is defined by setting the axis of phenyl (I) along z and that of phenyl (IV) in the $-x$, $-z$ quadrant. The zero of ϕ_1 is on the xz plane; each of the other three angles is measured from the vertical plane containing z and the axis of the respective phenyl group. The positive direction of rotations is shown

non-bonded atom pairs was: $U_{ij} = a_{ij} \exp(-b_{ij}r) - c_{ij}r^{-6}$ [r being the distance (Å) between atoms i and j] with the values of the constants [21] reported in Table 8.

TABLE 8

Non-bonded interaction parameters

	a_{ij} 10^{-11}erg mol^{-1}	b_{ij} Å^{-1}	c_{ij} 10^{-11}erg Å^6 mol^{-1}
C $\cdots$ C	1640	4·32	2·07
C $\cdots$ H	218	4·20	0·84
H $\cdots$ H	45·8	4·08	0·34

The boron atom contributes to the total energy with constant terms, which were not included. The terminal C–H moieties in the phenyl groups (i.e. those *trans* to B–C) were excluded for analogous reasons and for the neglect of the interactions >6 Å. Torsional energy terms arising from rotations about the B–C bonds were disregarded in view of the fact that a potential with six-fold rotational symmetry should not present deep minima.[22] The calculations have been performed on an IBM 1130 computer. One minimum

* The approximation involved stems largely from the distortions which each case exhibits with respect to the overall tetrahedral geometry, assumed for the model.

[21] J. L. De Coen, G. Elefante, A. M. Liquori, and A. Damiani, *Nature*, 1967, **216**, 910.
[22] D. A. Buckingham, I. E. Maxwell, A. M. Sargeson, and M. R. Snow, *J. Amer. Chem. Soc.*, 1970, **92**, 3617.

in the potential energy $U(\phi_1, \phi_2, \phi_3, \phi_4)$ in the region of symmetry-independent conformations, has been found, for the values 96, 36, 84, and 24° of the parameters, in the order ϕ_1—ϕ_4. The position of the minimum, which is largely determined by the geometry of the problem, is practically identical for models (a) and (b) and is essentially unchanged by slightly differing assumptions for the C–H distance. The conformation at the minimum possesses S_4 symmetry about an axis bisecting the C_I–B–C_{II} and C_{III}–B–C_{IV} angles [where C_I is the carbon atom of phenyl (I) bonded to boron, *etc.*]. In view of its symmetry this arrangement may be described by a single parameter, θ, measuring the rotation of each phenyl group about its B–C axis from a plane containing that axis and the S_4 direction.[20,23] The present value of θ (36°) compares with the corresponding values calculated for CPh$_4$ (35°) and SiPh$_4$ (37°) in the solid state.[20]

The difference between the minimum energy values for models (a) and (b) is ΔU 2·21 kcal mol^{-1}. Assuming that this amount is required to distort the phenyl rings from the regular geometry of model (a) to that of model (b), then a mean value of 42 kcal mol^{-1} radian^{-2} is obtained for the composite bending constants [24] ($K/2$) of the C–C–C aromatic angles. Values in the range 60—70 kcal mol^{-1} radian^{-2} are reported for angles in paraffins.[24] However, the estimate of ΔU may be expected to be strongly dependent on the nature of the expressions used to reproduce the non-bonded interactions. In fact, the use of low-energy expressions [25] or of high-energy expressions [26] yields values of 1·03 and 2·90 kcal mol^{-1}, respectively, for ΔU. On the other hand, the results to be discussed below are not so strongly dependent on the specific expressions adopted, as they are primarily conditioned by the geometry of the problem.

The energy of S_4 conformations with $\theta \neq 36°$ is not stationary with respect to distortions decreasing the symmetry. This should be obvious for low values of θ, at which pairs of phenyl groups tend to be coplanar. Examination of the values $U(\phi_1, \phi_2, \phi_3, \phi_4)$, which cannot be reported in detail, has revealed a region of some extention around the energy minimum, containing low-energy conformations which should be easily induced by asymmetric environments. The region extends mainly along ϕ_4, and ϕ_3, and least along ϕ_1. This enables plotting of $U(\phi_3, \phi_4)$ from that area, for constant values of ϕ_2, with ϕ_1 fixed at 96°, the value at the minimum. Figure 5 shows two of these plots, calculated for model (b). Although they provide only partial information, they are nevertheless of use in the discussion of the experimental results.

The conformation of the anion in the present complex, in [Co(np)I]BPh$_4$, [Ni(npe)Br]BPh$_4$ and [Co(qp)Cl]-BPh$_4$, may be described to a good approximation *

[23] F. A. Cotton and S. J. Lippard, *Inorg. Chem.*, 1966, **5**, 416.
[24] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, ' Conformational Analysis,' Wiley, New York, p. 448.
[25] T. L. Hill, *J. Chem. Phys.*, 1948, **16**, 399.
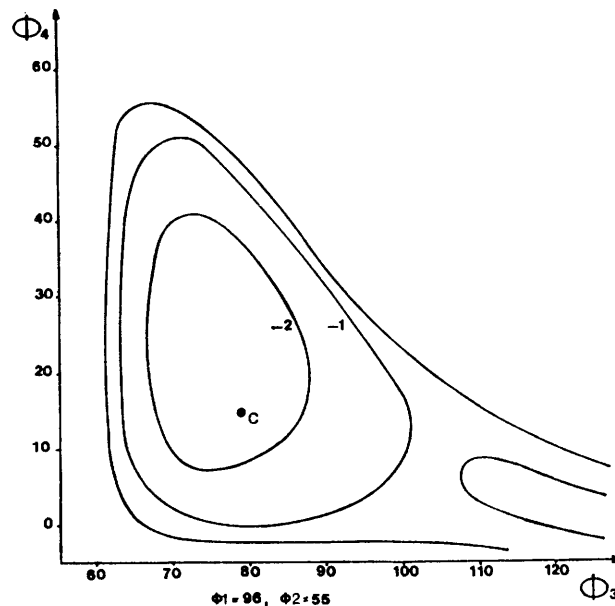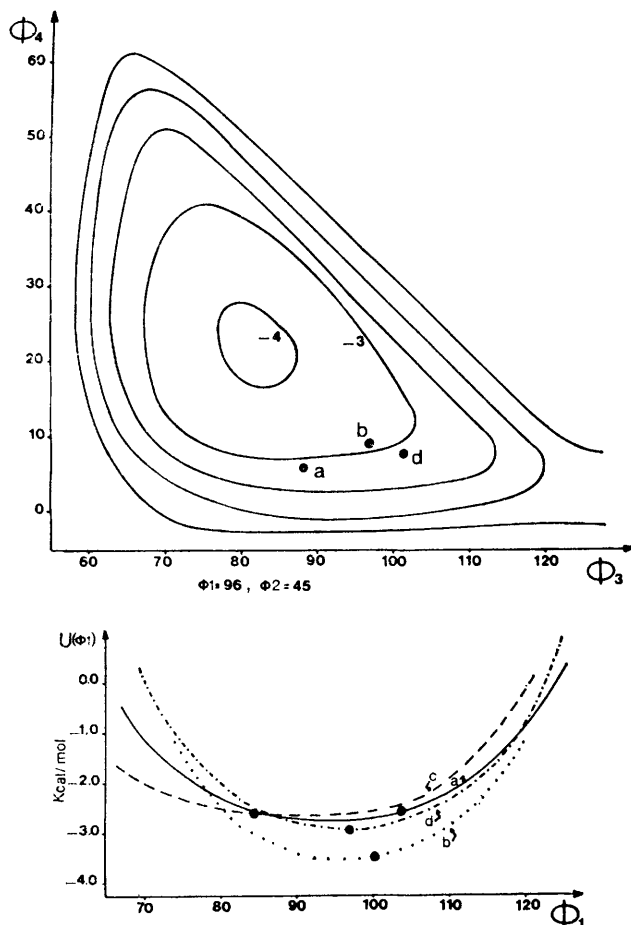[26] E. A. Mason and M. M. Kreevoy, *J. Amer. Chem. Soc.*, 1955, **77**, 5808.

FIGURE 5 Two sections of the $U(\phi_1, \phi_2, \phi_3, \phi_4)$ surface, for fixed values of ϕ_1 and ϕ_2 (see text), calculated for the model with distorted phenyl rings. Contours are at 1 kcal mol⁻¹ intervals and high-energy contours are omitted. The ϕ_3, ϕ_4 and (approximate) ϕ_2 values for the conformations found in: (a) [Ni(nas)(NCS)]BPh$_4$, (b) [Co(np)I]BPh$_4$, (c) [Ni(npe)Br]-BPh$_4$, and (d) [Co (qp)Cl]BPh$_4$ are indicated. Curves in the diagram showing U vs. ϕ_1, are calculated for those four cases: along each curve ϕ_2, ϕ_3, and ϕ_4 are fixed at the experimental values for the specific case considered. Dots mark the experimental ϕ_1 settings

by the sets of values for the four parameters: 104, 48, 88, and 6; 100, 40, 97, and 10; 85, 54, 79, and 15; and 97, 43, 102, and 7°. These are defined as in Figure 4, with the orientation of the right-handed reference system appropriate to each case, and are measured as the angles between least-squares planes through the phenyl groups and through other sets of atoms. The energies of these four conformations are respectively 1·80, 0·92, 1·74, and 1·52 kcal mol⁻¹ above the minimum, for the distorted-ring model. These conformations belong to the low-energy region, as indicated by their approximate locations on the two plots of Figure 5, which also shows the effect on the energy of ϕ_1 variations (not considered in the previous plots) corresponding to each of the experimental ϕ_2, ϕ_3, ϕ_4 arrangements. The value found for ϕ_1 in each case is seen to be essentially confined to the low-energy part of the curve. An analogous situation is found for the other three parameters, when these are separately considered, as has been reported for ϕ_1. It may be deduced from Figure 5 that even though a range of conformations appears to be possible, rotations of one phenyl group seem to be somewhat hindered, if the other three groups are considered to be fixed (it should be observed that a C · · · C interaction at 3·6 Å involves only 0·1
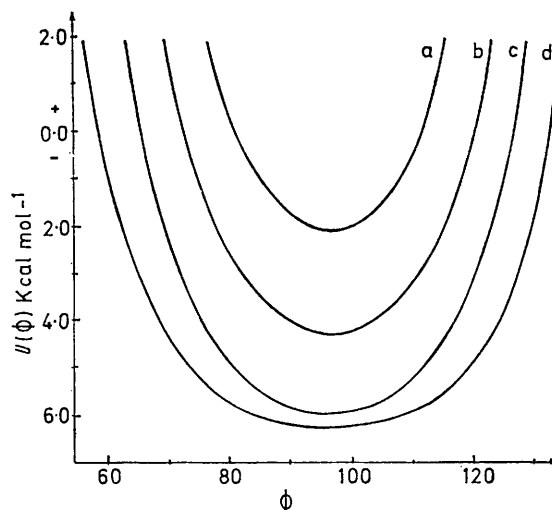

FIGURE 6 Variation of the conformational energy from the minimum value in model structures, due to rotation of one phenyl group; the other groups are fixed at the equilibrium conformation, which is virtually identical for the four cases considered. Curves are shown for: (a) BPh$_4^-$ with regular phenyl rings, (b) BPh$_4^-$ with distorted phenyl rings (see text), (c) PPh$_4^+$, and (d) AsPh$_4^+$. The P–C and As–C distances assumed in (c) and (d) (1·796 and 1·910 Å, respectively) are means of values in refs. 13 and 14

kcal mol⁻¹, in the computational scheme followed here).

The difference between BPh_4^- and other counterions having similar geometry but longer carbon–central atom distances, should appear from Figure 6, which shows the effect on the energy of rotations of one phenyl group from the equilibrium conformation, at which the four groups are equivalent. As may be seen, the distortion of the phenyl rings in BPh_4^- ion releases only partially their mutual hindrance. In conclusion, the calculation predicts a range of conformations, even larger than has been found experimentally, so far. However, the rotations of the four phenyl groups, required to cover that range, are not unrelated; individual rotations are in fact rather hindered. We assume this to be an indication of the limited flexibility for the anion.