59. Complexes of 2,2′,2″-Nitrilotriphenol

Part 2

Crystal and Molecular Structures of Three Boron Complexes

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Crystal and molecular structures of a complex between B(III) and the tripod ligand 2,2′,2″-nitrilotriphenol as well as of its pyridine and quinuclidine adducts are presented. The 2,2′,2″-nitrilotriphenyl borate (**III**) molecule shows a strained, tricyclic chelate system with a central N–B donor-acceptor bond of 1.681(5) Å. In the adducts with pyridine (**IV**) and quinuclidine (**III**-quin), this bond is broken, the N-atom inverts and is pushed out of the coordination sphere ($B-N_{intern}$ = 2.82 Å for Py and 2.85 Å for quin), and a new bond is formed between the boron atom and the external nucleophile ($B-N_{extern}$ = 1.631 Å for Py and 1.643 Å for quin).

Introduction. – In [1], we have reported on the temperature-dependent NMR spectra and structures of two complexes of B(III) with 2,2′,2″-nitrilotriphenol, namely **III** and **IV**. The results obtained were interpreted in terms of a nucleophilic substitution reaction **III** + Py⇌**IV**. In this paper, we report details of the X-ray structure determinations of **III**, **IV**, and **III**-quin (quin = quinuclidine).

The three complexes were obtained from reactions of trimethyl borate with solutions of 2,2′,2″-nitrilotriphenol in MeCN: **III** forms, when no additional reagents are present; in the presence of an excess of pyridine or quinuclidine [1] [2], the corresponding adducts **IV** and **III**-quin, respectively, are obtained.

Experimental. – *Crystals for X-Ray Structure Determinations.* The three compounds were synthesized as described previously [1] [2]. Crystals suitable for X-ray work were grown as follows.

III: 0.5 g of 2,2′,2″-nitrilotriphenol was dissolved in 10 ml of dry DMSO, 0.5 g of $B(OCH_3)_3$ was added, and the soln. kept overnight at 80°. The crystals deposited were isolated, washed with Et_2O, and dried *in vacuo*.

IV: 200 mg of crude **IV** (or **III**) was dissolved in a sufficient amount of dry pyridine (about 2 ml) at 90°, and the soln. was slowly cooled to r.t. at a rate of −10°/day.

III-*quin*: The crystals obtained from the synthesis were used directly [1].

X-Ray Data Collections. Table 1 summarizes crystal data and provides some details of data collection and structure refinement. Other relevant information: *Lorentz* and polarization corrections, direct methods (MULTAN 77 [3]); weighted least-squares refinements in the XRAY 72 [4] program system, weighting scheme of *Dunitz* and *Seiler* [5]. Real and imaginary scattering factors for neutral atoms [6]; all atoms refined; B, C, N, and O anisotropically.

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Table 1. *Crystal Data and Parameters Used in Data Collection and Structure Determination*

	III	**IV**	**III**-*quin*
Formula	$C_{18}H_{12}O_3BN$	$C_{23}H_{17}O_3BN_2$	$C_{25}H_{25}O_3BN_2$
Space group	monoclinic	orthorhombic	triclinic
	$P2_1/n$	*Pbca*	$P\bar{1}$
a [Å]	6.780(3)	14.745(3)	9.805(2)
b [Å]	13.626(5)	15.354(3)	10.570(4)
c [Å]	15.706(4)	16.419(3)	11.352(4)
α [°]	90.0	90.0	85.73(3)
β [°]	90.0	90.0	67.80(3)
γ [°]	99.32(3)	90.0	71.91(2)
V [Å^3]	1431.9	3717.3	1034
Z	4	8	2
Crystal size [mm]	0.3 × 0.3 × 0.2	0.2 × 0.2 × 0.2	0.2 × 0.2 × 0.2
Radiation	Mo$K\alpha$	(λ = 0.71069 Å)	
Theta max	25°	25°	25°
Scan type	$\omega/2\theta$	ω	$\omega/2\theta$
Total scan angle/reflection	1.5°	1.2°	1.5°
Max. measuring time/reflection	60 s	150 s	90 s
No. of independent reflections	2506	3281	3631
No. of reflections used in refinements	1538 ($> \sigma_F$)	1877 ($> 3\sigma_F$)	2378 ($> \sigma_F$)
No. of variables	257	331	382
Final R (R_w)[a])	0.050 (0.047)	0.045 (0.038)	0.077 (0.042)
Weighting, A[a])	10	10	8

[a]) $w = 1/\sigma^2(F) \times \exp(2 \times A \times (\sin\theta/\lambda)^2)$ [5].

Results and Discussion. – Positional and equivalent isotropic displacement parameters are given in *Tables 2, 3,* and *4*. Anisotropic displacement parameters have been given in [2].

Atomic numbering is indicated in *Fig. 1*. Chemically equivalent bond distances and angles have been averaged with respect to the non-crystallographic threefold axis. Values for the bi- and tricycloundecane cages are reported in *Table 5*. Additional geometric information and stereodiagrams of molecular packing are given in [2].

Complex **III** shows a tricyclo[3.3.3.0]undecane skeleton with approximate C_{3v} symmetry and a central N→B dative bond (1.681 Å). In **IV** and **III**-quin, this bond is broken (~ 2.83 Å) and replaced by an exocyclic B←N dative bond from the pyridine or quinuclidine N-atom to the B-atom (1.64 Å) *(Fig. 2a)*. The adducts, thus, show a bicyclo[3.3.3]undecane skeleton in which the NC_3 and BO_3 fragments deviate from the eclipsed arrangement by ~ 33°, *i.e.* the approximate symmetry is lowered to C_3 *(Fig. 2b)*. The differences in the overall conformations of **III** and **IV** are accompanied by changes in some other distances and angles [2].

Table 6 shows the geometry around the B-atom in boron-nitrilotriacetate [7], III, and nitrilotriethanol-borate (NTE-B) [8], together with the basicity of the O donor atoms. Boron-nitrilotriacetate, the weakest O-donor, shows the most pyramidalized BO_3-fragment and the shortest B–N bond; nitrilotriethanol-borate, the strongest O-donor, shows the most planar BO_3-fragment. Complex **III** is intermediate in its O-basicity, but its B–N bond is too long to fit into the correlation; a value of 1.64 Å, as found in the less strained adducts **III**-quin or **IV**, would fit much better. Possibly, the B–N bond in **III** is elongated as a consequence of angle strain in the five-membered rings, where the

Table 2. *Positional and Displacement Parameters* ($100 \times U_{eq}$ or $100 \times U_{iso}$) *for* **III**
(e.s.d.'s in terms of least significant digit)

Atom	*x*	*y*	*z*	U_{iso} or U_{eq}
N	1.1311(4)	0.7523(2)	0.2475(1)	3.3(1)
B	1.3646(6)	0.7286(3)	0.2620(2)	4.1(2)
O(1)	1.3809(3)	0.7187(2)	0.3528(1)	5.4(1)
O(2)	1.4902(3)	0.8153(2)	0.2260(1)	4.7(1)
O(3)	1.3691(3)	0.6395(2)	0.2138(2)	5.4(1)
C(11)	1.2136(4)	0.7395(2)	0.3907(2)	3.7(2)
C(12)	1.0657(4)	0.7597(2)	0.3362(2)	3.1(1)
C(13)	0.8864(5)	0.7831(2)	0.3639(2)	4.0(2)
C(14)	0.8574(5)	0.7855(3)	0.4519(2)	5.0(2)
C(15)	1.0043(6)	0.7652(3)	0.5066(2)	5.0(2)
C(16)	1.1824(5)	0.7413(3)	0.4776(2)	4.7(2)
C(21)	1.3712(5)	0.8753(2)	0.1884(2)	3.8(2)
C(22)	1.1687(4)	0.8457(2)	0.1985(2)	3.4(1)
C(23)	1.0283(5)	0.8978(3)	0.1648(2)	4.7(2)
C(24)	1.1007(7)	0.9827(3)	0.1189(2)	6.0(2)
C(25)	1.3029(7)	1.0124(3)	0.1077(2)	5.9(2)
C(26)	1.4412(6)	0.9599(3)	0.1423(2)	4.9(2)
C(31)	1.1853(5)	0.6057(2)	0.1831(2)	4.0(2)
C(32)	1.0418(4)	0.6637(2)	0.1995(2)	3.4(2)
C(33)	0.8458(5)	0.6385(3)	0.1740(2)	4.6(2)
C(34)	0.7956(6)	0.5515(3)	0.1277(2)	6.0(2)
C(35)	0.9378(7)	0.4946(3)	0.1089(2)	6.4(2)
C(36)	1.1342(6)	0.5192(3)	0.1357(2)	5.8(2)
H(13)	0.7657(37)	0.7902(19)	0.3193(16)	1.9(6)
H(14)	0.7324(48)	0.7975(24)	0.4735(21)	4.3(9)
H(15)	0.9740(55)	0.7648(28)	0.5680(25)	6.5(12)
H(16)	1.2907(52)	0.7279(26)	0.5140(22)	5.4(10)
H(23)	0.8523(44)	0.8628(23)	0.1732(20)	4.1(9)
H(24)	1.0184(61)	1.0203(32)	0.0946(28)	7.6(13)
H(25)	1.3533(56)	1.0690(29)	0.0774(26)	6.6(12)
H(26)	1.5790(52)	0.9832(27)	0.1375(23)	5.7(11)
H(33)	0.7316(34)	0.6778(17)	0.1884(15)	1.1(6)
H(34)	0.6546(61)	0.5332(34)	0.1084(27)	7.9(14)
H(35)	0.9071(57)	0.4397(30)	0.0792(25)	6.9(12)
H(36)	1.2218(57)	0.4856(31)	0.1228(25)	6.4(12)

Table 3. *Positional and Displacement Parameters* ($100 \times U_{eq}$ or $100 \times U_{iso}$) *for* **IV**
(e.s.d.'s in terms of least significant digit)

Atom	*x*	*y*	*z*	U_{iso} or U_{eq}
N(1)	0.7521(1)	0.2322(1)	0.7298(1)	3.3(1)
B	0.8716(2)	0.1096(2)	0.6608(2)	3.5(1)
O(1)	0.8232(1)	0.0624(1)	0.7243(1)	3.5(1)
O(2)	0.8156(1)	0.1344(1)	0.5915(1)	3.8(1)
O(3)	0.9311(1)	0.1780(1)	0.6884(1)	3.9(1)
C(11)	0.8055(2)	0.0999(2)	0.7976(1)	3.3(1)
C(12)	0.7712(2)	0.1844(2)	0.8023(1)	3.2(1)
C(13)	0.7585(2)	0.2226(2)	0.8779(2)	4.2(1)
C(14)	0.7776(2)	0.1768(2)	0.9488(2)	5.0(2)
C(15)	0.8079(2)	0.0919(2)	0.9436(2)	4.7(1)
C(16)	0.8211(2)	0.0529(2)	0.8685(2)	3.9(1)

Table 3 (cont.)

Atom	*x*	*y*	*z*	U_{iso} or U_{eq}
C(21)	0.7257(2)	0.1514(1)	0.6018(1)	3.3(1)
C(22)	0.6925(2)	0.1949(1)	0.6700(2)	3.3(1)
C(23)	0.5995(2)	0.2039(2)	0.6799(2)	4.2(1)
C(24)	0.5402(2)	0.1731(2)	0.6218(2)	5.1(2)
C(25)	0.5731(2)	0.1357(2)	0.5515(2)	5.1(2)
C(26)	0.6657(2)	0.1253(2)	0.5413(2)	4.2(1)
C(31)	0.9072(2)	0.2638(1)	0.6821(1)	3.6(1)
C(32)	0.8204(2)	0.2921(2)	0.7020(1)	3.4(1)
C(33)	0.7988(2)	0.3802(2)	0.6960(2)	3.9(1)
C(34)	0.8631(2)	0.4398(2)	0.6725(2)	4.6(1)
C(35)	0.9496(2)	0.4117(2)	0.6535(2)	5.0(2)
C(36)	0.9716(2)	0.3240(2)	0.6581(2)	4.6(1)
N(2)	0.9381(1)	0.0336(1)	0.6256(1)	3.7(1)
C(41)	0.9019(2)	–0.0316(2)	0.5825(2)	4.9(2)
C(42)	0.9519(2)	–0.1026(2)	0.5583(2)	6.0(2)
C(51)	1.0264(2)	0.0297(2)	0.6458(2)	5.4(2)
C(52)	1.0790(2)	–0.0395(2)	0.6223(2)	6.6(2)
C(2)	1.0414(3)	–0.1068(2)	0.5781(2)	6.0(2)
H(13)	0.7361(19)	0.2854(18)	0.8797(18)	4.9(8)
H(14)	0.7712(20)	0.2046(18)	1.0007(18)	5.7(9)
H(15)	0.8260(23)	0.0590(20)	0.9932(20)	6.6(9)
H(16)	0.8425(18)	–0.0069(17)	0.8647(17)	4.3(7)
H(23)	0.5781(20)	0.2342(19)	0.7272(18)	5.5(8)
H(24)	0.4787(20)	0.1796(18)	0.6278(19)	5.5(8)
H(25)	0.5307(22)	0.1161(20)	0.5080(21)	6.7(9)
H(26)	0.6922(19)	0.0977(19)	0.4940(19)	5.4(8)
H(33)	0.7391(19)	0.3991(17)	0.7111(16)	4.5(7)
H(34)	0.8478(20)	0.5013(19)	0.6680(18)	5.3(8)
H(35)	0.9959(20)	0.4538(19)	0.6387(20)	6.5(9)
H(36)	1.0318(20)	0.3019(18)	0.6434(18)	5.0(8)
H(41)	0.8366(21)	–0.0230(19)	0.5672(19)	5.4(8)
H(42)	0.9210(24)	–0.1468(22)	0.5250(22)	7.4(10)
H(51)	1.0478(22)	0.0793(20)	0.6800(19)	5.9(9)
H(52)	1.1392(26)	–0.0403(23)	0.6417(23)	8.2(11)
H(2)	1.0759(29)	–0.1595(27)	0.5583(25)	9.9(13)

Table 4. *Positional and Displacement Parameters* ($100 \times U_{eq}$ or $100 \times U_{iso}$) *for* **III**-*quin* (e.s.d.'s in terms of least significant digit)

Atom	*x*	*y*	*z*	U_{iso} or U_{eq}
N(1)	0.8976(3)	0.7946(2)	0.3415(2)	4.0(2)
B	0.8646(4)	0.7844(3)	0.1043(3)	3.7(2)
O(1)	1.0135(2)	0.6867(2)	0.0860(2)	4.1(1)
O(2)	0.7346(2)	0.7452(2)	0.1940(2)	3.9(1)
O(3)	0.8576(2)	0.9203(2)	0.1224(2)	4.1(1)
C(11)	1.1101(4)	0.7097(3)	0.1366(3)	4.0(2)
C(12)	1.0569(4)	0.7653(3)	0.2585(3)	4.1(2)
C(13)	1.1612(4)	0.7893(3)	0.3035(4)	5.2(2)
C(14)	1.3178(4)	0.7516(4)	0.2281(4)	6.5(3)
C(15)	1.3705(4)	0.6904(4)	0.1102(4)	6.5(3)
C(16)	1.2681(4)	0.6695(3)	0.0628(3)	5.1(2)
C(21)	0.7524(3)	0.6664(3)	0.2910(3)	3.6(2)
C(22)	0.8300(3)	0.6880(3)	0.3640(3)	3.8(2)

Table 4 (cont.)

Atom	*x*	*y*	*z*	U_{iso} or U_{eq}
C(23)	0.8431(4)	0.6055(3)	0.4624(3)	4.5(2)
C(24)	0.7759(4)	0.5036(3)	0.4921(3)	5.3(2)
C(25)	0.6980(4)	0.4837(3)	0.4200(3)	5.2(2)
C(26)	0.6849(4)	0.5639(3)	0.3210(3)	4.8(2)
C(31)	0.7764(4)	0.9856(3)	0.2393(3)	3.9(2)
C(32)	0.7943(4)	0.9274(3)	0.3484(3)	4.0(2)
C(33)	0.7099(4)	0.9965(3)	0.4653(3)	5.1(2)
C(34)	0.6088(4)	1.1225(4)	0.4736(4)	6.1(3)
C(35)	0.5920(4)	1.1802(3)	0.3654(4)	5.8(2)
C(36)	0.6754(4)	1.1138(3)	0.2678(3)	4.6(2)
N(2)	0.8469(3)	0.7827(2)	–0.0338(2)	3.7(1)
C(41)	0.8540(4)	0.6457(4)	–0.0699(3)	5.1(2)
C(42)	0.8410(5)	0.6425(3)	–0.1987(3)	6.2(2)
C(51)	0.6945(4)	0.8777(3)	–0.0281(3)	5.0(2)
C(52)	0.6722(5)	0.8746(4)	–0.1529(4)	6.3(3)
C(61)	0.9729(4)	0.8238(4)	–0.1372(3)	5.8(2)
C(62)	0.9531(5)	0.8279(4)	–0.2641(3)	6.6(2)
C(2)	0.8163(5)	0.7821(3)	–0.2501(3)	5.8(2)
H(13)	1.118(4)	0.831(3)	0.399(3)	6.5(10)
H(14)	1.389(4)	0.768(3)	0.257(3)	6.2(10)
H(15)	1.477(4)	0.663(3)	0.054(3)	6.6(10)
H(16)	1.300(3)	0.634(2)	–0.024(2)	3.2(8)
H(23)	0.902(3)	0.621(3)	0.511(3)	4.1(8)
H(24)	0.781(4)	0.450(3)	0.564(3)	8.2(12)
H(25)	0.651(3)	0.410(3)	0.442(3)	5.9(9)
H(26)	0.635(3)	0.555(3)	0.269(2)	3.8(8)
H(33)	0.721(3)	0.948(3)	0.546(2)	4.0(8)
H(34)	0.550(4)	1.172(3)	0.556(3)	7.8(12)
H(35)	0.523(4)	1.272(3)	0.370(3)	6.0(10)
H(36)	0.670(3)	1.150(3)	0.167(3)	4.2(9)
H(411)	0.955(3)	0.588(3)	–0.069(3)	5.8(10)
H(412)	0.768(5)	0.632(4)	0.003(4)	11.0(15)
H(421)	0.942(4)	0.580(3)	–0.262(3)	8.3(12)
H(422)	0.759(4)	0.611(3)	–0.193(3)	8.7(12)
H(511)	0.615(4)	0.853(3)	0.045(3)	7.0(11)
H(512)	0.691(4)	0.967(3)	–0.004(3)	7.8(11)
H(521)	0.584(4)	0.846(4)	–0.136(3)	8.4(12)
H(522)	0.653(4)	0.958(3)	–0.187(3)	6.5(10)
H(611)	0.967(4)	0.907(3)	–0.107(3)	8.9(12)
H(612)	1.074(5)	0.749(4)	–0.139(3)	10.5(14)
H(621)	0.938(4)	0.916(3)	–0.292(3)	7.9(11)
H(622)	1.056(4)	0.763(3)	–0.330(3)	7.6(11)
H(2)	0.804(4)	0.783(3)	–0.334(3)	5.8(10)

Table 5. *Average Geometries of the Tri- and Bicycloundecane Frameworks of* **III**, **III**-*quin, and* **IV** (bond lengths in Å; bond angles and torsional angles in deg)

	III	**III**-*quin*	**IV**
B–N(1)	1.681(5)	2.845(5)	2.816(4)
N(1)–C(12)	1.470(18)[a])	1.437(4)	1.434(3)
C(12)–C(11)	1.377(6)	1.387(5)	1.393(4)
C(11)–O(1)	1.356(9)	1.364(4)	1.363(3)
O(1)–B	1.443(16)	1.450(4)	1.451(3)

Table 5 (cont.)

	III	**III**-*quin*	**IV**
B–N(2)	–	1.643(5)	1.631(4)
C(12)–N(1)–C(22)	116.4(2)	117.7(2)	118.0(2)
B–N(1)–C(12)	101.1(2)	81.2(3)	81.8(2)
N(1)–C(12)–C(11)	109.6(3)	121.4(3)	121.1(2)
N(1)–C(12)–C(13)	127.3(3)	118.9(3)	119.3(2)
C(12)–C(11)–O(1)	115.7(3)	122.0(3)	121.5(2)
C(16)–C(11)–O(1)	124.9(3)	118.3(3)	119.0(2)
C(11)–O(1)–B	109.4(3)	120.5(3)	120.9(2)
O(1)–B–N(1)–(N(2)	103.9(3)	104.1(2)	103.7(2)
O(1)–B–O(2)	114.4(3)	114.2(3)	114.5(2)
B–N(1)–C(12)–C(11)	–3.1(9)	–18.9(28)	–19.7(22)
N(1)–C(12)–C(11)–O(1)	0.0(11)	0.8(45)	2.6(34)
C(12)–C(11)–O(1)–B	3.8(9)	44.9(50)	42.5(39)
C(11)–O(1)–B–N(1)	–5.3(4)	–39.3(29)	38.5(23)
O(1)–B–N(1)–C(12)	5.0(5)	33.0(21)	32.7(16)
O(1)–B–N(2)–C(41)		59.0(31)	(10.8(25))[b]

[a] E.s.d.'s of the averaged values estimated as $(\frac{1}{3}\sum_{3}\sigma_i^2)^{\frac{1}{2}}$.

[b] The smallest of the six torsion angles between an O–B and a pyridine N–C bond.

Table 6. *Correlation of the Geometry of the NBO_3 Fragment with the Basicity of the O-Donor Atoms*

Compound	Basicity of O-donors [pK]	B–O [Å]	O–B–O [°]	O–B–N [°]	B–N [Å]
Boron-nitrilotriacetate [7]	5	1.446	113.4	105.2	1.620
III	10	1.443	114.4	103.9	1.681
Nitrilotriethanol-borate [8]	18	1.439	115.5	103.0	1.677

N(1)–C(12)–C(11), C(12)–C(11)–O(1), and C(11)–O(1)–B angles are compressed relative to their values in **III**-quin, **IV** (*Table 5*), and also 2,2′,2″-trimethoxytriphenylamine [2].

Following *Murray-Rust et al.* [9], the individual B–O and B–N bond lengths of nitrilotriethanol-borate [8], boron-nitrilotriacetate [7], **III**, **IV**, and **III**-quin have been plotted against the corresponding N–B–O angles (*Fig. 3*). They lie close to the modified *Pauling* relationships[3]):

$$r(\text{B–N}) = r(\text{B–N})_0 - c \ln(-3\cos\varphi)$$

$$r(\text{B–O}) = r(\text{B–O})_0 - c \ln(4/3 + \text{cis}\,\varphi)$$

where r(B–N) and r(B–O) are the observed bond lengths, φ is the corresponding N–B–O angle and c is a constant with a value of about 0.35 Å [2].

[3] Derived from *Pauling*'s bond length/bond order relationship ($r = r_0 - c \ln(n)$, which allows to calculate the length r of an arbitrary bond if one knows its bond order n and the length of the corresponding single bond r_0), postulating a conservation of total bond order around a given central atom during any chemical transformations (in our case: $\Sigma n_i = 4$ around the B-atom). See [10].

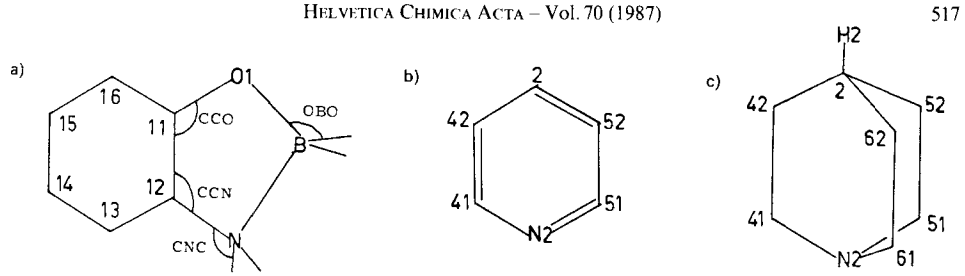

Fig. 1. *Atom numbering schemes:* a) *of the* **III** *skeleton* (labels are shown for chelate ring No. 1; the numbering of chelate rings No. 2 and No. 3 is analogous); b) *of the pyridine ligand;* c) *of the quinuclidine ligand.* The H-atoms carry the number of the C-atoms to which they are bound; if necessary, they are distinguished by an additional '1' or '2'; *e.g.* C-atom C(41) carries the H-atoms H(411) and H(412).

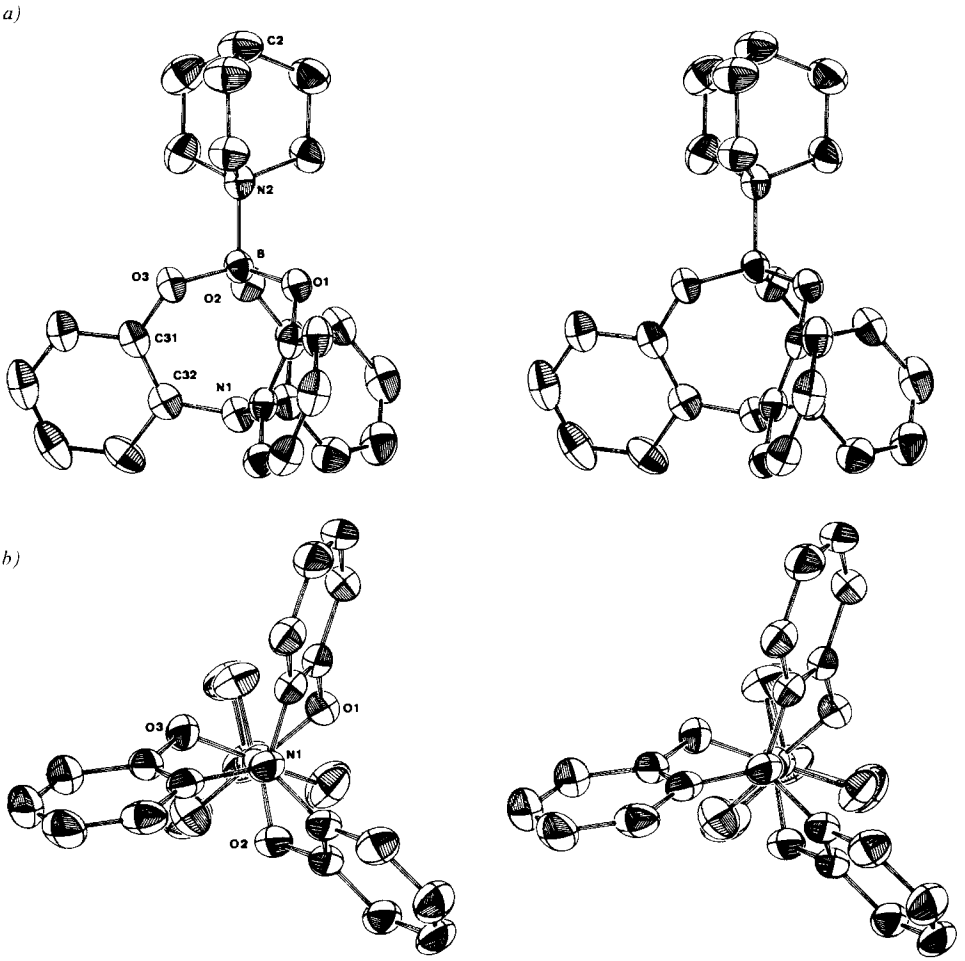

Fig. 2. a) *ORTEP [15] stereodrawing of the* **III**-*quin molecule,* b) *viewed along the molecular 3-fold axis*

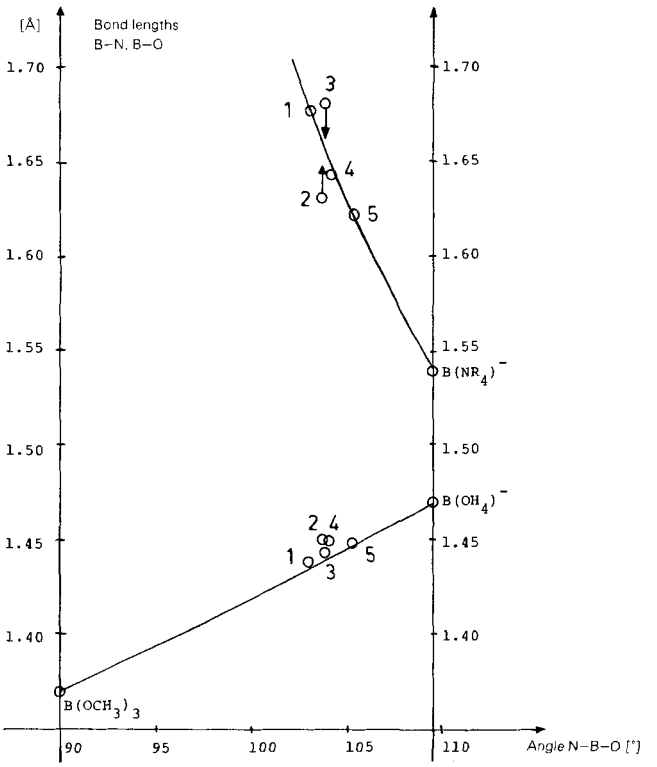

Fig. 3. *Structure correlation of the NBO_3 fragments of* 1) *nitrilotriethanol-borate [8]*; 2) **IV**; 3) **III**; 4) **III**-*quin, and* 5) *boron-nitrilotriacetate [7]*

The reference bond length for a B–N bond in a tetrahedral BN_4 fragment, $r(B–N)_0$ equals 1.54 Å (from tetrakis(1-pyrazolyl) borate [11]), whereas $r(B–O)$ is 1.47 Å (from $B(NO_3)_4^-$, $B(OAc)_4^-$ [13], and $B(OH)_4^-$ [14]). The B–N bond in **IV** seems short *(Fig. 3)*, but may be accounted for, if it is assumed that the shortening of bond length observed in going from $C(sp^3)–C(sp^3)$ to $C(sp^3)–C(sp^2)$ (about 0.02 Å [16]) applies to B–N bonds as well. Again, the B–N distance in **III** is clearly seen to be elongated by ~ 0.04 Å (arrow in *Fig. 3*).

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