47. Boron-nitrilotriacetate, $\mathrm{N(CH_2COO)_3B}$: Synthesis and Crystal-Structure Determinations at 293K and 110K

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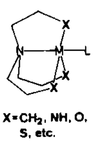
Summary

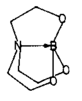
The title compound is insoluble in aprotic solvents and decomposes in protic ones. Its crystal structure consists of discrete molecules with non-crystallographic C_{3v}-symmetry and a transannular dative B–N bond (1.620(3) Å). The molecules pack tightly (density 1.804 g $\mathrm{cm^{-3}}$) interacting *via* O...C contacts between carbonyl groups (2.92–3.05 Å). The atoms show small vibrational motion which may be interpreted in terms of a rigid body model. Distances and angles obtained at 293 and 110 K were corrected for effects of rigid body motion and do not show significant differences.

Introduction. – In the course of our studies of nucleophilic displacement reactions at boron compounds in solution [1] the title compound was resynthesized [2]. It is insoluble in apolar and aprotic polar solvent and decomposes in protic ones. It was therefore useless for our purposes and it remained to be seen what features of its crystal structure, if any, could be held responsible for its insolubility.

Boron-nitrilotriacetate belongs to the family of inorganic compounds called 'atranes' by *Voronkov* [3]. These are closely related to the family of organic compounds called 'propellanes' [4] [5]. An [m,n,p]-propellane is a tricyclic C-compound whose (m + 2)-, (n + 2)- and (p + 2)-membered rings share a common C–C bond. An atrane is an [m,m,m]-propellane (m is mostly 3 or 4) whose common C–C bond is replaced by a metal and a N-atom. An optional apical ligand bonded to the metal may also be present (**I**).



I



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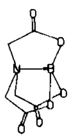

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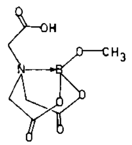

IV

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If the metal is boron, the corresponding family of compounds is called 'boratranes' (M = B). The neutral complex of boron with triethanolamine (**II**, boratrane proper) has been described [6] and its crystal and molecular structure determined [7]. This compound shows four-coordinate boron with a central N-B dative bond. The boron complex of nitrilotriacetic acid (**III**, boratranetrione, NTA-B) shows an analogous molecular structure; its crystal structure contains short intermolecular O...C contacts between carbonyl groups and the vibrational amplitudes of the atoms are relatively small. These observations are in qualitative agreement with the observed insolubility of the compound as well as with its unusually high density of 1.804 g cm^{-3}.

Synthesis and Properties of NTA-B (III). – *Voronkov & Mikhailova* [2] obtained NTA-B by reaction of boric acid with nitrilotriacetic acid (NTA) in boiling dimethyl sulfoxide (DMSO) or dimethylformamide (DMF):

$$N(CH_2COOH)_3 + B(OH)_3 \xrightarrow[150\,^\circ C]{\text{DMSO or DMF}} N(CH_2COO)_3B + 3\ H_2O$$

The resulting product is a fine, white powder, insoluble in common aprotic solvents and hydrolyzing in protic ones. In our work the synthesis was modified to obtain suitable crystals for X-ray structure determination:

$$N(CH_2COOH)_3 + B(OCH_3)_3 \xrightarrow[70\,^\circ C]{\text{DMSO}} N(CH_2COO)_3B + 3\ CH_3OH$$

The formation of **III** from NTA and $B(OCH_3)_3$ was followed by ^1H-NMR spectroscopy in (D_6)DMSO. At room temperature, an intermediate is formed within a few minutes. Its ^1H-NMR spectrum shows singulets at 4.28, 4.04 and 3.35 ppm relative to TMS with intensities in the ratio of 4:2:3. The signals may be explained in terms of

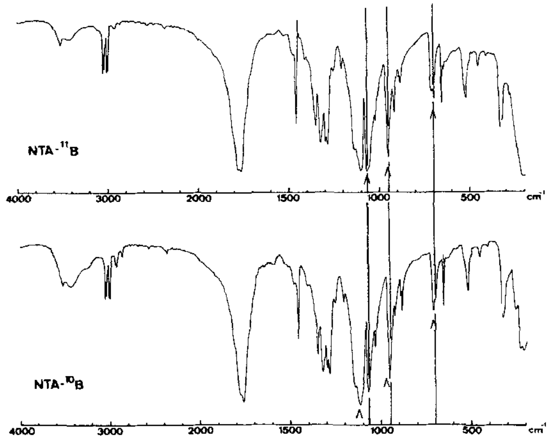

Fig. 1. *IR spectra of a KBr disc of* a) *NTA-*^{11}B (**III**), b) *NTA-*^{10}B (**III**). The main differences between the two spectra are marked by lines and arrows.

compound **IV**, they correspond to the methylene protons in the rings, the methylene protons of the acetate side chain and the methyl protons of the methoxy group. NTA-B (**III**) is produced only at elevated temperatures (approximately 2 hours at 100 °C). If the mixture is cooled to room temperature and kept there for about 1 day, the solution contains a mixture of **IV** and **III** in a ratio of 3:1 indicating the expected temperature-dependent equilibrium between CH_3OH, **III** and **IV**. Prolonged heating of the sample leads to crystallization of **III**.

Compound III was synthesized both with ^{11}B in natural abundance (80%) and with ^{10}B enriched to 95%. The IR spectra of both isotopic species *(Fig. 1)* show a very intense carbonyl absorption at 1765–1785 cm^{-1} and a nicely resolved multiplet of 6 sharp C–H stretching modes between 2985 and 3055 cm^{-1}. The main difference in the spectra of the two samples is in the intensities of the bands at 1070 and 1120 cm^{-1}. This difference may be interpreted as a consequence of an isotopic shift of the asymmetric B–O stretching vibrations from ≈ 1070 cm^{-1} in NTA-^{11}B to ≈ 1120 cm^{-1} in NTA-^{10}B. In tetrahedral $^{11}B(OH)_4^-$ these vibrations are at 945 cm^{-1}, in trigonal planar $^{11}B(OH)_3$ at 1450 cm^{-1} [8]; NTA-B is thus somewhere in between. Analogous, but smaller differences are observed at ≈ 700 and ≈ 950 cm^{-1}.

Discussion of the Crystal and Molecular Structure of NTA-B (III). – The structure consists of discrete molecules showing approximate non-crystallographic C_{3v}-symmetry *(Fig. 2)*. The five-membered chelate rings of **III** are planar to within the positional standard deviations whereas in boratrane (**II**) they are significantly puckered [7]. The central N–B bond is 1.62 Å, significantly shorter than in **II**, where it is 1.68 Å *(Table 1)*. Both B–N bonds are long, however, if compared to the B–N bonds of 1.57 Å in the cubic modification of boron nitride [9].

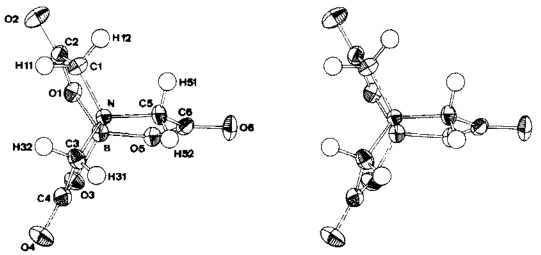

Fig. 2. *Stereoscopic drawing of NTA-B* (III) (drawn with program ORTEP [21]; 50% probability, 293 K)

The observed B–O bonds of length 1.44 Å are shorter than those in $B(OAc)_4^-$ or $B(OCH_3)_4^-$ (1.47 Å [10]) but longer than those in planar $B(OCH_3)_3$ (1.37 Å [11]). The O–B–O angles are larger, the O–B–N angles smaller than 109.5°. The coordination geometry at boron is thus C_{3v}-distorted tetrahedral; the structure can be regarded as a point on the reaction pathway delineating nucleophilic attack of nitrogen on electrophilic boron in the BO_3-fragment [1] [12]. The C–C, C–O and C=O bond lengths of the carboxyl groups agree with those of an average γ-lactone [13]. The C–C=O and

Table 1. *Bond Distances and Bond Angles of NTA-B* (**III**) *Uncorrected* (columns 1, 2) *and Corrected for Effects of Rigid Body Motions* (columns 3,4). Observed distances and angles for boratrane (**II**, column 5)[a]).

	NTA-B				Boratrane
T	110K	293 K	110 K	293 K	
N–B	1.622 (3) Å	1.620 (3) Å	1.623 Å	1.624 Å	1.677 (6) Å
B–O	1.449 (2)	1.446 (6)	1.450	1.450	1.439 (10)
O–C	1.339 (0)	1.336 (2)	1.340	1.339	1.423 (3)
C–C	1.517 (8)	1.510 (11)	1.519	1.514	1.519 (6)
C–N	1.502 (3)	1.499 (5)	1.503	1.503	1.487 (6)
C=O	1.207 (1)	1.198 (5)	1.208	1.201	–
N–B–O	105.4 (2)°	105.2 (4)°	105.4°	105.2°	103.0 (6)°
B–O–C	112.6 (1)	112.8 (2)	112.6	112.8	108.2 (1)
O–C–C	111.8 (2)	111.6 (3)	111.8	111.6	105.1 (6)
C–C–N	106.3 (2)	106.5 (2)	106.3	106.5	103.7 (2)
C–N–B	103.9 (1)	103.8 (2)	103.9	103.8	103.0 (3)
O–B–O	113.2 (3)	113.4 (8)	113.2	113.4	115.5 (2)
C–N–C	114.4 (3)	114.5 (2)	114.5	114.5	115.1 (6)
O–C=O	123.3 (3)	123.2 (5)	123.3	123.1	–
C–C=O	124.9 (2)	125.2 (3)	124.9	125.2	–

[a]) The values are averaged with respect to the non-crystallographic threefold axis. Numbers in brackets are the population e.s.d.'s in terms of the least significant digit, except for B–N where the e.s.d. obtained from the uncertainty in coordinates is given.

O=C–O angles are much more balanced (124.9°, 123.3°) than those in the average γ-lactone (128.6(8)°, 121.7(9)°) [13] [14].

The packing in the *bc*-plane is dominated by short O...C distances between carbonyl groups *(Fig. 3)* (O2...C4 3.000 Å, O2...C6 3.049 Å, O4...C2 2.943 Å, O4...C6 2.921 Å, O6...C2 2.978 Å, O6...C4 2.957 Å). Each carbonyl O- and carbonyl C-atom is involved in two such contacts. These interactions might be responsible for the insolubility of the compound. The molecules mesh together like cogwheels to achieve a highly efficient packing mode reflected by the high density of 1.804 g cm^{-3}.

The mean square vibrational amplitudes of the B-, C-, N- and O-atoms are in the range 0.0142 to 0.0551 Å^2 at 293 K and 0.0049 to 0.0183 Å^2 at 110 K. These rather low

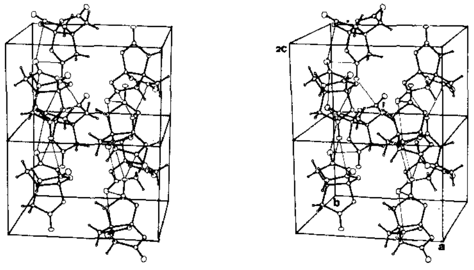

Fig. 3. *Stereoscopic drawing of molecular packing of NTA-B* (**III**). Two unit cells are shown along c. Nonbonded contacts between carbonyl O- and C-atoms are indicated with thin lines (drawn with program ORTEP [21]).

values may be another consequence of tight molecular packing. The *Hirshfeld* test for rigid bonds [15] shows that in good approximation the molecule behaves like a rigid body. The test was applied separately to bonded as well as intramolecular nonbonded distances. Average absolute differences ΔU along internuclear vectors are $< |\Delta U(\text{bonded})| > = 0.0014(8)$ Å^2 and $< |\Delta U(\text{nonbonded})| > = 0.0016(11)$ Å^2 at 293 K, $< |\Delta U(\text{bonded})| > = 0.0009(5)$ Å^2 and $< |\Delta U(\text{nonbonded})| > = 0.0008(6)$ Å^2 at 110 K. A rigid body model [16] explains the observed vibrational parameters with R-values of 0.104 and 0.119 at 239 K and 110 K, respectively. Root mean square deviations between observed and calculated U_{ij}'s are 0.0017 and 0.0008 Å^2, *i.e.* similar to the values obtained in the *Hirshfeld* test. Bond lengths and bond angles uncorrected and corrected for effects of rigid body motion are collected in the first four columns of *Table 1*. The distances are systematically longer in the structure at low temperature even though individual differences are statistically insignificant. Corrections are small, but corrected distances agree better with each other than do the uncorrected ones. The bond angles do not seem to be affected by vibrational corrections.

Experimental. – *Preparation.* A solution of 1 g nitrilotriacetic acid in 50 ml of hot DMSO, dried over molecular sieves, was cooled to 35°. Trimethoxyborate (1g) was added, the solution was mixed thoroughly and kept over night at 70°–80°. Clear, well-developed, diamond shaped crystals as long as one millimeter formed. These were isolated, washed with acetone and ether and dried *in vacuo*. Yield 0.68 g (65%). Anal. calc. for $C_6H_6B_3NO_6$ (198.93): C 36.23, H 3.04, N 7.04; found: C 36.33, H 3.10, N 6.89.

Properties. The compound does not melt below 350°, but decomposes on prolonged heating at this temperature. At 310°/0.001 Torr slow sublimation was observed.

The compound is insoluble in all of the common aprotic solvents, except for DMSO, where some sort of metastable solution could be obtained during the formation of the compound. The ^{1}H-NMR spectrum of the metastable solution in (D$_6$)DMSO shows a singulet at 4.56 ppm relative to TMS. In protic solvents, such as H_2O and alcohols, the compound solvolyses to nitrilotriacetic acid and boron-containing compounds of unknown composition.

Crystal Structure Determination. Crystal data and details of the X-ray diffraction experiments are given in *Table 2*. Preliminary investigations at r.t. were made with a precession camera, using CuK_α radiation. Lattice parameters and diffraction intensities were measured at 293 and 110 K on the same crystal with an automated *CAD4* diffractometer using graphite monochromatized MoK_α radiation ($\lambda = 0.71069$ Å) and an ENRAF-

Table 2. *Crystal Data and Parameters Pertaining to Data Collection*

Temperature	293 K	110 K
Crystal dimensions	0.2 × 0.2 × 0.3 mm^3	
Space group	Pn2$_1$a	
a	10.505 (2) Å	10.468 (2) Å
b	10.269 (1) Å	10.193 (7) Å
c	6.807 (1) Å	6.754 (3) Å
Volume	734.4 Å^3	720.6 Å^3
Z	4	4
Θ_{max}	27°	33°
Total scan width at $\Theta = 0°$	0.9°	1.2°
Reflections measured	844	1421
$F > \sigma(F)$	818	1296
No. of variables	151	150
Final R	0.024	0.037
Final R_w	0.028	0.043
Isotropic extinction g [17]	1.47 (2) × 10^{-3}	–

Table 3. *Positional and Equivalent Isotropic Temperature Factor Parameters of All Atoms at 293 K* (Temperature factor parameters as U^{a}) 100; e.s.d.'s in terms of least significant digit)

Atom	x	y	z	U or U_{eq}[a])
B	0.3000 (2)	0.2765 (3)	0.4592 (4)	1.94 Å^2
N	0.1676 (2)	0.1958 (3)	0.4616 (3)	1.71
O(1)	0.3911 (1)	0.1953 (3)	0.5591 (3)	2.37
O(2)	0.4023 (2)	0.0000 (0)	0.7027 (3)	3.95
O(3)	0.2720 (2)	0.3976 (3)	0.5591 (3)	2.55
O(4)	0.1085 (2)	0.4983 (3)	0.7010 (3)	4.03
O(5)	0.3292 (1)	0.2942 (3)	0.2525 (2)	2.20
O(6)	0.2485 (2)	0.2464 (3)	0.0411 (2)	3.47
C(1)	0.2018 (2)	0.0712 (3)	0.5649 (4)	2.50
C(2)	0.3419 (2)	0.0823 (4)	0.6191 (4)	2.39
C(3)	0.0788 (2)	0.2824 (3)	0.5728 (4)	2.50
C(4)	0.1512 (2)	0.4055 (4)	0.6182 (4)	2.52
C(5)	0.1350 (2)	0.1798 (3)	0.2486 (3)	2.17
C(6)	0.2416 (2)	0.2410 (4)	0.1345 (3)	2.18
H(11)	0.1504 (32)	0.0611 (34)	0.6911 (50)	4.19 (87)
H(12)	0.1933 (28)	0.0024 (33)	0.4843 (44)	2.85 (74)
H(31)	0.0050 (42)	0.3032 (41)	0.4985 (55)	5.01 (87)
H(32)	0.0564 (32)	0.2407 (35)	0.6996 (49)	4.82 (96)
H(51)	0.1272 (28)	0.0939 (34)	0.2141 (44)	3.30 (76)
H(52)	0.0575 (28)	0.2258 (32)	0.2148 (43)	3.18 (73)

[a]) $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

Table 4. *Positional and Equivalent Isotropic Temperature Factor Parameters of All Atoms at 110 K* (Temperature factor parameters as U^{a}) 100; e.s.d.'s in terms of least significant digit)

Atom	x	y	z	U or U_{eq}[a])
B	0.3012 (2)	0.2799 (2)	0.4579 (3)	0.71 Å^2
N	0.1675 (1)	0.1995 (2)	0.4616 (2)	0.69
O(1)	0.3924 (1)	0.1973 (2)	0.5598 (2)	0.87
O(2)	0.4016 (1)	0.0000 (0)	0.7063 (2)	1.38
O(3)	0.2752 (1)	0.4025 (2)	0.5594 (2)	0.92
O(4)	0.1114 (1)	0.5058 (2)	0.7063 (2)	1.47
O(5)	0.3307 (1)	0.2978 (2)	0.2499 (2)	0.80
O(6)	0.2489 (1)	0.2492 (2)	0.0471 (2)	1.26
C(1)	0.2006 (2)	0.0733 (2)	0.5654 (3)	0.95
C(2)	0.3417 (2)	0.0834 (2)	0.6196 (3)	0.94
C(3)	0.0788 (2)	0.2875 (2)	0.5745 (3)	0.94
C(4)	0.1540 (2)	0.4113 (2)	0.6210 (3)	0.95
C(5)	0.1339 (2)	0.1843 (2)	0.2466 (2)	0.83
C(6)	0.2423 (2)	0.2447 (3)	0.1311 (2)	0.85
H(11)	0.1842 (37)	0.0010 (39)	0.4830 (58)	1.27 (75)
H(12)	0.1466 (34)	0.0646 (39)	0.6800 (59)	1.21 (71)
H(31)	0.0503 (43)	0.2441 (48)	0.6996 (67)	2.63 (96)
H(32)	0.0093 (50)	0.3057 (48)	0.4966 (74)	2.79 (99)
H(51)	0.0605 (43)	0.2380 (50)	0.2165 (69)	2.79 (98)
H(52)	0.1272 (36)	0.0933 (41)	0.2109 (60)	1.57 (79)

[a]) $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

Nonius liquid N_2 cooling device. Integrated intensities were obtained from ω-scans in bisecting diffraction geometry. The first and last sixth of the total scan width were used to determine the intensity of background radiation. Scan time per reflection was such that $\sigma(I)/I \leq 0.01$ or scan time $\leqslant$ 180 s. Periodic controls of intensity standard reflections ($\bar{1}31$, 013 at 293 K; $\bar{1}\,\bar{3}\,\bar{1}$, $\bar{2}\bar{2}0$ at 110 K) showed no changes of the crystal during the measurements. After corrections for background, *Lorentz* and polarization factors, the structure was solved using direct methods (MULTAN 77 [18]). All positional parameters, anisotropic vibrational parameters for B, C, N and O and isotropic vibrational parameters for H were refined by least-squares methods using *Seiler-Dunitz* weighting [19] $w = \sigma^{-2}(F)\exp(10 \sin^2\Theta/\lambda^2)$. The ratio of shift/e.s.d. in the final cycle was less than 0.1, the maximum value applying to H-parameters (C–H bond lengths are in the range 0.91 to 1.00(5) Å). A final difference *Fourier*-synthesis showed significant feature related to chemical bonds and lone pair electrons. A more accurate determination of the electron density function for this molecule is underway. Most computations were performed with the XRAY72 package of programs [20]. Refined positional parameters and equivalent isotropic temperature factors for all atoms are given in *Table 3* (293K) and *4* (110K). Anisotropic vibrational parameters, rigid body motion parameters in a Cartesian crystal frame, corresponding transformation matrices and structure factor listings may be obtained on request from *H.B.B.*

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