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1,1,4,4-Tetramethyl-1,4-diazonia-2,5-diboratacyclohexane. Crystal Structure and a New Preparation

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A new preparation of 1,1,4,4-tetramethyl-1,4-diazonia-2,5-diboratacyclohexane from the reaction of eutectic sodium–potassium alloy with trimethylamine–bromoborane in trimethylamine solvent is described and previously unpublished mass spectra are tabulated. The crystal structure was determined by X-ray diffraction. The crystal is orthorhombic, space group *Pbca*, with $Z = 4$; $a = 10.227$ (1), $b = 7.946$ (1), $c = 12.044$ (1) Å; and $d_o = 0.958$, $d_c = 0.963$ g/cm^3. Intensity data for 2238 reflections (1119 independent) were obtained on an automated single-crystal diffractometer with Mo Kα radiation. The structure was solved by symbolic addition. Full-matrix least-squares refinement based on intensity (including isotropic secondary extinction) reduced $R(I)$ to 0.027, and $R_w(I)$ to 0.039. The six-membered ring has the chair conformation with C–B = 1.609 (2), B–N = 1.615 (2), and N–C = 1.511 (2) Å. The N–C bond lengths to equatorial and axial methyl carbon atoms are 1.482 (2) and 1.484 (2) Å, respectively.

Introduction

The compound 1,1,4,4-tetramethyl-1,4-diazonia-2,5-diboratacyclohexane, I, was first prepared by Miller and coworkers.[2a] Recently we also prepared this material, but by a different route.[2b] A preparation was being sought for the bis(trimethylamine) adduct of diborane(4), II, a substance differing in composition from I by only two hydrogen atoms. Continued study of the reaction first reported by Miller[3] yielded a material with properties somewhat different from those ascribed to II. These properties were contradictory when interpreted as being those of a diborane(4) adduct and an X-ray structure was sought. Successful interpretation of the X-ray analysis[4] unambiguously revealed the product to be I. This paper presents the determined molecular structure along with the alternative preparation and the previously unreported mass spectrum.

Experimental Section

A. Preparation and Characterization. General Data. Standard vacuum-line and inert-atmosphere techniques were used. Melting points were obtained using sealed capillaries filled with dry nitrogen gas. Nuclear magnetic resonance spectra (^{1}H and ^{11}B) were observed on a Varian 4311 high-resolution spectrometer. Mass spectra were obtained from an AEI MS-9 spectrometer[5] operated at 25-V ionizing potential.

Preparation. In a typical reaction, eutectic sodium–potassium alloy (3 ml, *ca.* 80 mequiv) and trimethylamine–bromoborane[6] (2.58 g, 17.0 mmol) were mechanically stirred along with trimethylamine (40 ml, dried and purified over P_2O_5) at 0° in an evacuated 100-ml round-bottom flask. After 48 hr the mixture, containing dark blue, finely divided solid, was cooled to −80°, and the trimethylamine was removed through U traps cooled to −80 and to −196°. The solid residue was warmed to room temperature and a pumping vacuum was then applied through the same traps for 1 hr. The solid material contained in the trap cooled to −80° was extracted at room temperature with 20 ml of dry, alkene-free hexane. The hexane was slowly removed from this solution *in vacuo* and well-formed crystals appeared (mp 89.5–90.5°). The yields thus obtained were in the range 15–20%, accompanied by complete conversion of starting material.

B. Crystal Structure Determination. General Data. A transparent well-formed single crystal of size 0.8 × 0.16 × 0.44 mm was sealed in a Lindemann-glass capillary. An orthorhombic system was demonstrated by Weissenberg and precession photographs. Systematic absences ($0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; $hk0$, $h = 2n + 1$) unambiguously implied the space group *Pbca* (No. 61). The cell constants, $a = 10.227$ (1), $b = 7.946$ (1), and $c = 12.044$ (1) Å, were obtained from a least-squares fit of 28 2θ values (averages of $\pm 2\theta$) collected on a Picker automated single-crystal diffractometer[5] with Mo Kα radiation. The density calculated on the basis of four molecules per unit cell is 0.963 g/cm^3, which compares well with the experimental value of 0.958 g/cm^3, measured by flotation using H_2O and methanol.

Collection and Reduction of Intensity Data. Three-dimensional intensity data (2238 reflections, 1119 independent, with $(\sin\theta)/\lambda < 0.65$) were collected at room temperature using Mo Kα (λ 0.71069 Å) radiation. The diffracted beam, filtered through 0.001-in. Nb foil, was detected by a scintillation counter equipped with a pulse height analyzer. The scan technique was θ–2θ at a scan rate of 1° in 2θ/min using a takeoff angle of 3.5°. Two stationary-counter, stationary-crystal background counts of 20 sec were taken at each end of the scan; the scan ranges were −0.5° from Kα_1 to +0.55° from Kα_2. The spindle axis was along a. The peak full width at half-maximum was about 0.4° in 2θ. During the data collection, the intensities of five standard reflections were remeasured periodically after each group of about 100 reflections. These standard intensities showed no significant variation with time.

The intensities were corrected for coincidence loss, $I_{\text{cor}} = I_{\text{measd}}/(1 - \tau I_{\text{measd}})$, where τ was determined from a set of reflections with intensities measured at 14- and 4-mA X-ray tube currents. The standard deviations of the intensities, I's, were obtained by the relation

$$\sigma(I) = [C + (t_s/2t_b)^2(B_1 + B_2) + (kI)^2]^{1/2}$$

where C is the total integrated peak count measured in time t_s, B_1 and B_2 are the background counts, each measured in time t_b, $I = C - (t_s/2t_b)(B_1 + B_2)$, and k (0.003) is a factor based on the analysis of standard reflections to account for instrumental instability. The two equivalent sets of intensity data were averaged, *i.e.*

$$\bar{R}_w{}' = \left[\sum_{i=1}^{1119}\sum_{j=1}^{2} w_{ij}(I_{ij} - \bar{I}_i)^2 / \sum_{ij} w_{ij}I_{ij}{}^2\right]^{1/2}$$

with $w_{ij} = 1/\sigma_{ij}{}^2(I)$, and were converted to structure factors after applying Lorentz and polarization correction in the usual manner.

Determination and Refinement of the Structure. The structure was solved by symbolic addition[7] using crystallographic programs (SIGMA2, PHASE) from the X-ray 70 system.[8] The carbon,[9] nitrogen,[9] boron,[10] and hydrogen[11] atom scattering factors were taken from the literature.

Two refinements of the structure were carried out (program CRYLSQ[8]), once minimizing the function $\sum w(|F_o| - |F_c|)^2$, where F_c is the calculated structure factor, F_o is the observed structure factor, and w is the error-theory weight, $1/\sigma(F_o)^2$, and, second, minimizing $\sum w(I_o - I_c)^2$, where I_c is the calculated intensity, I_o is the observed intensity, and w is $1/\sigma(I)^2$. The serial R indices are defined by

$$R_w(F) = \Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2$$

$$R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$$

$$R_w(I) = \Sigma w(I_o - I_c)^2/\Sigma wI_o{}^2$$

$$R(I) = \Sigma|I_o - I_c|/\Sigma I_o$$

The signs of the 90 reflections with $|E|$ greater than 1.49 were determined using origin-defining reflections (171), (178), and (3,10,1), with $|E| = 3.29$, 2.86, and 3.23, respectively. An E map computed with these 90 $|E|$ values and the determined signs clearly showed peaks

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Table I. Postional and Thermal Parameters ($\times 10^2$)[a]

Atom	x/a	y/b	z/c
N	0.00833 (7)	0.15817 (8)	0.07787 (6)
B	0.03575 (13)	0.16684 (15)	−0.05406 (9)
C3	−0.08360 (12)	0.01308 (13)	0.09972 (10)
C1	0.13095 (14)	0.13692 (18)	0.14198 (14)
C2	−0.05358 (18)	0.31744 (18)	0.11502 (14)
H1	−0.0639 (8)	0.2102 (7)	−0.0918 (6)
H2	0.1171 (7)	0.2652 (8)	−0.0670 (6)
H31	−0.1012 (8)	0.0099 (9)	0.1868 (7)
H32	−0.1700 (8)	0.0533 (10)	0.0636 (7)
H11	0.1115 (10)	0.1330 (13)	0.2222 (8)
H12	0.1763 (9)	0.0270 (10)	0.1196 (8)
H13	0.1881 (9)	0.2404 (11)	0.1228 (9)
H21	0.0122 (9)	0.4113 (10)	0.0991 (9)
H22	−0.1377 (10)	0.3317 (12)	0.0691 (9)
H23	−0.0712 (10)	0.3111 (12)	0.1948 (8)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N	6.51 (5)	4.00 (4)	5.84 (5)	0.03 (5)	−0.36 (4)	0.00 (4)
B	6.50 (8)	4.02 (6)	5.42 (7)	−0.39 (7)	0.21 (7)	0.58 (6)
C3	5.85 (7)	5.16 (6)	5.93 (8)	−0.31 (6)	0.46 (7)	0.48 (7)
C1	7.71 (10)	6.59 (10)	7.01 (9)	−0.74 (8)	−1.73 (8)	−0.29 (9)
C2	10.43 (13)	4.57 (7)	7.28 (10)	0.79 (8)	0.22 (10)	−1.06 (8)
H1	7.16 (54)	4.49 (52)	4.75 (51)	1.32 (48)	−1.82 (49)	0.00 (41)
H2	8.86 (67)	3.49 (42)	5.61 (59)	−0.13 (46)	2.11 (54)	0.52 (41)
H31	10.62 (76)	5.41 (61)	4.39 (54)	−0.78 (53)	2.19 (61)	−0.43 (57)
H32	2.51 (52)	7.29 (64)	9.72 (82)	−0.48 (47)	−1.15 (51)	−0.14 (56)
H11	9.11 (78)	12.29 (96)	4.68 (66)	−1.73 (73)	−3.04 (64)	0.26 (74)
H12	6.59 (70)	7.09 (68)	9.99 (94)	1.29 (57)	−2.08 (60)	−1.56 (70)
H13	9.87 (77)	6.93 (62)	12.54 (108)	−6.16 (59)	−5.06 (69)	1.55 (65)
H21	11.73 (104)	3.24 (52)	12.88 (101)	−2.86 (57)	1.19 (80)	−3.51 (59)
H22	10.66 (86)	7.31 (70)	8.44 (81)	5.50 (79)	−3.36 (64)	−2.88 (63)
H23	12.61 (86)	8.11 (76)	4.41 (62)	2.45 (62)	1.77 (66)	−1.60 (66)

[a] Estimated errors are in parentheses. Anisotropic temperature factors are expressed as $\exp[-2\pi^2 \Sigma_j \Sigma_i U_{ij} h_i h_j a_i^* a_j^*]$.

corresponding to all nonhydrogen atoms, and the structure factors calculated from the positions of these peaks gave $R(F) = 0.49$. An F_o Fourier synthesis with signs taken from these F_c values followed by two cycles of full-matrix, unit weight with 2σ cutoff, least-squares refinement on F, without hydrogen atoms and starting with individual isotropic temperature factors, gave $R(F) = 0.219$. The boron atom, which could not be distinguished from the ring carbon atom on the E and F_o maps, was put into the F_c calculations as a carbon atom. After least-squares refinement it was recognized by its bond length and abnormally high thermal parameters. Two more cycles of least-squares calculations with error-theory weights reduced $R_w(F)$ to 0.181. A difference Fourier synthesis was calculated; the ten highest peaks, electron densities ranging from 0.41 to 0.65 e/Å^3, were assigned as hydrogen atoms. Additional refinement with anisotropic temperature factors for nonhydrogen atoms and isotropic temperature factors for hydrogen atoms reduced $R_w(F)$ to 0.031.

At this point, the data were corrected for absorption.[12] The calculated linear absorption coefficient of the crystal is 0.58 cm^{-1} (Mo Kα); the transmission factors ranged from 0.97 to 0.99.

Another four cycles of refinement with anisotropic temperature factors for all atoms, including the isotropic secondary-extinction coefficient g which leveled to $g = 8.79 \times 10^{-4}$, then reduced $R_w(F)$ to 0.019. The extinction correction was of the form

$$F^{\text{cor}} = F_c(1 + 2gF_c^2\delta)^{-1/4}$$

where $\delta = (e^2/mc^2V)^2 (\lambda^3/\sin 2\theta)(p_2/p_1)\bar{T}$, and $\bar{T}$ is the mean path length through the crystal for each reflection, $p_n = (1 + \cos^{2n} 2\theta)$, and V is the unit cell volume.[13]

The last refinement was based on intensity (I), including negative net intensities. Three reflections were omitted: one, (112), had a large $w(\Delta F)$ value, $\Delta F \approx 10\sigma$, throughout the F refinement; the other two, (224) and (400), had large negative net intensities, $I \approx -10\sigma(I)$. The remaining 1116 reflections led to the final values $R_w(I) = 0.039$, $R(I) = 0.027$, and $g = 8.77 \times 10^{-4}$.

The final average and maximum parameter shifts were 0.044σ and 0.162σ. The difference Fourier calculated at the end of the I refinement had a peak height of 0.16 e/Å^3 between the boron and carbon atoms and a peak of 0.09 e/Å^3 between the boron and nitrogen atoms. The standard deviation of the difference density is estimated to be 0.03 e/Å^3, by using the formula $\sigma = (1/V)(\sum m\Delta F^2)^{1/2}$, where m is the multiplicity. The molecular structure (and numbering scheme) and the packing arrangement of the molecules in the unit cell are shown in Figures 1 and 2, prepared with Johnson's ORTEP program.[14] The final parameters, bond lengths, bond angles, and structure factors are listed in Tables I–III. (See paragraph at end of paper regarding the material listed in Table III.)

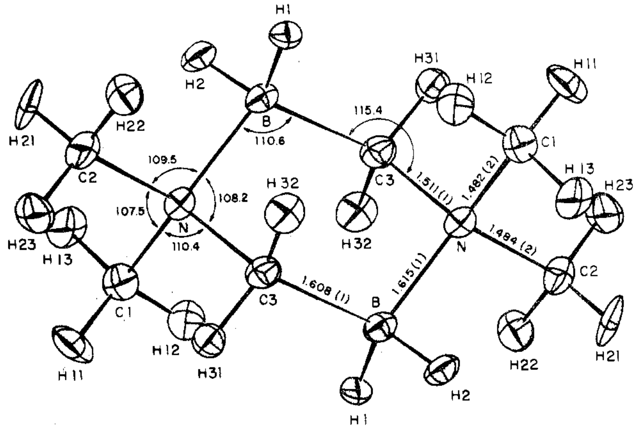


Figure 1. Molecular structure with the numbering scheme of the atoms and some bond lengths and angles.

Results and Discussion

A. Preparation and Characterization. The yields were somewhat less than those reported by Miller[2a] and they were not improved by the use of other reaction solvents (*e.g.*, hexane, benzene, ether, etc.). Major ir absorptions in CCl_4, benzene, or acetone compared well with previously reported values.[1] The ^{11}B nmr spectrum, a 1:2:1 triplet (+8.4 ± 0.5 ppm from $(C_2H_5)_2O{\cdot}BF_3$, $J = 93 \pm 5$ Hz), was also in agreement (+9.2 ppm, calculated from literature value of 27.4 ppm referenced to $B(OCH_3)_3$, $J = 98$ Hz) as was the ^1H spectrum. The ^1H spectrum B–H coupling constant, previously unreported, was 93 ± 15 Hz, consistent with ^{11}B results. The 25-V electron

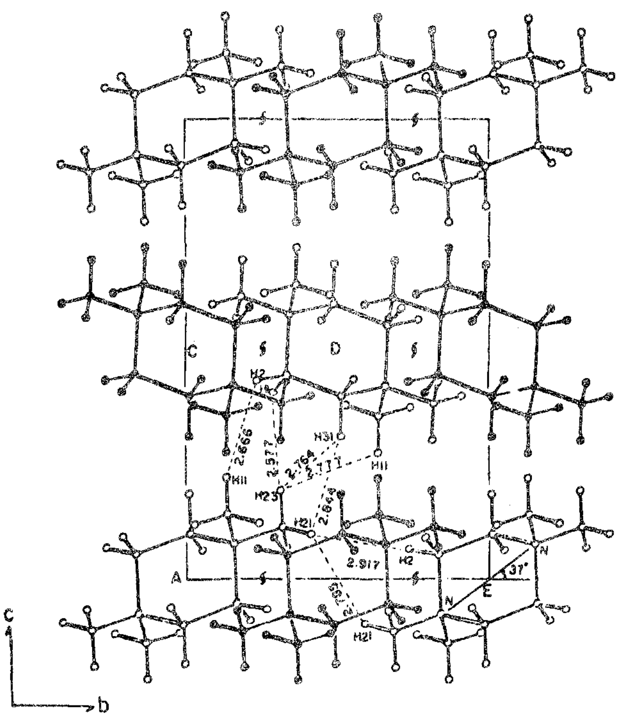


Figure 2. Packing diagram (projection onto the *bc* plane). Dashed lines indicate close intermolecular contacts.

Table II. Bond Distances (A) and Angles (deg)

	Distances		
N-B	1.615 (1)	C3-H31	1.064 (8)
N-C3	1.511 (1)	C3-H32	1.035 (8)
N-C1	1.482 (2)	C1-H11	0.987 (10)
N-C2	1.484 (2)	C1-H12	1.025 (9)
B-H1	1.168 (8)	C1-H13	1.034 (9)
B-H2	1.152 (7)	C2-H21	1.022 (9)
		C2-H22	1.029 (10)
		C2-H23	0.979 (10)
	Angles		
B-N-C3	108.2 (1)	B-C3-H31	111.5 (4)
B-N-C1	111.8 (1)	B-C3-H32	113.0 (4)
B-N-C2	109.5 (1)	H31-C3-H32	106.1 (7)
C3-N-C1	110.4 (1)	N-C1-H11	110.1 (6)
C3-N-C2	109.4 (1)	N-C1-H12	110.0 (5)
C1-N-C2	107.5 (1)	N-C1-H13	105.7 (5)
N-B-H1	104.1 (4)	H11-C1-H12	108.8 (8)
N-B-H2	106.7 (4)	H11-C1-H13	111.0 (8)
N-B-C3	110.6 (1)	H12-C1-H13	111.3 (7)
C3-B-H1	113.3 (3)	N-C2-H21	106.5 (5)
C3-B-H2	109.7 (4)	N-C2-H22	106.8 (6)
H1-B-H2	112.2 (5)	N-C2-H23	109.3 (6)
N-C3-H31	107.1 (4)	H21-C2-H22	111.7 (8)
N-C3-H32	102.8 (4)	H21-C2-H23	110.0 (9)
N-C3-B	115.4 (1)	H22-C2-H23	112.3 (9)

Table IV. Electron-Beam Mass Spectrum

Mass	Rel intens	Mass	Rel intens	Mass	Rel intens
142	6.43	98	1.01	58	100.00
141	72.44	97	8.19	57	3.38
140	38.95	96	7.58	56	50.08
139	36.65	95	3.81	55	13.96
138	16.49	94	1.10	54	11.70
137	2.05			53	3.60
		92	1.05	52	1.07
128	11.44				
127	9.31	90	3.44	46	3.29
126	3.03			45	1.98
125	4.73	86	11.18	44	20.26
124	2.58	85	98.93	43	2.63
123	1.71	84	61.24	42	7.72
		83	22.49	41	18.27
119	2.12	82	5.12	40	28.97
		81	1.70		
117	2.05	80	3.15	38	1.05
116	2.52	79	1.56		
115	36.39			36	2.18
114	11.20	72	17.82		
113	16.46	71	10.87	32	72.38
112	4.32	70	99.71		
		69	39.92	30	6.12
109	1.19	68	10.87	29	12.98
108	5.60	67	2.68		
107	2.11			18	13.79
106	19.39	63	1.54	17	2.31
105	4.42			16	4.99
		61	3.41	15	3.06
99	8.92	60	2.00	14	6.05
		59	10.89		

Table V. High-Resolution Mass Spectrum[a] of I

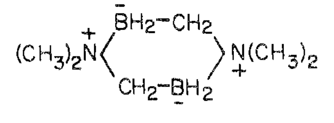
	Mass values	
Species	Calcd	Found
$^{11}B_2{}^{12}C_5{}^{13}C^{14}N_2H_{19}{}^+$	142.1767	142.1786 ± 0.0005[b]
$^{11}B_2{}^{12}C_6{}^{14}N_2H_{19}{}^+$	141.1733	141.1733[c]
$^{11}B^{10}B^{12}C_6{}^{14}N_2H_{19}{}^+$	140.1770	140.1772 ± 0.0005
$^{11}B_2{}^{12}C_5{}^{13}C^{14}N_2H_{17}{}^+$	140.1611	140.1621 ± 0.0005[b]
$^{10}B_2{}^{12}C_6{}^{14}N_2H_{19}{}^+$	139.1806	139.1801 ± 0.0005
$^{11}B_2{}^{12}C_6{}^{14}N_2H_{17}{}^+$	139.1577	139.1575 ± 0.0005
$^{11}B^{10}B^{12}C_6{}^{14}N_2H_{17}{}^+$	138.1613	138.1608 ± 0.0005

[a] Accelerating voltage 70 V; resolution 50 ppm (5% overlap). [b] Broad, weak, and ragged peaks difficult to calibrate. [c] This peak was the first peak matched and was set at the theoretical value; no improvement was discernible on changing the ratioing resistance values and the final mass was left at the theoretical value.

beam mass spectrum is presented in Table IV. Monoisotopic reduction[15] confirmed the product to be a two-boron molecule while a high-resolution study of the parent envelope, given in Table V, proved the presence of six carbon, two nitrogen, and at least nineteen hydrogen atoms.

There was ample precedent for postulating a coupling of boron atoms since this method is commonly used to produce tetrakis(dialkylamino)- and tetrakis(alkoxy)-substituted derivatives of B_2H_4 (see, *e.g.*, ref 16). However the presence of active hydrogen on carbon in trimethylamine–bromoborane is seen to lead to a different result. If a diborane(4) adduct was produced in the present reaction, it must have been in small amounts. The two major products appear to result from a predictable side reaction[17,18] to the Wurtz–Fittig coupling. The initial reaction is presumed to generate $(CH_3)_3NBH_2^-K^+$ for which evidence of existence has been presented.[3] As a base this can abstract a weakly acidic methyl hydrogen atom[19] from $(CH_3)_3N{\cdot}BH_2Br$ producing trimethylamine–borane and the carbanion $^-{:}CH_2N(CH_3)_2BH_2Br$, III. (The recovery of monodeuterated trimethylamine from the DCl–D_2O-treated products of the reaction between butyllithium tetramethylethylenediamine and trimethylamine–borane[2b] suggests the potential presence of III, but a free-radical mechanism cannot be ruled out.) A subsequent "head-to-tail" S_N2 dimerization of III with loss of two bromide ions would yield I; or bromide ions may be lost first resulting in zwitterions which could then dimerize.

B. Crystal Structure Determination. The molecules of I, centrosymmetric in the chair conformation, are well separated in the crystal with closest contact distance of 2.577 Å between H1 and H23. The close packing can be understood if the molecules, although centrosymmetric and nondipolar, are rather strongly multipolar, perhaps in the way that is indicated by the formal changes in the Lewis electronic formula



It is helpful to view I as sterically similar to a diatomic

Table VI. Short Intramolecular Nonbonded Distances (Å)[a]

H1–N	2.212 (7)	N–N	3.141
H2–N	2.237 (7)	B–B	3.043
H31–N	2.089 (8)	C3–C3	2.956
H32–N	2.012 (8)	H1–H32	2.497 (11)
H11–N	2.043 (10)	H1–H12	2.233 (11)
H12–N	2.071 (9)	H1–H22	2.293 (13)
H13–N	2.024 (8)	H2–H13	2.407 (13)
H21–N	2.028 (8)	H2–H21	2.550 (12)
H22–N	2.036 (10)	H31–H11	2.422 (13)
H23–N	2.030 (10)	H31–H23	2.415 (12)
H31–B	2.231 (8)	H32–H12	2.298 (13)
H32–B	2.227 (8)	H32–H22	2.238 (12)
H1–C3	2.331 (7)	H11–H23	2.368 (14)
H2–C3	2.272 (6)	H13–H21	2.272 (12)

[a] Estimated errors are in parentheses.

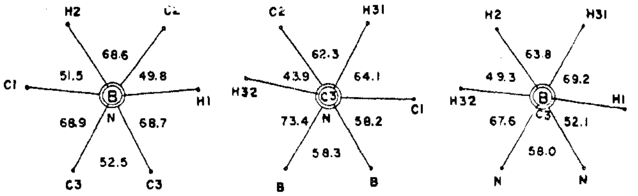


Figure 3. Torsional angles of the ring conformation.

molecule: two overlapping spheres with centers located at the two nitrogen atoms. It then becomes apparent that the packing is like a typical packing of diatomic molecules, *e.g.*, Cl_2.[20] The N–N axis of I (Figure 2) lies almost in the *bc* plane, making an angle with the *b* axis of 37°. In solid chlorine the Cl–Cl axis lies exactly in the plane and the angle is 55°. The difference may be due to the steric differences of the molecule from the diatomic molecule and to the presumed multipolar interaction.

This molecule and the neopentane molecule have similar methyl group conformations. The intermolecular and intramolecular H···H contact distances are given in Tables VI and VII. The shortest intramolecular distances, H12···H1, 2.233 Å, and H12···H32, 2.298 Å, are slightly smaller than the sum of the usual van der Waals radii, 2.4 Å. The rotational barrier, taking into consideration the adjacent B–N and C–N bonds, would be expected to be equal to or greater than that of neopentane,[21] 5.2 kcal/mol.

The torsional angles of the ring are shown in Figure 3; in cyclohexane the torsional angle is 54.5°. It will be seen that the distortion from the tetrahedral ideal (60°) is less for I, on balance, than for cyclohexane.

The X-ray determination of hydrogen positions is subject to various errors. The range of C–H bond length values gradually improved from the stage of refinement on isotropic hydrogen temperature factors (0.921–1.090 Å, about 10σ) to the refinement based on intensity and including the correction for isotropic secondary extinction (0.979–1.034 Å, about 5σ). The average for methyl C–H bonds is 1.013 Å, and the average for ring C–H bonds is 1.049 Å. The bond angles N–B–H1, N–B–H2, N–C1–H13, H31–C3–H32, and N–C2–H21, all significantly smaller than the tetrahedral ideal (109.5°), appear to correlate with intermolecular repulsion (Figure 2). The small C1–N–C2, N–C3–H32, and N–C2–H22 bond angles are probably the results of intramolecular repulsion.

The methyl C–N bond lengths (1.482 (2) and 1.484 (2) Å) are virtually identical and are comparable to the 1.477 (5) Å reported for ethylenediamine–bisborane[22] and the 1.479 (5) Å average for four-coordinated N given in Sutton's tables.[23] The ring C–N bond length (1.511 (1) Å) is longer, recalling those in $BF_3{\cdot}N(CH_3)_3$,[24] 1.50 Å, and $(CH_3)_4N^+$ in a polyhedral clathrate hydrate,[25] 1.499 Å. The B–N bond length (1.615 (1) Å) is also a bit greater than has been reported for B–N in comparable cases: 1.59 (3) Å in $BF_3N(CH_3)_3$,[24] 1.59

Table VII. Intermolecular Contacts[a]

Ref molecule	Molecule	Distance, Å
A	B	
H1	H13	2.594
H2	H22	2.623
H2	H32	2.611
H13	H12	2.668
A	C	
H11	H31	3.285
H12	H31	3.262
A	D	
H11	H2	2.666
H11	H31	3.191
H21	H11	3.055
H21	H31	2.844
H23	H1	2.577
H23	H31	2.746
H23	H11	2.777

[a] Molecules A, B, C, and D are indicated in Figure 2.

(3) Å in *N*-hexamethylcyclotriborazane,[26] and 1.600 (7) Å in ethylenediamine–bisborane.[22] The B–C bond length is comparable to that in $(CH_3)_2B_2H_4$ reported by Hedberg, *et al.*,[27] 1.61 Å.

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Supplementary Material Available. Table III, a listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number AIC402393.

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Copper(II) Complexes of Amino Alcohols. Molecular Structures of Chloro(2-diethylaminoethanolato)copper(II) and Bromo(2-dibutylaminoethanolato)copper(II)

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The crystal and molecular structures of chloro(2-diethylaminoethanolato)copper(II) and bromo(2-dibutylaminoethanolato)copper(II) have been determined from three-dimensional X-ray data collected by counter methods. The chloro complex crystallizes in the space group $P4_12_12$ (or $P4_32_12$) of the tetragonal system with 16 monomeric formula units in a cell of dimensions $a = 11.334$ (3) and $c = 27.791$ (8) Å. The observed and calculated densities are 1.59 and 1.602 g cm^{-3}, respectively. The bromo complex crystallizes in the space group $P2_12_12_1$ of the orthorhombic system with four formula units in a cell of dimensions $a = 21.16$ (2), $b = 15.15$ (2), and $c = 8.40$ (1) Å. The observed and calculated densities for this complex are 1.55 and 1.5 (1) g cm^{-3}, respectively. Least-squares refinement of the chloro and bromo structures has led to final values of the conventional R factor (on F) of 0.051 and 0.236, respectively. The chloro structure is tetranuclear with oxygen atoms bridging the adjacent copper(II) atoms. The bromo structure consists of oxygen-bridged, dimeric units. The analyses of these structures, therefore, support the classification by Uhlig and Staiger of complexes of the type Cu(OR)X (ROH = an amino alcohol) into three distinct structural classes and suggest that members of group 1 are dimeric while those in group 3 are tetrameric.

Introduction

The syntheses of a wide variety of compounds of the types CuCl(OR) and CuBr(OR), where ROH is an amino alcohol, have been reported by Hein and coworkers.[1,2] These workers postulated that the complexes should be formulated as dimers in which the amino alcohol acts as a chelating bridge, and this was recently confirmed by the report[3] of the structure of bromo(2-diethylaminoethanolato)copper(II). The geometry around the copper centers in this complex is roughly tetrahedral, with a Cu–O–Cu bridging angle, ϕ, of approximately 104.5°. More recently, Bertrand[4] has observed a similar dimeric unit in the structure of acetato(2-dibutylaminoethanolato)copper(II), with $\phi = 109°$. Uhlig and Staiger, however, have reported the room-temperature magnetic and spectroscopic properties of a number of compounds of this type[5,6] and deduced that they may be divided into three distinct groups according to their magnetic moments: (1) compounds which have greatly reduced moments at 20° (less than 1 BM); they assumed these to be oxygen-bridged dimers; (2) compounds which have normal magnetic moments; in this case the copper atom probably has a coordination number greater than 4; (3) compounds with only slightly reduced moments at 20° (about 1.5 BM); it was suggested[6] that these complexes might be tetrameric. It is noteworthy that Uhlig and Staiger placed bromo(2-diethylaminoethanolato)copper(II) in the first group, since the subsequent structure determination by Pajunen and Lehtonen lends credence to their scheme. The corresponding chloro complex ($\mu = 1.68$ BM) was assigned[5] to the third group, and Lehtonen later reported that the space group and cell constants are, in fact, different from those of the bromo complex; this strongly suggested that the two structures might be entirely different and that the chloro complex might not be an oxygen-bridged dimer.

In order to investigate further the structural properties of this class of complexes and especially to test the general classification of Uhlig and Staiger (*vide supra*), we have examined the crystal structures of two complexes of this type. One of the complexes chosen was chloro(2-diethylaminoethanolato)copper(II), which is in group 3, while the other was bromo(2-dibutylaminoethanolato)copper(II) which has been assigned[6] to group 1. The results of these structural investigations are reported here.

Experimental Section

(a) Chloro(2-diethylaminoethanolato)copper(II). The dark green chloro(2-diethylaminoethanolato)copper(II) was prepared by treating 1.34 g of copper(II) chloride (0.01 mol) in 150 ml of absolute ethanol with 2.34 g of 2-diethylaminoethanol (0.02 mol) in 50 ml of absolute ethanol. The reaction mixture was allowed to stand at room temperature. After several days dark green rhombic crystals formed. *Anal.* Calcd for Cu($C_6H_{14}NO$)Cl: C, 33.49; H, 6.55; N, 6.51; Cl, 16.47; mol wt 860.70. Found: C, 33.53; H, 6.36; N, 6.54; Cl, 16.41.

On the basis of Weissenberg and precession photographs the crystals were assigned to the tetragonal system. The observed systematic absences of $h00$ for h odd and $00l$ for l not equal to $4n$ are consistent with the space groups $P4_32_12$ and $P4_12_12$; the latter assignment was chosen. The cell constants, obtained by the least-squares procedure of Busing and Levy,[7] are $a = 11.334$ (3) and $c = 27.791$ (8) Å. These are in agreement with the cell constants previously reported by Lehtonen.[8] A density of 1.602 g cm^{-3} calculated for 16 formula units in the cell agrees well with the value of 1.59 g cm^{-3} which Lehtonen obtained by flotation in carbon tetrachloride and toluene.[8]

Diffraction data were collected at 17° using a Picker four-circle automatic diffractometer. The wavelength was assumed to be λ(Mo Kα_1) 0.7093 Å. Two rhombic crystals with faces (011), $(0\bar{1}1)$, $(\bar{1}01)$, (101), $(0\bar{1}\bar{1})$, $(01\bar{1})$, $(10\bar{1})$, and $(\bar{1}0\bar{1})$ were chosen for data collection. The face–face distance was 0.04 cm for all opposite pairs of faces in both crystals. The crystals were mounted on glass fibers roughly normal to the (011) planes, and in this orientation intensity data were