Isolation and Characterization of a New Polycyclic System from the Reaction of (Dimethylamino)diethylborane with 2,2'-Biimidazole

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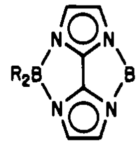
In a study of the interaction between (dimethylamino)diethylborane and 2,2'-biimidazole, the formation of discrete compounds such as **1** or **2** (R = C_2H_5) was expected. However, originally only a mixture of apparently macromolecular species of variable composition was obtained, on the basis of mass spectroscopic studies. During attempts to separate and purify this initial product, minor amounts of a crystalline material were isolated. The EI mass spectrum of the latter exhibited a very weak ion cluster at *m*/*z* 498 as the highest observed peak and two extremely strong clusters at *m*/*z* 469 (base peak) and 297, respectively. A high-resolution spectrum of the *m*/*z* 469 peak indicated a species of the composition $C_{22}H_{33}B_4N_8O$, suggesting partial hydrolysis of the original product. Indeed, when the reaction and crystallization were performed without stringent exclusion of moisture, the crystalline material became the major product and analyzed for a composition of $C_{24}H_{38}B_4N_8O$. Considering the starting materials and in consonance with the NMR data, two structures, **3** and **4** (R = C_2H_5), appeared to be most likely for the compound.



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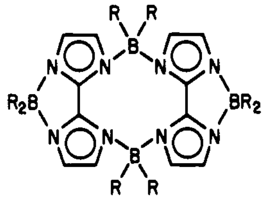

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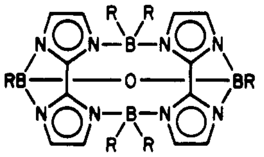

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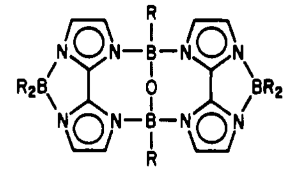

4

The correct structure, **4**, was established by a single-crystal X-ray analysis, and ORTEP plots of **4** are shown in Figure 1 (top view) and Figure 2 (side view). Due to the four ethyl groups in the molecule, the latter has the lowest point symmetry (C_1). The four boron atoms assume approximate tetrahedral symmetry. The two biimidazole planes form a dihedral angle of 106.7 (1)°. The B(2) and B(4) atoms are only slightly out of these two planes (~0.1 Å). The B–O–B angle is exceptionally large with 151 (3)°, almost certainly due to the steric strain imposed by the two biimidazole moieties and the B(2) and B(4) atoms. The average B–N length of 1.605 (11) Å and B–C distance of 1.607 (15) Å are comparable to those in similar compounds; the average B–O length of 1.422 (6) Å is in the normal range.

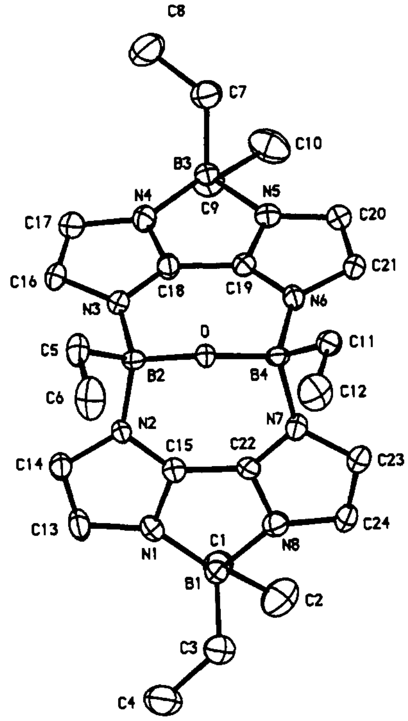

Figure 1. ORTEP plot of **4** (top view; 50% thermal ellipsoids, hydrogen atoms omitted for clarity).

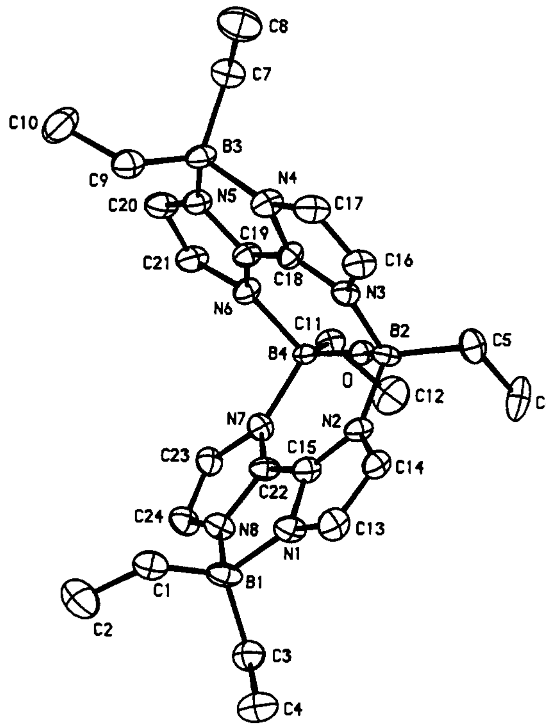

Figure 2. ORTEP plot of **4** (side view; 50% thermal ellipsoids, hydrogen atoms omitted for clarity).

The structural features of **4** indicate that **1** is unlikely to be formed in the reaction between (dimethylamino)diethylborane and 2,2'-biimidazole, since the latter structure involving four fused five-membered heterocycles would involve too much strain. On the other hand, a species such as **2** could be existent. However, the preparative observations seem to suggest the preferential formation of linear and/or macrocyclic oligomers in the initial process, and **4** ultimately results from their partial hydrolysis.

The formation of **4** is unusual inasmuch as it suggests the interaction with water results in a cleavage of B–C bonds in

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Table I. Positional Parameters for Non-Hydrogen Atoms in **4**[a]

atom	x	y	z	B (Å^2)[b]
O	0.9494 (6)	0.2613 (2)	0.6329 (2)	1.58 (8)
N(1)	0.6219 (8)	0.1198 (2)	0.6986 (3)	2.1 (1)
N(2)	0.7866 (7)	0.2003 (2)	0.7294 (3)	1.7 (1)
N(3)	0.7335 (8)	0.3079 (2)	0.7285 (3)	1.8 (1)
N(4)	0.5214 (8)	0.3779 (2)	0.6972 (3)	2.1 (1)
N(5)	0.5223 (8)	0.3776 (2)	0.5594 (3)	1.9 (1)
N(6)	0.7350 (7)	0.3082 (2)	0.5326 (3)	1.8 (1)
N(7)	0.7903 (7)	0.2001 (2)	0.5333 (3)	1.8 (1)
N(8)	0.6212 (8)	0.1206 (2)	0.5603 (3)	2.1 (1)
C(1)	0.291 (1)	0.0880 (3)	0.6271 (4)	2.6 (1)
C(2)	0.180 (1)	0.0600 (4)	0.5591 (5)	4.0 (2)
C(3)	0.617 (1)	0.0184 (3)	0.6275 (4)	2.5 (1)
C(4)	0.544 (1)	−0.0216 (3)	0.6917 (5)	3.5 (2)
C(5)	1.077 (1)	0.2688 (3)	0.7747 (4)	2.4 (1)
C(6)	1.249 (1)	0.2280 (4)	0.7616 (4)	3.3 (2)
C(7)	0.503 (1)	0.4793 (3)	0.6249 (4)	2.6 (1)
C(8)	0.429 (1)	0.5179 (3)	0.6896 (5)	3.9 (2)
C(9)	0.186 (1)	0.4065 (3)	0.6254 (4)	2.6 (1)
C(10)	0.078 (1)	0.4357 (3)	0.5567 (5)	4.0 (2)
C(11)	1.0765 (9)	0.2688 (3)	0.4934 (4)	1.9 (1)
C(12)	1.250 (1)	0.2281 (4)	0.5101 (4)	3.4 (2)
C(13)	0.631 (1)	0.1244 (3)	0.7793 (4)	2.4 (1)
C(14)	0.7346 (9)	0.1729 (3)	0.7980 (3)	2.0 (1)
C(15)	0.7155 (9)	0.1673 (3)	0.6719 (3)	1.9 (1)
C(16)	0.663 (1)	0.3315 (3)	0.7975 (3)	2.2 (1)
C(17)	0.533 (1)	0.3741 (3)	0.7784 (4)	2.5 (1)
C(18)	0.6438 (9)	0.3371 (3)	0.6720 (3)	1.8 (1)
C(19)	0.6428 (9)	0.3367 (3)	0.5873 (3)	1.8 (1)
C(20)	0.538 (1)	0.3743 (3)	0.4792 (4)	2.3 (1)
C(21)	0.669 (1)	0.3323 (3)	0.4633 (4)	2.2 (1)
C(22)	0.7156 (9)	0.1672 (3)	0.5888 (3)	1.8 (1)
C(23)	0.7409 (9)	0.1720 (3)	0.4641 (3)	1.9 (1)
C(24)	0.638 (1)	0.1239 (3)	0.4806 (4)	2.2 (1)
B(1)	0.527 (1)	0.0820 (3)	0.6285 (4)	2.3 (2)
B(2)	0.897 (1)	0.2596 (3)	0.7133 (4)	1.7 (1)
B(3)	0.419 (1)	0.4137 (3)	0.6267 (4)	2.0 (1)
B(4)	0.897 (1)	0.2590 (3)	0.5521 (4)	1.5 (1)

[a] In this and subsequent tables, esd's are given in parentheses. [b] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Table II. Selected Bond Distances (Å) in **4**

O–B(2)	1.426 (4)	N(7)–B(4)	1.581 (5)
O–B(4)	1.417 (4)	N(8)–C(22)	1.346 (4)
N(1)–C(13)	1.383 (4)	N(8)–C(24)	1.371 (4)
N(1)–C(15)	1.360 (4)	N(8)–B(1)	1.614 (5)
N(1)–B(1)	1.605 (5)	C(1)–C(2)	1.514 (6)
N(2)–C(14)	1.387 (4)	C(1)–B(1)	1.611 (6)
N(2)–C(15)	1.327 (4)	C(3)–C(4)	1.530 (5)
N(2)–B(2)	1.601 (5)	C(3)–B(1)	1.603 (6)
N(3)–C(16)	1.396 (4)	C(5)–C(6)	1.522 (5)
N(3)–C(18)	1.316 (4)	C(5)–B(2)	1.602 (6)
N(3)–B(2)	1.608 (5)	C(7)–C(8)	1.518 (5)
N(4)–C(17)	1.390 (5)	C(7)–B(3)	1.630 (6)
N(4)–C(18)	1.340 (4)	C(9)–C(10)	1.527 (6)
N(4)–B(3)	1.608 (5)	C(9)–B(3)	1.586 (6)
N(5)–C(19)	1.334 (4)	C(11)–C(12)	1.532 (5)
N(5)–C(20)	1.379 (4)	C(11)–B(4)	1.612 (5)
N(5)–B(3)	1.603 (5)	C(13)–C(14)	1.364 (5)
N(6)–C(19)	1.317 (4)	C(15)–C(22)	1.420 (5)
N(6)–C(21)	1.375 (4)	C(16)–C(17)	1.358 (5)
N(6)–B(4)	1.617 (5)	C(18)–C(19)	1.447 (5)
N(7)–C(22)	1.330 (4)	C(20)–C(21)	1.353 (5)
N(7)–C(23)	1.386 (4)	C(23)–C(24)	1.355 (5)

Table III. Selected Bond Angles (deg) for **4**

B(2)–O–B(4)	151.0 (3)	C(2)–C(1)–B(1)	116.6 (3)
C(13)–N(1)–C(15)	105.2 (3)	C(4)–C(3)–B(1)	115.2 (3)
C(13)–N(1)–B(1)	142.5 (3)	C(6)–C(5)–B(2)	113.0 (3)
C(15)–N(1)–B(1)	112.1 (3)	C(8)–C(7)–B(3)	114.8 (3)
C(14)–N(2)–C(15)	105.2 (3)	C(10)–C(9)–B(3)	114.9 (3)
C(14)–N(2)–B(2)	132.3 (3)	C(12)–C(11)–B(4)	112.7 (3)
C(15)–N(2)–B(2)	122.4 (3)	N(1)–C(13)–C(14)	107.8 (3)
C(16)–N(3)–C(18)	104.6 (3)	N(2)–C(14)–C(13)	109.0 (3)
C(16)–N(3)–B(2)	131.8 (3)	N(1)–C(15)–N(2)	112.8 (3)
C(18)–N(3)–B(2)	123.5 (3)	N(1)–C(15)–C(22)	110.3 (3)
C(17)–N(4)–C(18)	104.8 (3)	N(2)–C(15)–C(22)	136.9 (4)
C(17)–N(4)–B(3)	142.4 (3)	N(3)–C(16)–C(17)	108.6 (3)
C(18)–N(4)–B(3)	112.8 (3)	N(4)–C(17)–C(16)	107.8 (3)
C(19)–N(5)–C(20)	104.6 (3)	N(3)–C(18)–N(4)	114.2 (3)
C(19)–N(5)–B(3)	113.3 (3)	N(3)–C(18)–C(19)	136.0 (3)
C(20)–N(5)–B(3)	142.1 (3)	N(4)–C(18)–C(19)	109.9 (3)
C(19)–N(6)–C(21)	104.8 (3)	N(5)–C(19)–N(6)	113.9 (3)
C(19)–N(6)–B(4)	123.0 (3)	N(5)–C(19)–C(18)	109.8 (3)
C(21)–N(6)–B(4)	132.1 (3)	N(6)–C(19)–C(18)	136.3 (3)
C(22)–N(7)–C(23)	104.3 (3)	N(5)–C(20)–C(21)	108.0 (3)
C(22)–N(7)–B(4)	122.5 (3)	N(6)–C(21)–C(20)	108.8 (3)
C(23)–N(7)–B(4)	133.1 (3)	N(7)–C(22)–N(8)	113.2 (3)
C(22)–N(8)–C(24)	105.3 (3)	N(7)–C(22)–C(15)	136.6 (4)
C(22)–N(8)–B(1)	112.4 (3)	N(8)–C(22)–C(15)	110.5 (3)
C(24)–N(8)–B(1)	142.4 (3)	N(7)–C(23)–C(24)	109.1 (3)
N(8)–C(24)–C(23)	108.1 (3)	N(4)–B(3)–N(5)	94.3 (3)
N(1)–B(1)–N(8)	94.4 (3)	N(4)–B(3)–C(7)	110.8 (3)
N(1)–B(1)–C(1)	110.0 (3)	N(4)–B(3)–C(9)	111.5 (3)
N(1)–B(1)–C(3)	111.7 (3)	N(5)–B(3)–C(7)	108.6 (3)
N(8)–B(1)–C(1)	110.7 (3)	N(5)–B(3)–C(9)	112.9 (3)
N(8)–B(1)–C(3)	110.5 (3)	C(7)–B(3)–C(9)	116.5 (3)
C(1)–B(1)–C(3)	117.2 (3)	O–B(4)–N(6)	108.9 (3)
O–B(2)–N(2)	108.6 (3)	O–B(4)–N(7)	109.4 (3)
O–B(2)–N(3)	109.0 (3)	O–B(4)–C(11)	115.4 (3)
O–B(2)–C(5)	115.0 (3)	N(6)–B(4)–N(7)	105.4 (3)
N(2)–B(2)–N(3)	104.2 (3)	N(6)–B(4)–C(11)	107.0 (3)
N(2)–B(2)–C(5)	110.8 (3)	N(7)–B(4)–C(11)	110.3 (3)
N(3)–B(2)–C(5)	108.6 (3)		

preference to a hydrolysis of B–N bonds. This feature may be interpreted by assuming that the reacting boron is four-coordinate and, therefore, may exhibit an abnormal reactivity as compared to that of three-coordinate boron–nitrogen compounds.

Experimental Section

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Melting points (uncorrected) were determined on a Mel-Temp block.

NMR spectra were recorded for solutions in $CDCl_3$ on a Varian VXR-400 (^{11}B) or GEMINI-200 (^1H, ^{13}C) instrument. Chemical shift data are given in ppm with positive values indicating a downfield shift from the reference (internal $(CH_3)_4Si$ for ^1H and ^{13}C NMR, external $(C_2H_5)_2O{\cdot}BF_3$ for ^{11}B NMR); s = singlet, d = doublet, t = triplet, q = quartet, m = unresolved multiplet, and an asterisk denotes a broad signal. Coupling constants J are given in hertz. ^{13}C NMR spectra were recorded in the proton-decoupled mode. Electron impact (EI) mass spectral data (relative intensities in parentheses) were obtained on a VG ZAB-2F spectrometer under standard operating conditions; field desorption (FD) mass spectra were obtained on a Finnigan MAT-250 instrument (courtesy of Professor A. Meller, University of Göttingen, Germany).

Preparation of 4. A mixture of 1.5 g (11 mmol) of 2,2′-biimidazole[1] and 15 mL of (dimethylamino)diethylborane[2] was stirred at room temperature for 30 min and then heated to reflux. Strong dimethylamine evolution was observed, and heating was continued for 1 h to give a clear homogeneous solution. Excess aminoborane was distilled off under atmospheric pressure, and remaining traces were removed at 80 °C under vacuum. The material solidified on cooling to room temperature, and 30 mL of pentane was added. The stirred mixture was kept at 0 °C for 24 h, and 1.4 g (50%) of colorless crystals was collected. These were recrystallized from hexane to give an analytical sample of **4**, mp 154–155 °C. Anal. Calcd for $C_{24}H_{38}B_4N_8O$ (M_r = 497.87): C, 57.90; H, 7.69; B, 8.69; N, 22.51; O, 3.21. Found: C, 57.36; H, 7.60; B, 8.52; N, 22.54.

NMR data: $\delta(^1H)$ 7.11 (2 H, d, J = 1.4), 7.00 (2 H, d, J = 1.4), 0.9–0.8 (5 H, m), 0.6–0.5 (5 H, m), 0.43 (2 H, q, J = 7.3), 0.31 (3 H, t, J = 7.2); $\delta(^{11}B)$ 6.2 (1 B, s, $h_{1/2}$ = 500 Hz), 3.6 (1 B, s, $h_{1/2}$ = 250 Hz); $\delta(^{13}C)$ 138.6, 123.1, 121.8, 14.7*, 13.2*, 8.5, 8.24, 8.20. The EI mass spectrum showed two ion clusters of high abundance at m/z 469 and 297; 12 eV spectrum m/z 471 (3), 470 (26), 469 (100), 468 (94), 467 (34), 466 (6), 298 (4), 297 (24), 296 (17), 295 (4). The FD mass spectrum showed only an ion cluster at m/z 469 (calculated for $[M - C_2H_5]^+ = C_{22}H_{33}B_4N_8O$ m/z 470 (25), 469 (100), 468 (85), 467 (30), 466 (5); observed m/z 470 (24), 469 (100), 468 (90), 467 (34), 466 (6)).

Crystal data for 4, empirical formula $C_{24}H_{38}B_4N_8O$ with a formula weight of 497.9, were obtained on a material precipitated from hexane. The data were collected at 223 K using Cu Kα radiation, λ = 1.5418 Å, on an Enraf-Nonius CAD4 diffractometer equipped with a rotary anode tube. The colorless compound crystallizes in space group $P2_1/n$ with a = 6.784 (2) Å, b = 23.287 (5) Å, c = 17.080 (6) Å, β = 91.53 (2)°, V

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(1) Kaiser, S. W. Ph.D. Dissertation, University of Michigan, 1975.
(2) Alam, F.; Niedenzu, K. *Inorg. Synth.* **1983**, *22*, 209–211.

= 2697.2 Å^3, d_{calcd} = 1.226 cm^{-3}, Z = 4; μ = 5.665 cm^{-1}. Crystallographic computations were carried out on a DEC MicroVAX 3100 computer system using SDP (Structure Determination Package). The structure was solved by a combination of the direct method MULTAN 11/82 and difference Fourier syntheses. Full-matrix least-squares refinements were employed. One hydrogen atom in each methyl group was located from the difference Fourier maps; the remaining hydrogen atoms were calculated at 0.95 Å from the carbon atoms and were assigned thermal parameters B(H) = B(C) + 1. The hydrogen atoms were not refined in the least-squares refinements but were included in the structure factor calculations. R_F = 0.093, R_{wF} = 0.128 (334 variables refined) for 2884 reflections [$I \geq 3.0\sigma(I)$] of 4259 independent reflections collected over the range $1° \leq \theta \leq 67.5°$. Positional parameters are given in Table I, and selected bond distances and angles are presented in Tables II and III, respectively.

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Supplementary Material Available: Tables of crystal data, positional parameters, and isotropic thermal parameters (7 pages); a listing of calculated and observed structure factor amplitudes (29 pages). Ordering information is given on any current masthead page.