

## 2,6-Dibromo-4,4,8,8-tetraethylpyrazabole

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(Received 10 February 1976; accepted 11 February 1977)

**Abstract.**  $(\text{BrC}_3\text{N}_2\text{H}_2)_2\text{B}_2(\text{C}_2\text{H}_5)_4$ , monoclinic,  $P2_1/a$ ,  $a = 15.623$  (14),  $b = 12.420$  (10),  $c = 9.927$  (6) Å,  $\beta = 92.48$  (3)°,  $Z = 4$ ,  $D_c = 1.476$ ,  $D_m = 1.49$  g cm<sup>-3</sup> (floatation),  $\mu(\text{Mo } K\alpha) = 45.1$  cm<sup>-1</sup>. Each B atom is coordinated to two ethyl groups and a N of each pyrazolyl group. The two pyrazolyl rings are coplanar within experimental limits.

**Introduction.** Crystals of 2,6-dibromo-4,4,8,8-tetraethylpyrazabole were received from S. Trofimenko in a form suitable for crystal-structure analysis. Preliminary Weissenberg and precession photographs established the space group  $P2_1/a$  ( $h0l$ ,  $h = 2n$ ;  $0k0$ ,  $k = 2n$ ). A cube-like crystal of maximum dimension 0.4 mm was mounted on a Picker automated diffractometer for data collection. Cell dimensions were refined during the alignment procedure. Data were collected with a  $\theta$ - $2\theta$

scan of range  $2.4^\circ$  ( $1^\circ \text{ min}^{-1}$ ) ( $\sin \theta_{\text{max}} = 0.46175$ ) and Mo  $K\alpha$  radiation ( $\lambda = 0.71069$  Å). Background measurements were made at  $1.2^\circ$  on either side of the Bragg position for 20 s each. The intensities of three standard reflections were measured after every 40 reflections. The net intensities of these standards declined 19% over the data-collection period and the data were rescaled by multiplying each reflection (reflection number =  $N$ ) by  $(1 + N \times \text{SCL})$ , where  $\text{SCL} = 0.000113$ . The value of SCL was determined by a linear least-squares fit of the declining intensities of the standards to the original intensities as a function of  $N$ . The rescaled standards were then found to be constant to within 5%. Of the 1228 measured reflections, 444 were classed as observed ( $|F_o|/\sigma|F_o| > 1.5$ , where  $F_o$  is the observed structure amplitude and  $\sigma F_o$  its corresponding estimated standard deviation) after subtraction of background and correction for Lorentz

Table 1. Positional parameters ( $\times 10^3$ , for Br  $\times 10^4$ ) for 2,6-dibromo-4,4,8,8-tetraethylpyrazabole

The estimated standard deviations are given in parentheses in units of the last significant figure of the coordinate.

	<i>x</i>	<i>y</i>	<i>z</i>
Br(1)	4347 (4)	1825 (5)	-6467 (5)
Br(2)	928 (4)	638 (5)	2252 (5)
N(1)	342 (2)	136 (3)	-278 (3)
N(2)	266 (2)	158 (3)	-350 (3)
N(3)	188 (2)	125 (3)	-140 (3)
N(4)	260 (2)	103 (3)	-68 (3)
C(1)	411 (3)	142 (4)	-364 (4)
C(2)	365 (3)	165 (4)	-493 (5)
C(3)	281 (3)	178 (4)	-481 (4)
C(4)	111 (3)	118 (4)	-59 (5)
C(5)	159 (3)	89 (4)	64 (4)
C(6)	242 (3)	74 (4)	66 (4)
C(7)	166 (3)	316 (4)	-256 (4)
C(8)	161 (4)	385 (4)	-379 (5)
C(9)	106 (3)	144 (5)	-378 (4)
C(10)	112 (4)	-6 (4)	-390 (4)
C(11)	421 (3)	177 (5)	-36 (4)
C(12)	384 (4)	291 (5)	-30 (5)
C(13)	386 (3)	-37 (4)	-126 (4)
C(14)	329 (4)	-115 (4)	-207 (5)
B(1)	168 (4)	177 (5)	-294 (5)
B(2)	364 (4)	100 (5)	-112 (6)

Table 2. Bond distances (Å) and angles (°)

Br(1)-C(2)	1.92 (6)	C(1)-C(2)-C(3)	113 (4)
Br(2)-C(5)	1.97 (5)	C(2)-C(3)-N(2)	106 (4)
C(5)-C(6)	1.31 (6)	C(3)-N(2)-N(1)	111 (3)
C(5)-C(4)	1.45 (6)	N(2)-N(1)-C(1)	109 (3)
C(2)-C(1)	1.47 (7)	N(1)-C(1)-C(2)	100 (4)
C(2)-C(3)	1.33 (7)	C(4)-C(5)-C(6)	122 (4)
C(4)-N(3)	1.48 (6)	C(5)-C(5)-N(4)	101 (4)
C(6)-N(4)	1.42 (5)	C(6)-N(4)-N(3)	110 (3)
C(3)-N(2)	1.35 (5)	N(4)-N(3)-C(4)	113 (3)
C(1)-N(1)	1.42 (6)	N(3)-C(4)-C(5)	94 (4)
N(1)-N(2)	1.38 (5)	N(2)-B(1)-N(3)	97 (3)
N(3)-N(4)	1.34 (5)	N(2)-B(1)-C(7)	103 (4)
N(1)-B(2)	1.72 (6)	N(2)-B(1)-C(9)	109 (4)
N(2)-B(1)	1.67 (7)	N(3)-B(1)-C(7)	101 (3)
N(4)-B(2)	1.69 (7)	N(3)-B(1)-C(9)	114 (4)
N(3)-B(1)	1.67 (6)	C(7)-B(1)-C(9)	128 (5)
B(1)-C(7)	1.76 (9)	N(1)-B(2)-N(4)	95 (3)
B(1)-C(9)	1.47 (8)	N(1)-B(2)-C(11)	114 (4)
B(2)-C(11)	1.50 (8)	N(1)-B(2)-C(13)	102 (3)
B(2)-C(13)	1.74 (9)	N(4)-B(2)-C(11)	114 (4)
C(7)-C(8)	1.49 (7)	N(4)-B(2)-C(13)	104 (4)
C(9)-C(10)	1.50 (8)	C(11)-B(2)-C(13)	123 (5)
C(11)-C(12)	1.52 (9)	N(1)-N(2)-B(1)	129 (3)
C(13)-C(14)	1.53 (7)	N(4)-N(3)-B(1)	133 (4)
		N(2)-N(1)-B(2)	133 (3)
		N(3)-N(4)-B(2)	132 (3)

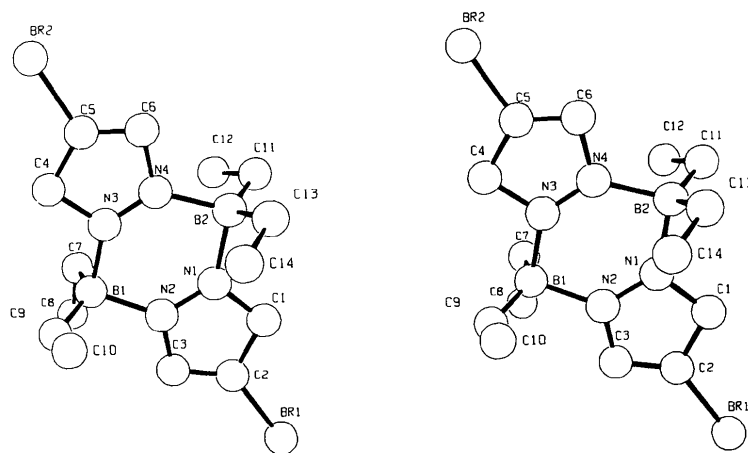


Fig. 1. A projection of 2,6-dibromo-4,4,8,8-tetraethylpyrazabole onto the  $xz$  plane.

and polarization factors. Absorption corrections were not made.

The structure was solved with conventional heavy-atom techniques. Full-matrix refinement of the positional parameters and isotropic temperature factors for all 22 non-hydrogen atoms gave  $R = 17.2\%$ . A difference Fourier map revealed anisotropic motion about the Br atoms and ethyl groups. The temperature factors for these ten atoms were converted to their anisotropic equivalents, and six cycles of refinement of all positional and thermal parameters gave a final  $R$  of 6.2%. On the final cycle the maximum ratio of a parameter to its corresponding standard deviation was 0.05. A final difference map showed no peak higher than  $0.36 \text{ e } \text{\AA}^{-3}$ . Unit weights were used throughout.

Atomic coordinates are given in Table 1, bond lengths and angles in Table 2.\* Fig. 1 shows a projection of the structure onto the  $xz$  plane of the cell.

**Discussion.** Di- and tripyrazolyl borates have been studied crystallographically in various coordinations to heavy atoms (Trofimenko, 1971, 1972). In the tri-pyrazolyl borate structures the pyrazolyl rings have been shown to display various modes of skew about the boron-heavy-metal axis (Avitabile, Ganis & Nemiroff, 1971; Holt, Holt & Watson, 1973; Holt, Holt, Cavalito & Watson, 1976; Churchill, Gold & Maw, 1970; Cotton, Frenz & Shaver, 1973; Davies & Payne, 1974; Holt & Holt, 1973). Dipyrazolyl borate has been studied in a situation where the structure was constrained as a result of hydrogen bonding (Kosky, Ganis

Table 3. Equations of the least-squares planes, and deviations ( $\text{\AA}$ ) of atoms from the planes

Plane 1: Br(1), N(1), N(2), C(1), C(2), C(3)

$$0.169x + 0.121y + 0.193z = 0.169$$

[Br(1) 0.004, N(1) -0.004, N(2) -0.006, C(1) 0.017, C(2) -0.031, C(3) 0.021]

Plane 2: Br(2), N(3), N(4), C(4), C(5), C(6)

$$0.158x + 0.120y + 0.244z = 0.145$$

[Br(2) 0.008, N(3) -0.002, N(4) 0.021, C(4) -0.010, C(5) 0.007, C(6) -0.024]

& Avitabile, 1971). The reported structure was undertaken to provide an observation of a pyrazabole in normal unstrained circumstances.

Coordination about each B atom is distorted tetrahedral [ $97(3)$ – $128(5)^\circ$ ] with each B atom being bonded to a N of each of two pyrazolyl groups and also to two ethyl groups. The B–N distances are longer than those found in other pyrazolyl borate structures [ $1.67(6)$ – $1.72(6) \text{ \AA}$ ] as opposed to the reported range of  $1.50$ – $1.60 \text{ \AA}$ . Each B has one significantly shorter bond ( $1.47$ – $1.50 \text{ \AA}$ ) and one longer bond ( $1.74$ – $1.76 \text{ \AA}$ ) to C. The bromopyrazolyl rings are planar (maximum deviation from plane:  $0.03 \text{ \AA}$ ) (Table 3). The angle between the planes of the two rings is  $177^\circ$ . Calculations show that B(1) and B(2) lie  $0.15$ ,  $0.20 \text{ \AA}$  and  $-0.08$ ,  $0.04 \text{ \AA}$  respectively from the planes of the rings.

Calculations were performed on an XDS Sigma 7 with the XRAY system (1976).

We thank the North Atlantic Treaty Organization for a grant to support this work and S. Trofimenko, E. I. du Pont de Nemours & Co., for the crystalline material.

\* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32491 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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*Acta Cryst.* (1977). **B33**, 1988–1990

### 18(17 → 16)abeo-Yohimbine Acetate Methanol Solvate

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(Received 13 January 1977; accepted 7 February 1977)

**Abstract.**  $C_{23}H_{28}N_2O_4 \cdot CH_4O$ , monoclinic,  $P2_1$ ,  $a = 6.734$  (5),  $b = 14.465$  (9),  $c = 12.114$  (10) Å,  $\beta = 105.2$  (2)°,  $Z = 2$ , final  $R$  value 0.07. The  $C/D$  ring junction is *trans*-quinolizidine; the  $D/E$  ring junction is *trans*. The six-membered rings  $C$  and  $D$  have half-chair and chair conformations, the five-membered ring  $E$  has a half-chair conformation.

**Introduction.** In a study of ring closure by mercury oxidation, demethylcorynantheine led mostly to a new derivative of the 18(17 → 16)abeo-yohimbine type (Djakouré, Jarreau & Goutarel, 1975). Recently, the reaction mechanism has been established (Boivin, Païs & Goutarel, 1976). The present X-ray structure determination was undertaken to ascertain the stereochemistry at C(20).

Data were collected from a crystal  $0.3 \times 0.3 \times 0.6$  mm on a Philips PW 1100 diffractometer with graphite-monochromated Cu  $K\alpha$  radiation ( $\lambda = 1.5418$  Å), for  $\theta$  between 3 and 68°. 2266 independent reflexions were measured, of which 1972 were considered observed with  $I > 3\sigma(I)$ ,  $\sigma(I)$  being derived from counting statistics.

The structure was solved by straightforward application of *MULTAN* (Germain, Main & Woolfson,

Table 1. Final coordinates ( $\times 10^4$ ) and their e.s.d.'s

	$x$	$y$	$z$
N(1)	7051 (5)	506 (0)	2066 (3)
C(2)	5242 (6)	952 (3)	1495 (4)
C(3)	5071 (6)	1965 (3)	1319 (4)
N(4)	2823 (5)	2205 (3)	1022 (3)
C(5)	1661 (8)	1610 (4)	97 (4)
C(6)	1599 (7)	610 (4)	479 (4)
C(7)	3709 (7)	326 (3)	1162 (4)
C(8)	4553 (7)	-565 (3)	1532 (4)
C(9)	3710 (9)	-1458 (4)	1485 (5)
C(10)	4995 (11)	-2189 (4)	1964 (5)
C(11)	7056 (11)	-2034 (4)	2477 (5)
C(12)	7923 (8)	-1154 (4)	2546 (4)
C(13)	6652 (7)	-430 (3)	2086 (4)
C(14)	6248 (6)	2540 (3)	2335 (4)
C(15)	5969 (6)	3544 (3)	2032 (4)
C(16)	6896 (6)	4314 (3)	2901 (4)
C(17)	9196 (7)	4416 (4)	2987 (4)
C(18)	5636 (7)	5178 (3)	2372 (4)
C(19)	3802 (7)	4842 (3)	1401 (4)
C(20)	3675 (6)	3805 (3)	1636 (3)
C(21)	2539 (7)	3189 (3)	681 (4)
O(22)	10114 (5)	5098 (3)	3844 (3)
C(23)	10842 (7)	5876 (4)	3504 (5)
O(24)	10665 (6)	6071 (3)	2531 (4)
C(25)	11889 (11)	6476 (5)	4479 (7)
C(26)	6696 (8)	4035 (3)	4068 (4)
O(27)	7942 (6)	3618 (3)	4765 (3)
O(28)	4874 (5)	4303 (3)	4243 (3)
C(29)	4452 (12)	3957 (6)	5301 (5)
O(30)	11023 (5)	1604 (3)	2838 (4)
C(31)	12360 (11)	1256 (9)	3789 (7)

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