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Structures of Three Pyrazaboles:* 1,3,5,7-Tetramethylpyrazabole, $C_{10}H_{18}B_2N_4$; 4,4-Bis(1-pyrazolyl)pyrazabole, $C_{12}H_{14}B_2N_8$; and 4,4,8,8-Tetrakis(1-pyrazolyl)-pyrazabole, $C_{18}H_{18}B_2N_{12}$

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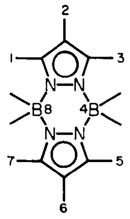
Abstract. 1,3,5,7-Tetramethylpyrazabole (hereafter, ME4PZB): $M_r = 215{\cdot}9$, monoclinic, $P2_1/c$, $a = 7{\cdot}552\,(1)$, $b = 12{\cdot}047\,(4)$, $c = 13{\cdot}814\,(6)$ Å, $\beta = 91{\cdot}27\,(2)°$, $V = 1256{\cdot}5\,(7)$ Å^3, $Z = 4$, $D_x = 1{\cdot}141$ g cm^{-3}, Mo $K\alpha$, graphite monochromator, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}65$ cm^{-1}, $F(000) = 464$, $T = 295$ K, final $R = 0{\cdot}055$ for 199 variables and 1424 reflections. 4,4-Bis(1-pyrazolyl)pyrazabole (hereafter BISPZB): $M_r = 291{\cdot}9$, triclinic, $P\bar{1}$, $a = 8{\cdot}721\,(2)$, $b = 9{\cdot}351\,(2)$, $c = 9{\cdot}407\,(2)$ Å, $\alpha = 93{\cdot}75\,(2)$, $\beta = 100{\cdot}75\,(2)$, $\gamma = 92{\cdot}73\,(2)°$, $V = 750{\cdot}7\,(2)$ Å^3, $Z = 2$, $D_x = 1{\cdot}291$ g cm^{-3}, Mo $K\alpha$, graphite monochromator, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}79$ cm^{-1}, $F(000) = 304$, $T = 295$ K, $R = 0{\cdot}035$ for 255 variables and 1957 reflections. 4,4,8,8-Tetrakis(1-pyrazolyl)pyrazabole (hereafter TETPZB): $M_r = 424{\cdot}0$, monoclinic, $P2_1/n$, $a = 8{\cdot}849\,(2)$, $b = 21{\cdot}765\,(2)$, $c = 11{\cdot}672\,(1)$ Å, $\beta = 109{\cdot}51\,(1)°$, $V = 2118{\cdot}9\,(5)$ Å^3, $Z = 4$, $D_x = 1{\cdot}329$ g cm^{-3}, Mo $K\alpha$, graphite monochromator, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}82$ cm^{-1}, $F(000) = 880$, $T = 296$ K, final $R = 0{\cdot}036$ for 362 variables and 1880 reflections. In all three structures the pyrazabole adopts a pronounced boat conformation. A comparison with the nine other known pyrazabole structures, however, shows that the central B_2N_4 ring is quite flexible, and that its observed conformation is sensitive to substituent and packing effects.

Introduction. The pyrazaboles, which have the general structure and numbering scheme shown below,



are a class of heterocycles containing four-coordinate boron and exhibiting remarkable chemical and thermal stability. Recent efforts by one of us to exploit this stability (Clarke, Niedenzu, Niedenzu & Trofimenko, 1985) have focused on synthesizing polymeric pyrazaboles containing B atoms as spiro centers. In

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* Alternative name for pyrazabole: 3a,4a,7a,8a-tetraaza-4,8-dibora-*s*-indacene.

† Contribution No. 151 in the series 'Chemistry of Boron'.

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such a polymer the B_2N_4 ring must be approximately planar; however, if an analogy is made with 9,10-dihydroanthracene, the pyrazabole skeleton might just as well be expected to adopt a boat conformation [for discussion of the potential-energy surface of 9,10-dihydroanthracene see Rabideau (1978) and Lipkowitz, Rabideau, Raber, Hardee, Schleyer, Kos & Kahn (1982)]. The three structure determinations reported here were undertaken in order to increase the information available about the pyrazabole ring system and its conformational flexibility.

Experimental. The structures of ME4PZB and BISPZB were determined at the University of Munich using a Syntex *P*3 diffractometer and the *SHELXTL* program package (Sheldrick, 1978). ME4PZB: crystals (Trofimenko, 1967*a*) grown from CH_2Cl_2 as plates having faces of the forms $\{100\}$, $\{010\}$, and $\{001\}$ (needles are obtained from toluene); crystal $0{\cdot}3 \times 0{\cdot}2 \times 0{\cdot}5$ mm; ω–2θ scans, $2\theta \leq 45°$; 3785 reflections (2 quadrants); after averaging, 1424 with $F^2 > 3\sigma(F^2)$ treated as observed; 2 standard reflections; no absorption correction; decomposition (corrected) less than 2% overall; 21 reflections for measuring lattice parameters; $-8 \leq h \leq 8$, $k \leq 12$, $-14 \leq l \leq 14$; all C, B, and N atoms refined anisotropically; H atoms refined with fixed isotropic *U*'s of 0·070 Å^2; there was some difficulty in refining the methyl H atoms; final values of agreement indices [refinement on *F*, $w^{-1} = \sigma^2(F_o) + (0{\cdot}04F_o)^2$] are $R = 0{\cdot}055$, $wR = 0{\cdot}055$ for 199 variables; error in an observation of unit weight 1·94; most important features in a final difference-Fourier map have heights +0·17 and −0·19 e Å^{-3}; $(\Delta/\sigma)_{\max} = 0{\cdot}73$, $(\Delta/\sigma)_{\text{mean}} = 0{\cdot}14$. BISPZB: crystals (Niedenzu & Niedenzu, 1984) grown from $CHCl_3/C_6H_{12}$ as prisms; crystal $0{\cdot}2 \times 0{\cdot}3 \times 0{\cdot}25$ mm; ω–2θ scans, $2\theta \leq 45°$; 4226 reflections (full sphere); after averaging, 1957 with $F^2 > 3\sigma(F^2)$ treated as observed; 2 standard reflections; no absorption correction; decomposition (corrected) less than 1·8% overall; 14 reflections for measuring lattice parameters; $-9 \leq h \leq 9$, $-10 \leq k \leq 10$, $l \leq 10$; all C, B, and N atoms refined anisotropically; H atoms refined isotropically; final values of agreement indices [refinement on *F*, $w^{-1} = \sigma^2(F_o) + (0{\cdot}02F_o)^2$] are $R = 0{\cdot}035$, $wR = 0{\cdot}037$ for 255 variables; error in an observation of unit weight 1·89; most important features in a final difference-Fourier map have heights +0·09 and −0·21 e Å^{-3}; $(\Delta/\sigma)_{\max} = 0{\cdot}44$, $(\Delta/\sigma)_{\text{mean}} = 0{\cdot}07$.

The structure of TETPZB was determined at the University of Kentucky using an Enraf–Nonius CAD-4/F diffractometer and a program package described previously (Brock & Webster, 1976). TETPZB: crystals (Trofimenko, 1967*b*) grown from $CHCl_3/C_6H_{12}$ as prisms elongated along **a** and bounded by faces of the forms $\{010\}$, $\{011\}$, and $\{10\bar{1}\}$; crystal $0{\cdot}15 \times 0{\cdot}22 \times 0{\cdot}38$ mm (all thicker crystals examined were twinned); θ–2θ scans, $2\theta \leq 55°$; 4839 reflections; 1880 with $F^2 > 2\sigma(F^2)$ treated as observed; 3 standard reflections; no absorption correction; correction for decomposition of 1·7% overall ; 24 reflections having $22 < 2\theta < 24°$ for measuring lattice parameters; $0 \leq h \leq 11$, $0 \leq k \leq 28$, $-15 \leq l \leq 15$; all C, B, and N atoms refined anisotropically, H atoms isotropically; an extinction factor (Zachariasen, 1967), final value 2·76 (11) $\times 10^{-5}$, improved agreement significantly; final agreement indices [refinement on *F*, $w = 4F_o^2/\sigma^2(F_o^2)$ where $\sigma^2(F_o^2)$ includes a term $(0{\cdot}02F_o^2)^2$] are $R = 0{\cdot}036$, $wR = 0{\cdot}033$ for 362 variables; error in an observation of unit weight 1·38; most important features in a final difference-Fourier map have heights ±0·17 e Å^{-3}; $(\Delta/\sigma)_{\max} = 0{\cdot}05$.

Table 1. *Atom coordinates* ($\times 10^4$) *and temperature factors for ME4PZB*

$B_{\text{eq}} = \frac{4}{3}\text{Tr}(\beta.\mathbf{G})$.

	x	y	z	B_{eq}(Å^2)
B(1)	256 (4)	898 (3)	7196 (2)	4·2
B(2)	−857 (4)	2778 (3)	6045 (2)	4·1
N(1)	1682 (2)	1732 (2)	6842 (1)	3·7
N(2)	1158 (2)	2624 (2)	6294 (1)	3·8
N(3)	−1526 (2)	1593 (2)	5750 (1)	3·5
N(4)	−999 (2)	701 (2)	6300 (1)	3·4
C(1)	3451 (3)	1783 (2)	6971 (2)	4·3
C(2)	4042 (3)	2719 (3)	6512 (2)	5·1
C(3)	2594 (3)	3232 (2)	6086 (2)	4·5
C(4)	−2569 (3)	1228 (2)	5016 (2)	3·6
C(5)	−2705 (3)	92 (2)	5098 (2)	3·7
C(6)	−1705 (3)	−218 (2)	5906 (2)	3·4
C(11)	4454 (5)	931 (4)	7536 (3)	6·3
C(31)	2458 (4)	4266 (3)	5505 (3)	6·6
C(41)	−3364 (4)	1983 (3)	4275 (2)	5·0
C(61)	−1416 (4)	−1339 (2)	6328 (2)	4·7
H(11)	874 (35)	133 (20)	7446 (18)	*
H(12)	−566 (33)	1337 (20)	7814 (17)	*
H(21)	−1501 (34)	3074 (21)	6696 (19)	*
H(22)	−995 (34)	3322 (21)	5444 (19)	*
H(2)	5093 (32)	2982 (19)	6441 (17)	*
H(5)	−3311 (33)	−346 (20)	4682 (17)	*
H(11*A*)	5590 (39)	1107 (23)	7497 (20)	*
H(11*B*)	4451 (36)	197 (25)	7228 (19)	*
H(11*C*)	4229 (38)	921 (23)	8181 (23)	*
H(31*A*)	3579 (34)	4524 (19)	5409 (17)	*
H(31*B*)	1945 (33)	4145 (20)	4852 (18)	*
H(31*C*)	1793 (33)	4840 (21)	5795 (18)	*
H(41*A*)	−3870 (37)	1612 (22)	3769 (21)	*
H(41*B*)	−2656 (36)	2595 (22)	4089 (20)	*
H(41*C*)	−4339 (33)	2381 (21)	4512 (18)	*
H(61*A*)	−2213 (38)	−1494 (23)	6785 (21)	*
H(61*B*)	−346 (37)	−1444 (22)	6619 (20)	*
H(61*C*)	−1593 (36)	−1870 (22)	5898 (21)	*

* Fixed at 5·5 Å^2.

Discussion. Positional parameters for ME4PZB, BISPZB and TETPZB are in Tables 1, 3 and 4, respectively*. Some bond lengths and angles are in Table 2. The molecular structures are illustrated in Figs. 1, 2 and 3, respectively.

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* The refined atomic displacement parameters and observed and calculated structure-factor amplitudes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42253 (37 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

If an analogy is made with 9,10-dihydroanthracene, the six-membered B_2N_4 ring of the pyrazabole would be expected to adopt either a boat or a planar conformation; however, the first structure of a member of this class [4,8-bis(3,5-dimethyl-1-pyrazolyl)-1,3,5,7-tetramethylpyrazabole; Alcock & Sawyer (1974)] revealed a flattened chair conformation. The authors invoked steric interactions to explain this observation, and it is true that no other pyrazabole with comparable crowding has been studied crystallographically. The second structure determined [2,6-dibromo-4,4,8,8-tetraethylpyrazabole; Holt, Tebben, Holt & Watson (1977)] contains a somewhat asymmetrical B_2N_4 ring that is approximately planar.

Quite recently ten more pyrazabole structures have been determined (Niedenzu & Nöth, 1983; Hanecker, Hodgkins, Niedenzu & Nöth, 1985; this work) and it is now possible to compare B_2N_4 ring conformations across a variety of substituents and crystal-packing arrangements. Two dihedral angles have been chosen to describe ring geometries: an angle θ_1 between the plane of the four N atoms and a plane defined by a N—B—N grouping, and an angle θ_2 between the plane of the four N atoms and a bridging pyrazolyl ring. In the absence of imposed symmetry each molecule has two θ_1 and two θ_2 values, but in all cases but one (see below) the two corresponding values differ by at most a few degrees. The average value of the angle θ_1 measures the deviation of the B_2N_4 ring from planarity, and the average value of θ_2 describes the extent to which the bridging pyrazolyl rings are folded back in a butterfly arrangement. In all twelve structures the four N atoms of the B_2N_4 ring and the five atoms of the N_2C_3 rings form good planes; most deviations are much smaller than the maximum value of 0·02 Å.

Table 2. *Selected bond lengths* (Å) *and bond angles* (°)

	ME4PZB	BISPZB	TETPZB
B(1)—N(1)	1·560 (4)	1·549 (2)	1·545 (3)
B(1)—N(4)	1·561 (3)	1·558 (2)	1·551 (3)
B(2)—N(2)	1·563 (4)	1·563 (2)	1·555 (3)
B(2)—N(3)	1·566 (4)	1·564 (2)	1·557 (3)
B(1)—N(5)		1·515 (2)	1·516 (3)
B(1)—N(7)		1·519 (2)	1·510 (3)
B(2)—N(9)			1·513 (3)
B(2)—N(11)			1·519 (3)
N(1)—N(2)	1·368 (3)	1·368 (1)	1·370 (2)
N(3)—N(4)	1·369 (3)	1·358 (1)	1·369 (2)
N(5)—N(6)		1·373 (2)	1·367 (3)
N(7)—N(8)		1·368 (1)	1·364 (3)
N(9)—N(10)			1·362 (3)
N(11)—N(12)			1·372 (3)
N(1)—C(1)	1·345 (3)	1·346 (2)	1·340 (3)
N(2)—C(3)	1·345 (3)	1·335 (2)	1·342 (3)
N(3)—C(4)	1·344 (3)	1·336 (2)	1·337 (3)
N(4)—C(6)	1·339 (3)	1·342 (2)	1·331 (3)
N(5)—C(7)		1·355 (2)	1·356 (3)
N(7)—C(10)		1·357 (2)	1·354 (3)
N(9)—C(13)			1·349 (3)
N(11)—C(16)			1·351 (3)
N(6)—C(9)		1·322 (2)	1·326 (3)
N(8)—C(12)		1·331 (2)	1·324 (3)
N(10)—C(15)			1·318 (3)
N(12)—C(18)			1·338 (4)
C(1)—C(2)	1·373 (4)	1·370 (2)	1·361 (4)
C(2)—C(3)	1·377 (4)	1·369 (2)	1·360 (4)
C(4)—C(5)	1·378 (4)	1·372 (2)	1·367 (4)
C(5)—C(6)	1·385 (4)	1·364 (2)	1·364 (4)
C(1)—C(11)	1·486 (5)		
C(3)—C(31)	1·488 (4)		
C(4)—C(41)	1·486 (4)		
C(6)—C(61)	1·485 (4)		
C(7)—C(8)		1·358 (2)	1·358 (4)
C(10)—C(11)		1·362 (2)	1·352 (5)
C(13)—C(14)			1·359 (4)
C(16)—C(17)			1·362 (4)
C(8)—C(9)		1·385 (2)	1·379 (4)
C(11)—C(12)		1·382 (2)	1·370 (5)
C(14)—C(15)			1·367 (4)
C(17)—C(18)			1·364 (5)
B(1)—H(11)	1·086 (25)		
B(1)—H(12)	1·190 (24)		
B(2)—H(21)	1·091 (27)	1·151 (13)	
B(2)—H(22)	1·061 (26)	1·067 (13)	
N(1)—B(1)—N(4)	105·1 (2)	105·6 (1)	105·6 (2)
N(2)—B(2)—N(3)	104·8 (2)	103·6 (1)	105·3 (2)
N(1)—B(1)—N(5)		111·2 (1)	109·4 (2)
N(4)—B(1)—N(5)		109·2 (1)	110·8 (2)
N(1)—B(1)—N(7)		109·7 (1)	110·7 (2)
N(4)—B(1)—N(7)		110·5 (1)	110·0 (2)
N(2)—B(2)—N(9)			109·3 (2)
N(3)—B(2)—N(9)			109·6 (2)
N(2)—B(2)—N(11)			110·9 (2)
N(3)—B(2)—N(11)			109·5 (2)
N(5)—B(1)—N(7)		110·5 (1)	110·2 (2)
N(9)—B(2)—N(11)			112·0 (2)
B(1)—N(1)—N(2)	119·1 (2)	119·6 (1)	121·2 (2)
B(1)—N(4)—N(3)	118·9 (2)	121·0 (1)	121·6 (2)
B(2)—N(2)—N(1)	118·9 (2)	121·0 (1)	122·3 (2)
B(2)—N(3)—N(4)	118·9 (2)	119·7 (1)	121·9 (2)
H(11)—B(1)—H(12)	112·1 (18)		
H(21)—B(2)—H(22)	113·9 (19)	115·7 (10)	

Table 3. *Atom coordinates* (×10^4) *and temperature factors for BISPZB*

$$B_{eq} = \tfrac{4}{3}\mathrm{Tr}(\boldsymbol{\beta}.\mathbf{G}).$$

	x	*y*	*z*	B_{eq} or B(Å^2)
B(1)	6515 (2)	2269 (2)	7138 (2)	3·2
B(2)	8782 (2)	4539 (2)	6679 (2)	4·4
N(1)	6286 (1)	2975 (1)	5674 (1)	3·5
N(2)	7339 (1)	4037 (1)	5466 (1)	3·8
N(3)	8094 (1)	4599 (1)	8101 (1)	3·9
N(4)	7094 (1)	3515 (1)	8327 (1)	3·5
N(5)	4988 (1)	1586 (1)	7392 (1)	3·5
N(6)	3642 (1)	2313 (1)	7231 (1)	4·4
N(7)	7734 (1)	1159 (1)	7163 (1)	3·5
N(8)	8486 (1)	723 (1)	8457 (1)	4·4
C(1)	5161 (2)	2788 (2)	4474 (1)	4·2
C(2)	5498 (2)	3720 (2)	3494 (2)	4·9
C(3)	6854 (2)	4486 (2)	4148 (2)	4·7
C(4)	8290 (2)	5548 (2)	9254 (2)	4·9
C(5)	7427 (2)	5084 (2)	10230 (2)	5·4
C(6)	6690 (2)	3812 (2)	9618 (2)	4·5
C(7)	4747 (2)	317 (2)	7957 (2)	4·3
C(8)	3248 (2)	210 (2)	8165 (2)	5·2
C(9)	2611 (2)	1463 (2)	7690 (2)	4·5
C(10)	8005 (2)	272 (1)	6048 (2)	4·3
C(11)	8944 (2)	−753 (2)	6619 (2)	5·2
C(12)	9208 (2)	−432 (2)	8103 (2)	4·8
H(21)	9673 (15)	3667 (13)	6693 (13)	4·3 (3)
H(22)	9202 (16)	5594 (14)	6514 (14)	5·2 (3)
H(1)	4263 (15)	2079 (13)	4457 (14)	4·8 (3)
H(2)	4870 (18)	3782 (15)	2585 (17)	5·4 (3)
H(3)	7417 (18)	5285 (16)	3866 (17)	6·5 (4)
H(4)	8954 (18)	6369 (16)	9228 (16)	6·2 (3)
H(5)	7352 (19)	5581 (17)	11097 (18)	7·2 (4)
H(6)	5962 (17)	3181 (15)	9949 (15)	4·8 (3)
H(7)	5550 (17)	−298 (14)	8136 (14)	4·3 (3)
H(8)	1553 (17)	1736 (15)	7655 (15)	5·6 (3)
H(9)	2738 (19)	−553 (17)	8497 (17)	6·3 (4)
H(10)	7585 (16)	442 (14)	5069 (14)	5·2 (3)
H(11)	9342 (18)	−1445 (15)	6086 (16)	6·2 (3)
H(12)	9857 (18)	−884 (16)	8878 (17)	5·9 (3)

Table 4. *Positional and thermal parameters for TETPZB*

$B_{eq} = \frac{4}{3}\mathrm{Tr}(\beta.\mathbf{G})$.

	x	y	z	B_{eq} or B (Å^2)
N(1)	0·2693 (2)	0·44465 (9)	−0·08711 (16)	2·9
N(2)	0·3173 (2)	0·43257 (9)	0·03503 (16)	2·9
N(3)	0·3821 (2)	0·32562 (9)	−0·00359 (17)	2·9
N(4)	0·3342 (2)	0·33808 (9)	−0·12546 (17)	3·1
N(5)	0·0471 (2)	0·37466 (10)	−0·20291 (17)	3·3
N(6)	−0·0083 (3)	0·31939 (11)	−0·25603 (19)	4·3
N(7)	0·2405 (2)	0·41195 (10)	−0·29988 (17)	3·5
N(8)	0·3874 (3)	0·42733 (11)	−0·030525 (20)	4·6
N(9)	0·4552 (2)	0·36386 (9)	0·21086 (16)	3·4
N(10)	0·6107 (3)	0·37695 (11)	0·22437 (19)	4·8
N(11)	0·1664 (2)	0·34424 (10)	0·08784 (17)	3·5
N(12)	0·0891 (3)	0·37726 (12)	0·1518 (2)	5·1
C(1)	0·2696 (3)	0·50575 (13)	−0·1012 (3)	3·6
C(2)	0·3166 (4)	0·53323 (15)	0·0099 (3)	4·1
C(3)	0·3466 (3)	0·48689 (13)	0·0927 (3)	3·6
C(4)	0·4722 (3)	0·27481 (13)	0·0169 (3)	3·7
C(5)	0·4831 (4)	0·25451 (15)	−0·0909 (3)	4·3
C(6)	0·3965 (3)	0·29495 (13)	−0·1772 (3)	3·9
C(7)	−0·0746 (4)	0·40801 (16)	−0·1883 (3)	4·1
C(8)	−0·2113 (4)	0·37448 (17)	−0·2319 (3)	4·6
C(9)	−0·1639 (4)	0·32060 (17)	−0·2720 (3)	4·8
C(10)	0·1277 (5)	0·41810 (19)	−0·4110 (3)	6·2
C(11)	0·2014 (5)	0·4371 (2)	−0·4892 (3)	8·0
C(12)	0·3601 (5)	0·44229 (17)	−0·4203 (3)	6·0
C(13)	0·4395 (5)	0·35468 (15)	0·3206 (3)	4·9
C(14)	0·5864 (5)	0·36251 (16)	0·4061 (3)	5·8
C(15)	0·6871 (4)	0·37568 (15)	0·3426 (3)	5·3
C(16)	0·0790 (4)	0·29476 (15)	0·0345 (3)	4·1
C(17)	−0·0576 (4)	0·29467 (20)	0·0640 (3)	5·4
C(18)	−0·0463 (4)	0·3455 (2)	0·1346 (3)	5·7
B(1)	0·2200 (4)	0·39235 (14)	−0·1818 (3)	3·1
B(2)	0·3286 (3)	0·36608 (14)	0·0860 (2)	3·1
H(1)	0·245 (3)	0·5225 (10)	−0·181 (2)	3·9 (6)
H(2)	0·327 (3)	0·5733 (12)	0·025 (2)	3·6 (6)
H(3)	0·383 (3)	0·4855 (10)	0·177 (2)	3·8 (6)
H(4)	0·512 (3)	0·2598 (10)	0·097 (2)	3·6 (6)
H(5)	0·540 (3)	0·2223 (12)	−0·100 (2)	4·6 (7)
H(6)	0·378 (3)	0·2960 (11)	−0·266 (2)	4·9 (6)
H(7)	−0·053 (3)	0·4488 (13)	−0·152 (2)	4·6 (7)
H(8)	−0·315 (4)	0·3888 (13)	−0·235 (3)	6·9 (9)
H(9)	−0·226 (3)	0·2846 (12)	−0·304 (2)	5·0 (7)
H(10)	0·019 (4)	0·4114 (15)	−0·416 (3)	8·7 (11)
H(11)	0·150 (4)	0·4413 (17)	−0·577 (3)	10·8 (11)
H(12)	0·452 (4)	0·4547 (14)	−0·443 (3)	7·1 (9)
H(13)	0·337 (3)	0·3473 (12)	0·325 (2)	5·6 (8)
H(14)	0·613 (4)	0·3581 (14)	0·486 (3)	7·5 (9)
H(15)	0·807 (4)	0·3849 (12)	0·370 (2)	6·1 (8)
H(16)	0·113 (3)	0·2681 (13)	−0·020 (2)	6·3 (8)
H(17)	−0·142 (4)	0·2661 (14)	0·034 (3)	7·2 (9)
H(18)	−0·117 (4)	0·3630 (13)	0·175 (2)	6·8 (8)

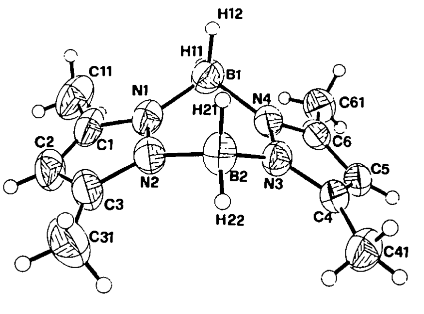

Fig. 1. Perspective drawing of the molecular structure of ME4PZB. In this and the following drawings the shapes of the ellipsoids for the non-H atoms correspond to 50% probability contours of atomic displacement.

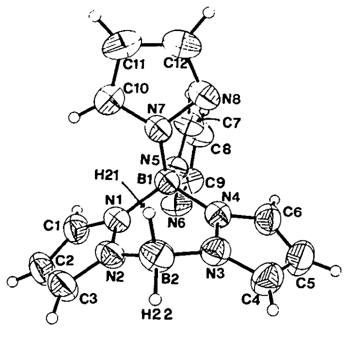

Fig. 2. Perspective drawing of the molecular structure of BISPZB.

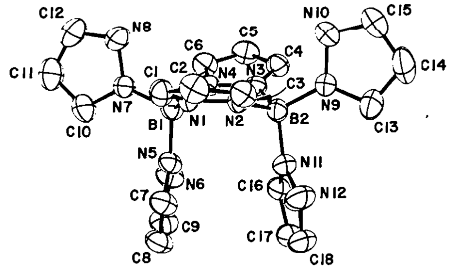

Fig. 3. Perspective drawing of the molecular structure of TETPZB.

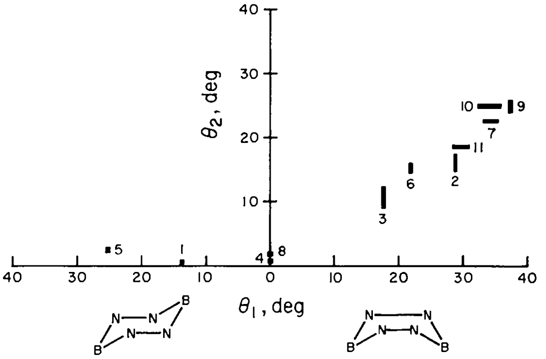

Fig. 4. A scatterplot showing the relationship between the dihedral angles θ_1 of the planes [B(1),N(1),N(4)] and [B(2),N(2),N(3)] with the plane [N(1),N(2)N(3),N(4)], and the angles θ_2 of the planes [N(1),N(2),C(1),C(2),C(3)] and [N(3),N(4),C(4),C(5),-C(6)] with the plane [N(1),N(2),N(3),N(4)] for 11 pyrazabole structures (see Figs. 1–3 for the atom-numbering scheme). The structures are (1) 4,8-bis(3,5-dimethyl-1-pyrazolyl)-1,3,5,7-tetramethylpyrazabole (Alcock & Sawyer, 1974); (2) 4,4,8,8-bis(ethylenedithio)pyrazabole, (3) 4,4,8,8-tetrakis-(methylthio)pyrazabole, (4) 4,4,8,8-tetrachloropyrazabole, (5) 4,8-diphenyl-4,8-bis(1-pyrazolyl)pyrazabole, (6) 4,8-dibromo-2,6-dichloropyrazabole (Niedenzu & Nöth, 1983); (7) pyrazabole, (8) 4,4,8,8-tetrabromopyrazabole (Hanecker, Hodgkins, Niedenzu & Nöth, 1985); (9) 1,3,5,7-tetramethylpyrazabole, (10) 4,4-bis(1-pyrazolyl)pyrazabole, and (11) 4,4,8,8-tetrakis(1-pyrazolyl)pyrazabole (this paper). The rectangle for each structure covers the range of the two θ_1 and two θ_2 values that is observed in the absence of imposed symmetry (see text).

A plot of θ_2 *vs* θ_1 for eleven of the twelve structures (Fig. 4) shows that a wide range of ring conformations has been observed. The interconversion of boat and chair forms must require only a small amount of energy, and must therefore be sensitive to substituent and packing effects. The boat form is, however, observed most frequently, and so is probably the favored conformation.* The plot also confirms the expected correlation between θ_1 and θ_2: the more pronounced the boat conformation, the greater the bending back of the pyrazolyl rings. Evidence from molecular-mechanics and quantum-mechanical calculations for the related hydrocarbon 9,10-dihydroanthracene (Lipkowitz *et al.*, 1982) and from various studies of its derivatives (Rabideau, 1978) suggests that the energy difference between the boat and planar conformations in such ring systems is very small, perhaps less than 2·1 kJ mol^{-1} for a θ_2 value of 10°. In the pyrazaboles, which may be even more flexible than the hydrocarbon, the chair conformation is also accessible.

The one structure omitted from Fig. 4 is that of 2,6-dibromo-4,4,8,8-tetraethylpyrazabole (Holt, Tebben, Holt & Watson, 1977). Its two angles θ_2 are similar at 1·2 and 3·2°, but the two values of θ_1, −0·5 and 12·2°, vary considerably. One end of the B_2N_4 ring is nearly planar, while the B atom at the other end is 0·24 Å out of the plane of the four N atoms. None of the other eleven structures even approaches this degree of asymmetry.

Differences in bond lengths and angles between bridging and terminal pyrazolyl rings are best examined in the structure of TETPZB. Not only is extensive averaging possible over the chemically equivalent bonds, but the internal consistency of the four (or in two cases, two) independent length and angle determinations is excellent. Fig. 5 shows some of the average values; bond angles in the B_2N_4 ring are in general sensitive to ring conformation and so are not included. There is clear evidence of localization of double bonds in the terminal rings. Although the differences within the pairs of N—C and C—C average bond lengths are small, they bracket the corresponding average values for the bridging rings. The same is true for the bond angles. Although a correction for the effects of thermal motion might increase the absolute values of these averages by *ca* 0·003–0·006 Å, the pattern shown is probably insensitive to that kind of systematic error. A very similar pattern is also seen in the structure of BISPZB. The structures of BISPZB and TETPZB show that a B—N bond to a terminal ring is about 0·040 (4) Å shorter than a B—N bond to a bridging ring.

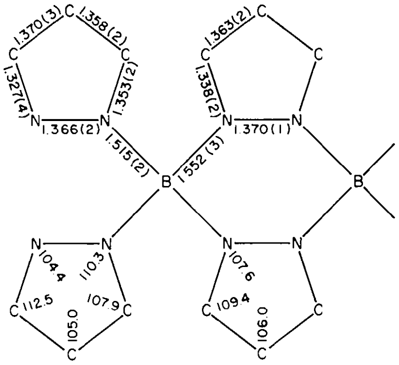

Fig. 5. Diagram showing some average bond lengths (Å) and angles (°) for 4,4,8,8-tetrakis(1-pyrazolyl)pyrazabole. The numbers in parentheses are the e.s.d.'s of the means. The e.s.d.'s for the angles range from 0·1 to 0·4°, and average 0·2°.

The B_2N_4 rings in both BISPZB and TETPZB adopt pronounced boat conformations (see Fig. 4); the arrangements of the two terminal rings on each B atom are also very similar (see Figs. 2 and 3). The orientations of the terminal rings in 4,8-diphenyl-4,8-bis(1-pyrazolyl)pyrazabole (Niedenzu & Nöth, 1983; site symmetry $\bar{1}$) are also related to those of BISPZB and TETPZB. The planes of the equatorial phenyl rings are almost perpendicular to the plane of the four N atoms and approximately bisect the N—B—N angles. The planes of the axial pyrazolyl rings are approximately perpendicular to both the equatorial rings and the central N-atom plane. The appearance of this same general arrangement of the terminal rings across three structures, two boat forms and one chair, suggests that it is the favored conformation for *cis* disubstitution by aromatic rings. In both BISPZB and TETPZB the uncoordinated N atoms of the pseudo-equatorial pyrazolyl rings are oriented so that the N—N bonds approximately eclipse the B—B vectors.

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* The recently completed structure determination of 4,4,8,8-tetrafluoropyrazabole (Nöth & Hanecker, 1985) also contains boat-shaped molecules with $\theta_1 \simeq 30°$.

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Structure of an Epipolysulfide: 3a,6-Dihydro-1-methylcyclopenta[6,7][1,2]dithiepino-[5,4-*b*][1]benzothiophen-2(3*H*)-one

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Abstract. $C_{15}H_{12}OS_3$, $M_r = 304{\cdot}4$, m.p. 441–443 K, orthorhombic, $P2_12_12_1$, $a = 8{\cdot}747\ (1)$, $b = 8{\cdot}787\ (2)$, $c = 18{\cdot}173\ (6)$ Å, $U = 1396{\cdot}8\ (9)$ Å^3, $Z = 4$, $D_x = 1{\cdot}445$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}458$ mm^{-1}, $F(000) = 632$, $T = 296$ K, final $R = 0{\cdot}062$ for 767 observed $[I > 3\sigma(I)]$ diffractometer data. The S atoms of the dithiepine ring are disordered, as a result of which the ring conformation adopted is a chair for the major component (75%) and a twist-boat for the minor.

Introduction. Cyclodehydration of the *C*-secosteroid, *B*-nor-6,12-bisthia-*B*,14-secoestra-1,3,5(10),8-tetraene-14,17-dione with excess of *p*-toluenesulfonic acid in refluxing benzene afforded the unexpected title compound (I) in 20% yield, along with the expected compound *B*-nor-6,12-bisthiaestra-1,3,5(10),8,14-pentaen-17-one (II) in 10% yield (Ramadas, Appa Rao, Chenchaiah & Kumaresan, 1983). Because of the possibility of its being a member of a new type of tetracyclic organosulfur system and the current interest in the conformation of epipolysulfides, the X-ray crystal structure determination was undertaken.

Experimental. Light-pink crystals from 2-propanol, $0{\cdot}30 \times 0{\cdot}25 \times 0{\cdot}25$ mm. Enraf–Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation, graphite monochromator. 1484 reflections ($\omega/2\theta$ scan mode, $6° < 2\theta < 52°$), 767 unique observed reflections $[I > 3\sigma(I)]$. Reflections $2\bar{2}2$, $0\bar{2}2$ maintained intensity within 8% during data collection. Lp correction applied; absorption and extinction neglected. Structure solved by direct methods for nonhydrogen atoms. A difference Fourier map with phases of non-hydrogen atoms revealed two extra peaks, close to the S atoms of the dithiepine ring. With occupancy factors based on peak heights (Hamilton, 1959), refinement led to occupancies of 0·750 (4) and 0·250 (4) for the two S atoms. Refinement on F: non-hydrogen atoms with anisotropic temperature factors and H atoms (from ΔF map) with isotropic temperature factors. Final $R = 0{\cdot}062$, $wR = 0{\cdot}040$, $R_G = 0{\cdot}029$, $w^{-1} = \sigma^2|F_o|$. $(\Delta/\sigma)_{\max}$ in final cycle 0·100. Final difference map: no electron density $>0{\cdot}15$ e Å^{-3}. Programs: *MULTAN*80 (Main *et al.*, 1980), *SHELX*76 (Sheldrick, 1976) and *ORTEP* (Johnson, 1965).

Discussion. Table 1 gives the coordinates of the atoms of the structure.† The atom numbering and thermal ellipsoids are given in Fig. 1. Bond lengths and bond angles are in Table 2.

The bond lengths and bond angles in the thianaphthene and the dithiepin fragments, with the exception of C(5)—S(1) (in the major conformer), correspond closely to similar parameters in heterocyclic compounds containing S as hetero-atom: *e.g.*

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† Lists of structure factors, anisotropic thermal parameters and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42288 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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