

Acta Cryst. (1974). B30, 2899**Bis-(3,5-dimethylpyrazolyl)borane Dimer**

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Abstract. $C_{20}H_{30}B_2N_8$, orthorhombic, $Pbcn$, $a = 14.042$ (2), $b = 11.094$ (1), $c = 14.298$ (2) Å at 20°C, $Z = 4$, $D_m = 1.19$ (floatation), $D_x = 1.21$ g cm⁻³. The dimers have the *trans* configuration; they lie on centres of symmetry in the flattened chair conformation. This isomer and conformer minimizes both transannular and *peri* interactions.

Introduction. The compound was prepared by the reaction of 3,5-dimethylpyrazole and triethylamine borane (Davies & Wallbridge, 1974; Trofimenko, 1967) and was recrystallized slowly from chloroform/cyclohexane, appearing as laths developed along (110). Systematic absences $h0l$, $l \neq 2n$; $hk0$, $h+k \neq 2n$; $0kl$, $k \neq 2n$, indicate space group $Pbcn$, and the value of Z requires the molecule to be centrosymmetric. Cell constants and errors were obtained by least-squares refinement of the positions of 15 reflexions. Data were collected on a Syntex $P2_1$ diffractometer with Mo $K\alpha$ radiation to a 2θ of 50° and $\omega/2\theta$ scans over the range

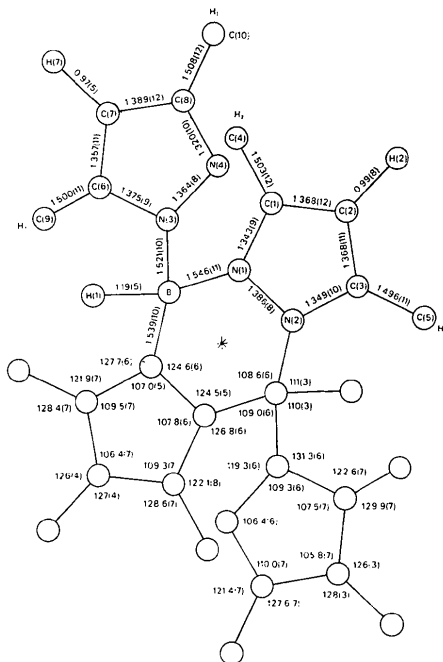


Fig. 1. Skeletal atomic numbering, bond lengths and angles (with standard errors in parentheses). Primed atoms are related to unprimed ones by the centre of symmetry (*) Methyl hydrogen atoms are numbered H(41), H(42), H(43), for those attached to C(4) etc. The methyl groups have tetrahedral angles and C-H = 0.95 Å (Churchill, 1973). H(1)-B-N(1) = 109 (2); N(3)-B-N(2)' = 108.5 (6)°.

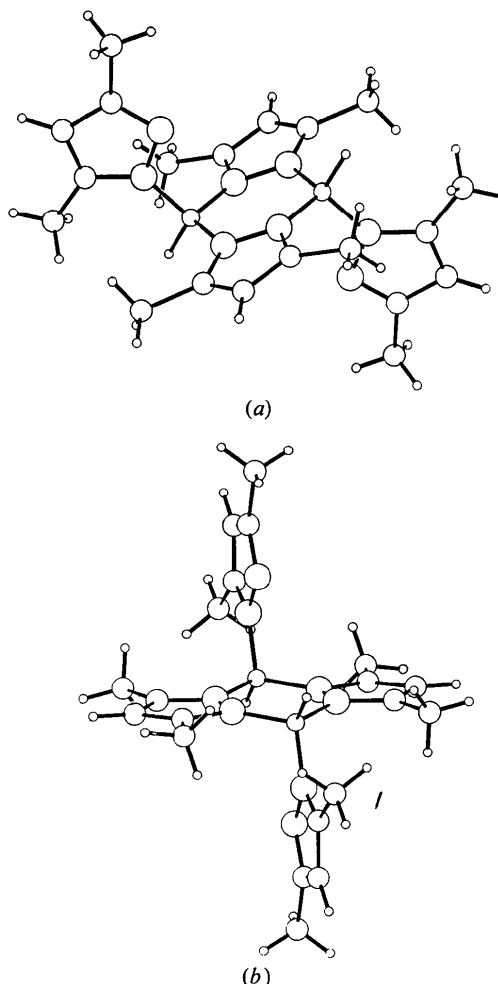


Fig. 2. Two views of the molecule: (a) along c , (b) about 10° from b . The circles are graded in size, $N > C > B > H$.

$(K\alpha_1 + 0.75) - (K\alpha_2 - 0.75)$ with a variable scan rate, 0.7–29.3° min⁻¹ depending on the intensity of a 2s preliminary count. 2238 reflexions were examined and used to obtain E values and to solve the structure by direct methods with the programs *NORMAL* and *MULTAN* (Germain & Woolfson, 1968). In the refinement only the 467 reflexions with $I/\sigma(I) > 3.5$ were used, with unit weights. Final refinement was with N, C and B anisotropic. Hydrogen atoms were included but it was found that some of the methyl hydrogen atoms were unstable. For the penultimate refinement cycles, therefore, rigid groups C-CH₃ were used, and in the

Table 1. Atomic coordinates ($\times 10^4$) and temperature factors ($\times 10$)

Standard errors in the last figures quoted as given by the final cycle of least-squares refinement are shown in parentheses. The anisotropic temperature factors were calculated from $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{23}klb^*c^* + 2B_{13}hla^*c^* + 2B_{12}hka^*b^*)]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
B	388 (6)	1301 (8)	-259 (6)	26 (4)	26 (4)	29 (4)	2 (3)	0 (4)	-1 (4)
N(1)	510 (4)	150 (6)	-860 (4)	25 (3)	34 (3)	21 (3)	3 (2)	3 (2)	-5 (3)
N(2)	283 (4)	-1009 (5)	-564 (4)	27 (3)	25 (3)	29 (3)	3 (3)	3 (3)	4 (3)
N(3)	1355 (4)	1669 (5)	135 (4)	26 (3)	28 (3)	27 (3)	2 (3)	-1 (3)	-4 (3)
N(4)	1845 (4)	876 (6)	686 (4)	25 (3)	30 (3)	27 (3)	0 (3)	-6 (3)	0 (3)
C(1)	994 (5)	54 (8)	-1668 (5)	43 (4)	36 (4)	30 (4)	-4 (4)	4 (4)	-12 (4)
C(2)	1063 (5)	-1139 (8)	-1912 (5)	25 (4)	52 (5)	36 (4)	-9 (4)	7 (3)	-7 (4)
C(3)	631 (6)	-1779 (7)	-1211 (6)	32 (4)	34 (4)	42 (4)	-4 (4)	-3 (3)	-2 (4)
C(4)	1371 (7)	1142 (8)	-2178 (6)	65 (6)	48 (5)	50 (6)	14 (4)	24 (5)	-11 (5)
C(5)	480 (6)	-3115 (7)	-1143 (6)	52 (5)	31 (4)	45 (4)	-7 (4)	12 (4)	5 (4)
C(6)	1859 (5)	2731 (7)	68 (6)	35 (4)	26 (3)	33 (4)	2 (3)	1 (3)	-5 (3)
C(7)	2675 (6)	2594 (8)	569 (5)	29 (4)	44 (4)	38 (4)	-10 (4)	3 (4)	-5 (4)
C(8)	2639 (5)	1433 (7)	938 (5)	27 (4)	36 (4)	29 (4)	-6 (3)	-3 (4)	-6 (4)
C(9)	1530 (6)	3774 (7)	-520 (6)	47 (5)	35 (4)	57 (5)	7 (4)	-8 (4)	-15 (4)
C(10)	3366 (6)	826 (9)	1558 (6)	45 (5)	61 (5)	46 (5)	-5 (5)	-12 (4)	2 (5)

	x	y	z	B	x	y	z	B	
H(1)	76 (37)	2102 (44)	-727 (35)	-10 (12)	H(53)*	-170	-3324	-1265	55 (21)
H(2)	1398 (54)	-1483 (63)	-2458 (55)	31 (19)	H(91)*	950	4098	-305	45 (15)
H(7)	3185 (37)	3178 (49)	623 (38)	-6 (12)	H(92)*	1459	3532	-1164	50 (29)
H(41)*	896	1738	-2234	32 (14)	H(93)*	2009	4411	-511	16 (58)
H(42)*	1576	905	-2799	48 (57)	H(101)*	3367	1182	2167	79 (47)
H(43)*	1913	1465	-1859	84 (47)	H(102)*	3992	896	1298	71 (32)
H(51)*	640	-3405	-527	16 (19)	H(103)*	3222	-19	1626	8 (14)
H(52)*	876	-3538	-1583	43 (47)					

* In rigid bodies.

final cycle the methyl hydrogen atoms were fixed and all other atoms refined freely. The final R was 0.043. Computing was carried out with the programs of Dr D. Russell on an ICL 4130 computer.

Fig. 1. shows the atomic numbering, bond lengths and angles, and Fig. 2 gives two views of the molecule. Atomic coordinates and temperature factors are given in Table 1, and molecular planes in Table 2.*

Table 2. Equations of mean planes (in orthogonal \AA coordinates), deviations (\AA) of atoms and angles ($^\circ$) between planes

Plane (1): N(1), N(2), C(1)-C(5) and corresponding primed atoms

$$0.861X - 0.0668Y + 0.5038Z = 0.0$$

[N(1) -0.014, N(2) 0.010, C(1) -0.003, C(2) -0.007, C(3) 0.023, C(4) 0.005, C(5) -0.013; B 0.186]

Plane (2): B, N(1), N(2)

$$0.7869X - 0.2685Y + 0.5556Z = -0.1646$$

Plane (3): N(3), N(4), C(6)-C(10)

$$-0.4652X + 0.3628Y + 0.8074Z = -0.0596$$

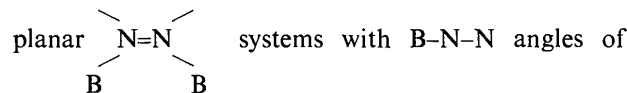
[N(3) 0.002, N(4) -0.002, C(6) 0.023, C(7) 0.013, C(8) -0.005, C(9) -0.021, C(10) -0.009]

Interplanar angles

$$(1)-(2) 12.7 \quad (2)-(3) 89.1 \quad (1)-(3) 89.0$$

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30615 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion. Pyrazolylborate anions have recently received attention because of their behaviour as ligands (Trofimenko, 1971). The neutral pyrazolylborane dimers are also potential ligands, but the present compound is the first whose structure has been determined. In a corresponding gallane, pyrazolylbideuterogallane dimer (Rendle, Storr & Trotter, 1973), the central ring has the boat conformation (dihedral angle 127.4°). The same conformation would be expected *a priori* for the present compound (both compounds being regarded as derivatives of cyclohexa-1,4-diene); this would provide



120° and N-B-N of 109° . However, the structure determination shows that instead each molecule (the *trans* isomer) lies on a centre of symmetry and is slightly chair-shaped (dihedral angle of 12.7° between the N-B-N plane and the central plane, B 0.19 \AA out of the central plane). This is apparently due to the bulky terminal pyrazolyl groups on each boron, as compared with the hydrogen atoms of the gallium compound. In the boat conformation, substituents on boron can be either pseudo-axial or pseudo-equatorial. Equatorial groups would be involved in severe *peri* interactions with the methyl groups of the ring pyrazoles (brought together by the fold of the central ring), and so only the axial positions are possible [*cf.* 9-*t*-butyl-9,10-dihydroanthracene (Brennan, Putkey & Sundaralingam, 1971), with axial *t*-butyl]. Thus the

boat conformation is unfavourable for the *trans* isomer because one substituent would be equatorial, and only an approximately planar conformation is available, even though this involves angle strain in the B_2N_4 ring. In fact, the conformation is slightly towards the chair form, presumably to reduce the *peri* interactions still further, although the ring nitrogen atoms are then slightly pyramidal. However, the angle strain at these nitrogen atoms is probably small, because the constraining of the C–N–N angle to 107–108° should allow the B–N–N angle to open to the observed 124° fairly easily.

That the *trans* rather than the *cis* isomer is formed in the reaction is also to be expected, because the *cis* isomer in the boat conformation with both substituents pseudo-equatorial would have severe *peri* interactions, while if they were pseudo-axial there would be very large transannular interactions, and these would still be present, although less marked, if the molecule were planar.

The same B_2N_4 ring system has been examined (Thomas & Paul, 1968) in $(C_4H_{11}NB_2)_4$ and found to have a boat conformation. However this is not directly

comparable with the present structure as the ring is saturated, and the main controlling factor for its geometry is the overall cage structure of the molecule.

Bond lengths in the terminal pyrazole do not depart significantly from those in free pyrazole (Krebs Larsen, Lehmann, Søtofte & Rasmussen, 1970), while those in the ring pyrazole are similar but with equal C–C and C–N distances.

References

- BRENNAN, T., PUTKEY, E. F. & SUNDARALINGAM, M. (1971). *Chem. Commun.* pp. 1490–1491.
 CHURCHILL, M. R. (1973). *Inorg. Chem.* **12**, 1213–1214.
 DAVIES, N. & WALLBRIDGE, M. G. H. (1974). In preparation.
 GERMAIN, G. & WOOLFSON, M. M. (1968). *Acta Cryst.* **B24**, 91–96.
 KREBS LARSEN, F., LEHMANN, M. S., SØTOFTE, I. & RASMUSSEN, S. E. (1970). *Acta Chem. Scand.* **24**, 3248–3258.
 RENDLE, D. F., STORR, A. & TROTTER, J. (1973). *J. Chem. Soc. Dalton*, pp. 2252–2255.
 THOMAS, P. C. & PAUL, I. C. (1968). *Chem. Commun.* pp. 1130–1131.
 TROFIMENKO, S. (1967). *J. Amer. Chem. Soc.* **89**, 4948–4952.
 TROFIMENKO, S. (1971). *Acc. Chem. Res.* **4**, 17–22.

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Cadmium Fluorophosphate, $Cd_2(PO_4)F$

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Abstract. Monoclinic, $C2/c$, $a = 13.879$ (2), $b = 6.693$ (1), $c = 10.519$ (1) Å, $\beta = 120.22$ (1)°, $Z = 8$, $D_x = 5.385$ g cm⁻³. The crystals were grown from a melt containing excess CdF_2 . $Cd_2(PO_4)F$ is isostructural with $Mn(PO_4)F$.

Introduction. Cadmium fluorophosphate was first reported by Engel (1970) to crystallize in the space group $C2/c$, who pointed out its structural relationship to the minerals of the wagnerite group [$M_2(PO_4)X$]. In a detailed investigation (Rea & Kostiner, 1972) of $Mn_2(PO_4)F$, a synthetic end member of the series represented by the mineral triplite [$(Mn, Fe)_2(PO_4)F$], we discussed a possible explanation for the disorder found at the fluorine position in the mineral in terms of cation size. The fluorine atom in synthetic $Mn_2(PO_4)F$ is not disordered. To help resolve this question, we have

carried out a refinement of the crystal structure of $Cd_2(PO_4)F$.

Crystals were grown by cooling a melt of $Cd_3(PO_4)_2$ and excess CdF_2 from 1075°C at 20°C⁻¹. A sphere was ground to a radius of 0.0055 cm; precession photographs confirmed the space group as $C2/c$. The lattice parameters were determined in a PICK II least-squares refinement program using 48 reflections, each automatically centered on a Picker FACS-I four-circle diffractometer using Mo $K\alpha_1$ radiation.

Diffraction intensities were measured using Zr-filtered Mo $K\alpha$ radiation at a take-off angle of 2.5° with the diffractometer operating in the θ - 2θ scan mode. Scans were made at 1° per min over 1.5° with allowance for dispersion and with 40 s background counts taken at both ends of the scan. Of the 1411 independent data investigated in the angular range $2\theta < 62^\circ$, 1344 were considered observable according to the criterion $|F_o| > 0.8\sigma_F$, where σ_F is defined as $0.02|F_o| + [C + k^2B]^{1/2}/2|F_o|Lp$; the total scan count is

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