Table 7. *Deviations from mean planes*

′ Denotes mirror image.

Equations of planes	Atoms in plane	Atom out of plane	Deviation
$(-0{\cdot}7884)x+(0{\cdot}0000)y+(-0{\cdot}6152)z-(-1{\cdot}5391)=0$	C(2), C(2′), C(3), C(3′)	C(1)	−0·28 (6) Å
$(-0{\cdot}8188)x+(0{\cdot}0000)y+(-0{\cdot}5741)z-(-1{\cdot}7059)=0$	C(02), C(02′), C(03), C(03′)	C(01)	−0·11 (8)
$(-0{\cdot}8435)x+(0{\cdot}0000)y+(-0{\cdot}5371)z-(4{\cdot}0206)=0$	C(5), C(5′), C(6), C(6′)	C(4)	−0·11 (5)
$(-0{\cdot}8643)x+(0{\cdot}0000)y+(-0{\cdot}5030)z-(3{\cdot}9024)=0$	C(05), C(05′), C(06), C(06′)	C(04)	−0·03 (4)
$(-0{\cdot}1317)x+(-0{\cdot}0897)y+(-0{\cdot}9872)z-(1{\cdot}7916)=0$	Cr(1), Cr(2), N(3)		
$(-0{\cdot}1317)x+(-0{\cdot}0897)y+(-0{\cdot}9872)z-(2{\cdot}2066)=0$	Cr(1), Cr(2), N(3′)		

Wheatley (1967) proposed a Cr–ring (centre) distance of 1·77 Å in unperturbed Cr π-cp complexes. In this case, the average value of the Cr–ring (centre) distance determined is 1·89 Å. This lengthening of the Cr–ring (centre) distance may be due to π back-donation of electrons of the NO group to the metal atom rather than to the electrophilicity of the NO groups proposed by Wheatley (1967).

The two disordered orientations of each cyclopentadiene ring make an angle of less than 3° between themselves. The rings are non-parallel and subtend an angle of at leat 5° (taking the planes nearest parallel in pairs), somewhat higher than the usual maximum of 3°. This may be explained by a combination of the following factors: (i) in the parent molecule, the NO and NH_2 groups will not allow mirror symmetry. They provide an asymmetric electronic distribution about the chromium atoms, thus causing a different tilt for each of the cyclopentadiene rings; (ii) disordering of both the cyclopentadiene rings and the parent molecule has the effect of blurring the images of the structure.

We wish to thank Dr N. Flitcroft for supplying us with a sample of the compound and for his interest in this work. Our thanks are also due to Dr F. R. Ahmed (National Research Council, Ottawa) and Dr B. R. Penfold (University of Canterbury, New Zealand) for supplying their computer programs. This work was supported by operating grants from the National Research Council of Canada.

References

AHMED, M., BRUCE, R. & KNOX, G. (1966). *Z. Naturf.* B, **21**, 289.

AHMED, F. R. & HALL, S. R. (1968). Private communication.

BAIRD, M. C. (1968). *Progr. Inorg. Chem.* **9**, 122.

BUSH, M. A., SIM, G. A., KNOX, G. A., AHMAD, M. & ROBERTSON, C. G. (1969). *Chem. Comm.* p. 74.

CARTER, O. L., MCPHAIL, A. T. & SIM, G. A. (1966). *J. Chem. Soc.* A, p. 1095.

COTTON, F. A. & RICHARDSON, D. C. (1966). *Inorg. Chem.* **5**, 1851.

COTTON, F. A. & WILKINSON, G. (1966). *Advanced Inorganic Chemistry*, 2nd Ed. New York: Interscience.

FLITCROFT, N. (1968). *J. Organometallic Chem.* **15**, 254.

GELLER, S. (1961). *Acta Cryst.* **14**, 1026.

HODGSON, D. J. & IBERS, I. A. (1968). *Inorg. Chem.* **7**, 2345.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

KETTLE, S. F. A. (1965). *Inorg. Chem.* **4**, 1661.

THOMAS, J. T., ROBERTSON, J. H. & COX, E. G. (1958). *Acta Cryst.* **11**, 599.

TULLBERG, A. & VANNERBERG, N.-G. (1967). *Acta Chem. Scand.* **21**, 1462.

WHEATLEY, P. J. (1967). *Perspectives in Structural Chemistry*, **1**, p. 27.

Acta Cryst. (1970). B**26**, 1905

The Crystal Structure of Diethylaminoborondifluoride

BY I. A. S. EDWARDS AND H. P. STADLER

School of Chemistry, The University, Newcastle upon Tyne, England

(*Received* 8 *December* 1969)

The crystal structure of diethylaminoborondifluoride $(C_2H_5)_2NBF_2$, has been solved, using low-temperature photographic data, and refined to a residual of 11·3% with $\sigma_x \simeq 0{\cdot}01$ Å. The space group is $P4_2/n$ with $a=b=14{\cdot}2$, $c=6{\cdot}44$ Å, $Z=4$ (dimers). The molecule has been confirmed as dimeric with the $(B–N)_2$ ring similar to other $(B–N)_2$ rings but with the B–N bond (1·64 Å) significantly longer.

Introduction

Substituted aminoboranes of the type R_2NBX_2, where R is methyl or ethyl and X is Cl or F, can exist either as monomers, *e.g.* Et_2NBCl_2 (Ostoff & Brown, 1952) or as dimers in which $(BN)_2$ forms a four-membered ring as in (Me_2NBF_2) (Hazell, 1966; Bannister, Greenwood, Straughan & Walker, 1964). Diethylaminoborondifluoride, $(C_2H_5)_2NBF_2$, was first described by Gerrard, Lappert & Pearce (1957). Infrared and nuclear magnetic resonance spectra (Greenwood & Walker, 1967) suggested that the molecules exist as dimers in the solid state. Walker, who prepared all the crystals used in this investigation, also carried out some preliminary X-ray work. His data were collected at room temperature, at which the crystals decompose even when sealed into glass capillary tubes to protect them from moisture. He therefore abandoned his attempt to solve the structure.

To reduce the rate of decomposition and to improve the accuracy and amount of data in general, a Weissenberg low-temperature attachment was designed and built in this laboratory which allowed the crystal to be cooled to temperatures below 100°K in a stream of evaporating nitrogen (Edwards, 1968). Equi-inclination Weissenberg photographs of the (*hk*0) to (*hk*4) layers were taken with the crystal at 100°K, using filtered Cu $K\alpha$ radiation and a four film pack. The intensities were estimated visually and the layers were correlated using the double-slit method (Stadler, 1950).

Table 1. *Final atomic parameters*

The standard deviations are given in brackets.

	x (Å)	y (Å)	z (Å)	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
N(1)	−0·059 (4)	1·150 (4)	0·295 (6)	0·013 (2)	0·017 (2)	0·003 (4)	−0·004 (4)	0·009 (4)	−0·001 (3)
F(1)	1·286 (3)	−0·381 (3)	1·786 (5)	0·021 (2)	0·024 (2)	0·008 (3)	0·009 (4)	−0·022 (3)	−0·012 (3)
F(2)	2·211 (3)	0·179 (3)	−0·279 (5)	0·007 (1)	0·019 (1)	0·022 (3)	0·000 (3)	0·016 (3)	−0·003 (3)
B(1)	1·033 (5)	−0·062 (6)	0·448 (9)	0·009 (2)	0·019 (3)	0·014 (6)	0·005 (6)	0·000 (6)	−0·002 (4)
C(1)	−0·589 (6)	1·666 (7)	1·662 (9)	0·016 (2)	0·034 (3)	0·013 (6)	−0·029 (7)	0·006 (6)	0·007 (4)
C(2)	0·393 (5)	2·283 (5)	−0·675 (9)	0·014 (2)	0·018 (2)	0·030 (6)	0·026 (6)	0·007 (6)	−0·005 (4)
C(3)	−1·765 (6)	2·640 (7)	1·488 (10)	0·021 (3)	0·034 (3)	0·037 (7)	−0·037 (7)	−0·007 (7)	0·013 (4)
C(4)	1·479 (5)	3·213 (6)	−0·027 (9)	0·014 (2)	0·024 (3)	0·034 (6)	0·008 (6)	−0·001 (6)	−0·004 (4)

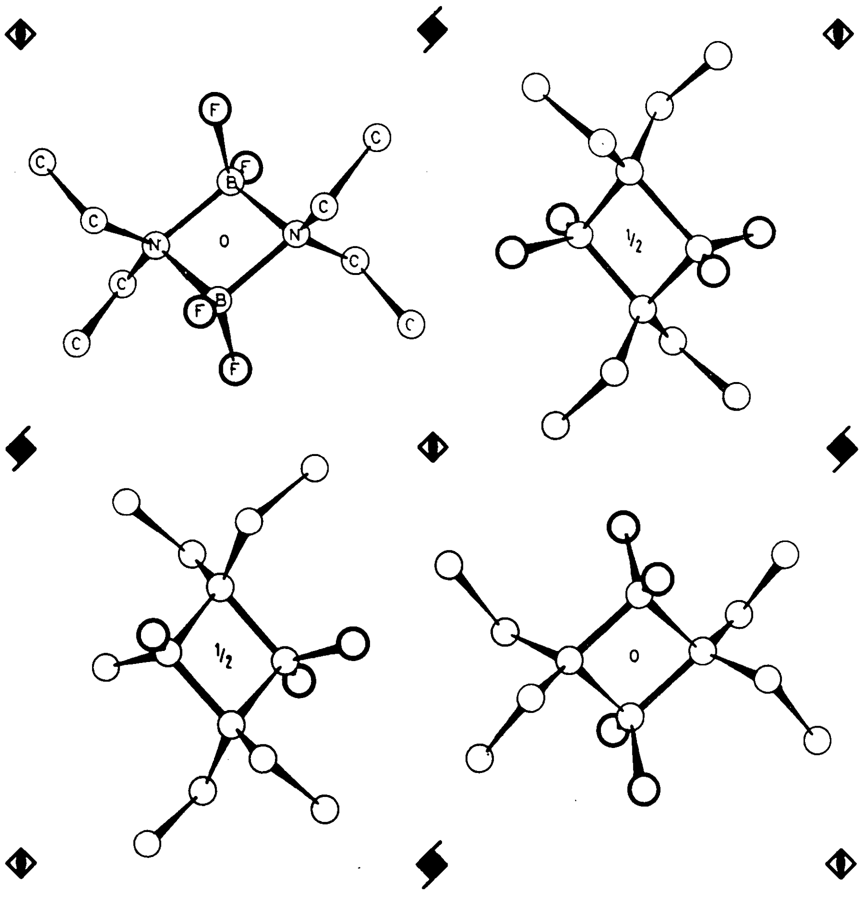

Fig. 1. The structure viewed along the c axis.

Table 2. *Observed and calculated structure factors*

Values for the unobserved reflexions are primed.

h	F_o	F_c
	h00	
2	-	131.3
4	9.0	5.1
6	40.9	41.4
8	44.8	31.8
10	21.5	22.1
12	31.1	28.5
14	[illegible]	4.0
16	12.8	-14.3
	h10	
1	-	9.7
3	15.6	19.7
5	*43.9	-52.1
7	10.0	9.3
9	22.4	-19.4
11	4'	-2.7
13	4'	-2.8
15	12.5	-11.8
17	3'	-2.3
	h20	
2	20.2	20.6
4	22.2	-16.0
6	15.3	-10.5
8	32.9	-30.9
10	3'	-2.4
12	22.8	22.1
14	22.1	22.4
16	13.6	-12.7
	h30	
1	13.0	8.7
3	*47.0	67.6
5	*49.3	61.5
7	16.3	11.5
9	8.4	-4.2
11	37.5	42.7
13	34.7	41.1
15	3'	0.6
17	2'	1.0
	h40	
2	33.1	-37.2
4	*81.5	-132.0
6	44.2	-46.6
8	41.0	-42.4
	h40	
10	27.5	[illegible]
12	22.3	[illegible]
14	19.9	[illegible]
16	16.6	-17.7
	h50	
1	30.8	[illegible]
3	2'	-3.3
5	42.5	41.2
7	3'	-1.4
9	17.2	14.9
11	[illegible]	[illegible]
13	[illegible]	15.5
15	3'	5.3
17	10.3	9.3
	h60	
2	9.3	3.5
4	50.1	-56.3
6	3'	-0.4
8	24.0	-20.9
10	30.8	-31.5
12	19.4	21.3
14	7.2	8.1
16	3'	-4.0
	h70	
1	15.3	10.7
3	15.3	11.4
5	6.6	-5.3
7	51.3	-65.7
9	49.7	-49.1
11	18.0	-17.1
13	8.6	-8.2
15	13.7	-13.7
	h80	
2	3'	-4.3
4	6.8	5.4
6	18.7	-13.4
8	32.6	-35.9
10	16.8	-17.7
12	28.4	29.8
14	11.8	11.2
16	9.0	-8.3
	h90	
1	21.3	15.2
3	3'	1.9
5	3'	2.2
7	14.2	-9.9
9	32.6	-34.8
11	4'	1.1
13	3'	-0.9
15	6.9	-7.0
	h10,0	
2	15.2	-12.9
4	16.2	13.9
6	4'	4.6
8	11.5	-11.0
10	12.9	-12.5
12	3'	3.6
14	15.5	18.1
	h11,0	
1	4'	1.0
3	4'	7.0
5	31.6	29.0
7	20.4	20.2
9	13.7	-13.0
11	15.9	17.3
13	11.5	12.8
	h12,0	
2	45.1	49.5
4	32.8	33.6
6	11.5	10.5
8	9.5	-8.7
10	5.1	4.7
12	15.4	16.5
	h13,0	
1	18.0	-16.3
3	[illegible]	[illegible]
5	14.5	13.3
7	13.9	-12.9
9	12.3	-14.6
11	3'	2.2
	h14,0	
2	17.6	16.8
4	4'	4.2
6	8.3	8.4
8	11.0	-10.9
10	3'	-0.8
	h15,0	
1	12.7	-11.0
3	8.9	-7.9
5	22.9	23.8
7	3'	0.5
9	14.6	-13.2
	h16,0	
2	11.2	-9.7
4	3'	-3.2
6	15.0	-13.5
8	16.1	-19.9
	h17,0	
1	10.4	11.9
3	5.9	5.1
5	14.7	19.3
	h01	
1	-	-10.5
2	22.3	21.4
3	8.0	10.6
4	36.2	-42.2
5	14.3	15.7
6	17.8	14.4
7	50.9	52.3
8	3'	1.4
9	53.4	61.6
10	16.9	-13.9
11	17.9	15.7
12	8.1	6.3
13	4'	0.3
14	8.6	-7.7
15	4.8	3.4
16	6.9	-4.7
17	3.5	-4.6
	h11	
1	-	115.4
2	17.9	-15.6
3	25.4	-31.3
4	26.2	-28.4
5	40.5	48.3
6	11.1	-9.6
7	37.1	36.5
8	3'	-3.0
9	12.3	10.3
10	12.9	14.1
11	17.7	14.0
12	4'	4.4
13	32.7	33.5
14	18.3	-17.8
15	11.0	9.1
16	11.0	-9.3
17	5.4	7.4
	h21	
1	*30.2	-40.1
2	24.5	-27.9
3	6.2	-4.8
4	14.5	11.3
5	7.5	-4.6
6	26.5	22.3
7	39.1	38.4
8	4.1	-5.5
9	25.6	21.7
	h21	
10	30.3	-32.2
11	5.1	-5.5
12	4'	0.2
13	4'	4.2
14	4'	-2.0
15	3'	-6.0
16	6.5	4.4
17	20.4	-16.8
	h31	
1	26.0	25.9
2	*61.7	-94.4
3	47.1	-54.3
4	*55.5	-68.1
5	23.3	-19.5
6	32.5	-30.8
7	18.2	-17.0
8	4.2	1.3
9	33.3	-32.5
10	16.4	14.9
11	7.9	8.4
12	4'	0.2
13	26.0	27.1
14	4'	0.6
15	3'	4.5
16	6.3	4.4
17	11.0	-8.3
	h41	
1	29.8	25.5
2	24.2	-22.2
3	32.7	-32.5
4	22.8	23.3
5	47.6	-52.2
6	22.6	21.2
7	7.9	6.4
8	18.6	16.9
9	3'	0.6
10	8.3	9.3
11	10.1	-9.3
12	20.0	20.6
13	5.2	-6.2
14	9.7	8.0
15	7.6	-9.8
16	3.9	3.3
17	3.1	-4.3
	h51	
1	23.2	24.6
2	6.8	-6.1
3	43.7	-41.4
4	47.8	-49.0
5	27.2	-30.1
6	31.8	-36.3
7	7.1	7.0
8	20.1	17.8
9	26.5	-27.9
10	19.7	19.2
11	4'	-1.9
12	4'	1.4
13	4'	-0.3
14	3'	-0.9
15	14.9	-12.9
16	3'	-1.2
17	11.6	-12.9
	h61	
1	9.9	8.1
2	52.9	-59.9
3	17.4	-13.7
4	3'	-3.0
5	19.6	-19.2
6	22.6	18.7
7	24.8	-21.5
8	18.8	-16.0
9	4'	2.7
10	17.6	-14.4
11	11.3	11.1
12	9.7	-8.7
13	4'	-3.8
14	3'	-0.5
15	7.5	-6.9
16	2'	-1.4
	h71	
1	17.6	15.7
2	48.9	44.1
3	3'	-1.2
4	3'	-2.0
5	7.4	-6.6
6	17.2	15.3
7	5'	-3.2
8	21.6	21.3
9	27.4	-29.1
10	5.2	5.7
11	4'	-0.9
12	8.6	9.8
13	13.6	13.5
14	4.5	-4.0
15	9.2	-9.6
16	13.2	-15.2
	h81	
1	17.8	-17.6
2	19.7	-15.1
3	12.4	-11.0
4	14.7	-10.0
5	16.8	-13.7
6	4.2	6.0
7	13.9	-15.2
8	31.6	32.5
9	8.7	9.3
10	12.3	-11.1
11	4.7	4.4
12	4'	-2.5
13	3'	0.9
14	10.5	-10.1
15	3'	-2.7
	h91	
1	7.6	-6.8
2	19.5	17.9
3	37.4	-39.7
4	17.1	-16.1
5	30.1	-27.8
6	12.4	15.0
7	18.6	-19.9
8	12.6	11.7
9	8.2	-8.7
10	5.3	1.7
11	4'	-1.5
12	4.8	5.1
13	13.0	11.2
14	3.8	-2.0
15	7.2	-7.3
	h10,1	
1	5'	2.6
2	3'	-1.2
3	4'	3.2
4	17.2	15.3
5	24.0	-27.2
6	36.3	38.7
7	8.1	-7.9
8	4'	6.4
9	19.1	18.0
10	5.1	3.2
11	12.3	12.9
12	10.9	12.2
13	8.8	8.0
14	2'	-0.8
	h11,1	
1	14.9	14.1
2	11.8	-9.6
3	8.5	-7.8
4	20.0	-18.6
	10.2	8.1
	18.4	-14.2
7	8.5	-6.5
8	9.4	-8.4
9	4'	-3.5
10	7.9	3.8
11	3'	3.1
12	6.9	7.0
13	14.9	14.0
	h12,1	
1	17.6	16.6
2	8.8	-8.0
3	13.1	12.7
4	16.9	16.1
5	5.3	-4.8
6	12.2	9.2
7	4'	-1.4
8	10.6	-4.4
9	5.1	7.7
10	8.1	-6.3
11	21.2	20.9
12	14.3	13.8
13	10.1	12.9
	h13,1	
1	33.0	36.2
2	5.3	-7.0
3	16.3	15.7
4	8.8	-7.6
5	11.1	10.2
6	8.8	-8.3
7	7.3	7.1
8	5.1	-5.8
9	10.2	9.1
10	9.7	-8.7
11	19.2	21.9
12	2.8	4.5
	h14,1	
1	18.4	19.1
2	23.5	-23.4
3	5.1	2.3
4	4'	-2.0
5	4'	-1.8
6	3'	-2.6
7	8.0	-8.0
8	12.7	-13.9
9	3.8	-1.9
10	12.3	-14.5
	h15,1	
1	4.8	-3.8
2	11.1	9.1
3	3'	0.5
4	7.6	-6.7
5	4.4	-3.0
6	3'	-2.0
7	3'	1.6
8	3'	-0.7
9	2'	-3.4
	h16,1	
1	8.5	5.9
2	3'	-3.2
3	3'	1.6
4	13.3	10.1
5	9.3	-8.4
6	12.7	12.0
7	15.5	-15.1
	h17,1	
1	3.5	-5.1
2	3.4	4.5
3	2'	0.4
4	2'	0.7
5	9.2	-11.4
	h02	
1	10.2	-11.2
2	1'	-0.0
3	16.3	-15.9
4	28.8	33.2
5	7.0	-5.6
6	29.8	28.5
7	3'	0.8
8	17.3	16.0
9	3'	-3.9
10	7.2	5.6
11	7.5	-6.8
12	32.3	36.9
13	4'	-3.7
14	26.0	28.6
15	3'	-3.0
16	3'	-1.0
17	2.2	0.0
	h12	
1	*44.4	-55.5
2	22.6	23.2
3	*43.7	-51.4
4	24.0	-23.1
5	16.7	15.8
6	14.4	-14.3
7	33.1	31.1
8	18.8	16.3
9	28.1	-30.1
10	3'	-0.7
11	26.7	-28.0
12	4'	-2.6
13	14.4	-14.9
14	9.0	8.5
15	3'	4.4
16	6.8	-6.2
17	2'	4.5
	h22	
1	19.5	21.5
2	20.6	-22.8
3	19.2	18.0
4	14.3	-17.0
5	20.7	19.1
6	49.7	55.8
7	3'	-0.1
8	3'	0.4
9	8.8	-7.9
10	7.3	-8.3
11	4'	-7.1
12	23.2	23.5
13	4'	-3.8
14	28.7	31.6
15	3'	-2.7
16	10.8	12.1
17	2'	-8.1
	h32	
1	16.0	-17.7
2	7.6	[illegible]
3	6.8	-4.5
4	[illegible]	-44.4
5	7.1	5.5
6	29.2	-26.7
7	18.9	16.6
8	3'	4.3
9	10.6	-10.5
10	13.7	-13.4
11	24.5	-26.4
12	13.8	-11.9
13	4'	0.9
14	3'	1.9
15	6.5	4.4
16	3'	-5.6
17	9.3	11.8
	h42	
1	21.6	-20.6
2	17.2	17.9
3	28.2	-30.0
4	24.9	-23.0
5	24.2	-19.9
6	5.8	4.8
7	22.0	-19.4
8	27.5	-26.4
9	20.7	-19.4
10	3'	-0.8
11	15.4	-14.6
12	4'	3.0
13	4'	-2.3
14	15.9	-16.6
15	3'	0.1
16	10.2	-13.1
	h52	
1	35.1	-38.8
2	8.7	9.5
3	49.1	-47.4
4	12.1	-11.3
5	16.3	16.6
6	3'	0.5
7	25.0	25.6
8	23.8	23.4
9	4'	-0.3
10	12.8	12.5
11	13.8	-14.8
12	4'	4.3
13	4'	2.7
14	10.9	10.4
15	7.8	-6.5
16	2'	3.6
	h62	
1	2'	-3.4
2	8.7	-7.6
3	11.0	-10.5
4	14.5	13.4
5	6.1	-5.6
6	21.5	18.1
7	3'	0.8
8	7.2	-4.2
9	17.0	-14.0
10	17.5	-16.5
11	7.8	-7.0
12	4'	-3.9
13	9.3	5.5
14	12.3	-13.7
15	3'	-1.3
16	10.0	-14.1
	h72	
1	41.0	-44.0
2	12.8	10.1
3	63.0	-62.4
4	9.8	4.8
5	31.7	29.4
6	6.8	6.2
7	19.5	17.3
8	22.8	22.8
9	21.1	-21.4
10	11.0	10.9
11	10.9	-9.7
12	4'	-1.9
13	3'	-1.2
14	3'	5.7
15	3'	-1.9
	h82	
1	25.1	25.5
2	35.9	-34.8
3	10.2	8.5
4	35.3	-31.8
5	13.8	13.0
6	28.1	-23.4
7	24.8	20.8
8	4'	4.1
9	4'	-2.9
10	4'	-5.1
11	4'	-0.5
12	10.2	8.7
13	14.7	10.0
14	3'	-5.2
15	3'	-1.9
	h92	
1	3'	-0.4
2	3'	-4.8
3	12.7	-13.4
4	14.2	-14.0
5	25.9	23.1
6	6.8	6.2
7	22.7	21.2
8	4'	3.3
9	7.8	7.4
10	4'	-5.2
11	13.6	14.2
12	15.2	-14.0
13	9.6	-9.1
14	12.3	-13.7
	h10,2	
1	11.4	10.6
2	35.9	-34.8
3	9.0	-7.2
4	44.2	-43.0
5	4'	2.0
6	22.0	-19.8
7	11.0	11.2
8	10.0	-7.4
9	4'	0.5
10	4'	-1.8
11	3'	4.2
12	3'	4.6
13	13.8	14.2
14	2'	-5.1
	h11,2	
1	15.1	-14.9
2	7.6	-5.1
3	17.4	17.0
4	9.9	-9.8
5	27.0	25.8
6	4'	-3.5
7	15.4	[illegible]
8	4'	6.9
9	9.4	-8.3
10	3'	4.6
11	6.3	3.8
12	3'	0.1
13	4.6	6.3
	h12,2	
1	4'	5.2
2	4'	3.2
3	4'	-6.2
4	7.8	-5.1
5	4'	2.0
6	9.8	12.3
7	13.2	10.5
8	3'	-3.9
9	3'	0.5
10	17.5	15.7
11	3'	-0.1
12	11.9	12.3
	h13,2	
1	4'	-4.6
2	4'	-7.9
3	4'	-8.1
4	4'	-3.7
5	10.5	-8.4
6	7.2	5.1
7	6.9	-7.2
8	10.4	8.6
9	15.5	-12.4
10	8.6	7.5
11	5.6	-7.0
	h14,2	
1	17.0	16.1
2	10.4	9.1
3	3'	1.4
4	3'	-1.4
5	3'	-0.8
6	11.4	12.0
7	10.8	8.8
8	19.5	16.9
9	2.5	-2.8
10	21.1	23.3
	h15,2	
1	3'	-0.7
2	15.2	-14.1
3	10.4	-8.7
4	10.0	-9.7
5	9.3	8.5
6	7.4	-5.6
7	8.6	-8.2
8	2'	-1.9
	h16,2	
1	3'	2.0
2	3'	-1.4
3	[illegible]	-9.9
4	3'	-1.7
5	13.5	-12.0
6	7.1	-7.7
	h17,2	
1	2'	1.6
2	8.3	-9.3
3	2'	-2.3
	h03	
1	24.6	29.3
2	19.8	19.3
3	9.8	-7.6
4	32.0	38.2
5	34.8	-38.9
6	3'	-2.7
7	3'	1.5
8	12.6	8.0
9	3'	1.9
10	3'	2.6
11	4'	2.6
12	14.7	-10.6
13	17.6	19.6
14	3'	-0.2
15	11.7	10.5
16	2'	2.4
	h13	
1	*48.8	55.2
2	36.1	38.1
3	2'	-1.0
4	31.1	33.7
5	17.8	17.7
6	9.5	8.8
7	14.1	12.3
8	10.3	3.0
9	14.8	13.0
10	12.7	-12.3
11	13.1	11.9
12	12.0	-9.4
13	18.3	19.3
14	11.8	10.2
15	3'	3.3
16	2'	-0.6
	h23	
1	19.7	20.8
2	5.6	-4.1
3	21.5	-22.5
4	17.7	14.9
5	31.5	-34.4
6	20.2	22.2
7	22.1	-20.4
8	11.5	11.5
9	3'	-4.1
10	12.8	-12.8
11	16.0	-13.8
12	14.2	13.0
13	12.6	-11.6
14	11.6	9.6
15	3	-1.5
16	2'	2.3
	h33	
1	27.0	26.7
2	28.8	33.5
3	19.2	-17.4
4	20.5	18.9
5	17.9	-14.2
6	3'	-1.5
7	[illegible]	-15.9
8	21.1	-18.8
9	23.7	-21.6
10	27.3	-29.1
11	12.0	10.6
12	11.9	-9.3
13	3'	6.1
14	3'	-2.7
15	3'	-1.8
16	12.3	-11.6
	h43	
1	2'	-6.2
2	22.3	20.8
3	2'	6.7
4	20.5	20.6
5	15.2	-13.3
6	12.9	9.7
7	10.3	4.2
8	11.0	10.7
9	16.3	18.0
10	4'	0.5
11	4'	-1.3
12	16.6	17.9
13	3'	4.6
14	3'	4.1
15	5'	5.8
16	2'	-7.5
	h53	
1	2'	-4.7
2	27.7	-29.7
3	25.5	-25.1
4	18.5	-18.1
5	27.1	-26.4
6	3'	2.4
7	15.1	-18.1
8	27.8	-31.5
9	22.2	-22.5
10	29.3	-32.1
11	4'	4.0
12	3.4	0.4
13	3'	-5.0
14	3'	5.2
15	2'	-6.2
	h63	
1	9.5	7.9
2	21.7	-21.0
3	3'	2.7
4	10.5	-8.8
5	3'	2.1
6	13.0	10.4
7	40.6	42.9
8	16.4	-17.0
9	33.4	38.0
10	17.0	-19.2
11	4'	1.9
12	3'	-4.0
13	12.8	15.2
14	3'	4.7
15	12.8	15.0
	h73	
1	3'	-9.7
2	3'	-4.1
3	3'	4.3
4	3'	-0.7
5	3'	-0.2
6	3'	8.3
7	3'	-3.7
8	11.8	-6.1
9	13.1	-12.1
10	3.6	-7.9
11	12.7	8.9
12	3'	3.5
13	14.0	17.8
14	11.5	11.4
15	2'	2.7
	h83	
1	12.6	11.6
2	10.4	8.5
3	11.7	-9.5
4	3'	-5.8
5	21.9	-16.8
6	3'	1.2
7	13.0	11.3
8	23.6	-23.5
9	4'	3.9
10	11.7	-6.9
11	13.7	-13.5
12	3'	-3.3
13	3'	-7.7
14	2'	-3.2
	h93	
1	3'	5.6
2	15.7	16.2
3	11.3	-6.3
4	17.8	17.3
5	3'	-2.1
6	11.8	9.2
7	4'	-7.8
8	4'	5.3
9	4'	-2.1
10	3'	-0.5
11	3'	6.1
12	13.6	14.3
13	8.3	7.8
14	15.3	19.9
	h10,3	
1	11.6	-7.6
2	3'	6.0
3	22.9	-22.5
4	11.9	9.3
5	4'	-5.4
6	14.7	13.7
7	4'	-0.2
8	3'	-2.4
9	11.3	-10.0
10	3'	-6.7
11	13.1	-15.0
12	3'	0.2
13	8.5	-10.9
	h11,3	
1	13.1	11.3
2	11.3	8.8
3	4'	-1.6
4	4'	-1.6
5	22.4	19.7
6	16.7	15.9
7	3'	-7.1
8	15.0	13.9
9	13.0	-14.1
10	3'	-3.8
11	3'	-1.2
12	10.3	11.1
	h12,3	
1	16.0	-15.3
2	4'	-3.6
3	15.9	-14.3
4	4'	7.8
5	3'	4.0
6	3'	-2.0
7	14.7	16.2
8	3'	-4.0
9	12.9	14.7
10	8.6	-9.3
11	2'	-2.5
	h13,3	
1	18.3	19.1
2	16.3	16.6
3	3'	4.3
4	3'	-3.6
5	13.4	11.8
6	12.8	12.6
7	3'	2.5
8	10.1	8.6
9	2'	1.6
10	2'	-2.6
	h14,3	
1	23.1	-23.7
2	5'	-6.3
3	14.4	-15.7
4	3'	6.3
5	3'	-5.6
6	3'	3.6
7	3'	6.4
8	2'	2.9
9	2'	6.5
	h15,3	
1	3'	-9.7
2	3'	-0.8
3	5'	0.5
4	12.4	-10.4
5	2'	3.4
6	2'	-2.7
7	2'	2.3
	h16,3	
1	15.0	-15.4
2	2'	5.1
3	17.8	-18.9
4	16.2	16.5
	h04	
1	4.1	2.6
2	22.8	23.3
3	8.1	7.6
4	10.4	-7.1
5	18.3	18.0
6	8.6	-8.4
7	3'	4.6
8	12.2	11.9
9	3'	-1.2
10	13.2	13.1
11	12.3	12.9
12	3'	-2.2
13	6.9	5.3
14	12.0	-9.5
15	2.2	0.3
	h14	
1	4.7	5.4
2	10.6	-9.2
3	2'	-0.9
4	33.2	-38.1
5	9.0	-7.9
6	3'	1.3
7	20.0	22.0
8	32.8	34.6
9	3'	0.1
10	17.7	18.1
11	12.7	11.1
12	3'	0.3
13	7.5	7.9
14	3'	0.9
15	7.1	-6.7
	h24	
1	4.7	2.7
2	11.5	10.5
3	11.8	-11.8
4	7.3	8.7
5	26.6	-28.7
6	3'	1.1
7	3'	-4.2
8	7.2	-5.1
9	3'	3.6
10	16.4	15.1
11	7.6	-7.2
12	3'	-0.3
13	3'	-2.4
14	3'	1.7
15	4.9	-3.5
	h34	
1	24.0	26.4
2	10.3	-8.6
3	27.4	25.7
4	35.8	-36.4
5	26.3	29.2
6	19.5	-18.5
7	16.9	16.4
8	16.6	14.3
9	3'	-1.3
10	3'	2.5
11	21.6	21.7
12	12.5	-11.5
13	22.9	22.6
14	7.8	-7.8
15	14.5	-12.3
	h44	
1	18.8	-17.8
2	12.5	-11.1
3	39.8	-35.6
4	29.4	-29.7
5	30.9	-33.3
6	20.4	-19.2
7	12.3	-12.4
8	13.9	-16.9
9	8.5	-8.8
10	3'	-1.0
11	3'	-1.3
12	3'	4.0
13	3'	3.8
14	2'	0.1
15	2'	-1.0
	h54	
1	19.7	15.2
2	3'	1.7
3	17.4	-16.8
4	22.7	-23.4
5	3'	-2.0
6	9.4	-7.0
7	8.0	-8.6
8	23.6	25.0
9	3'	0.5
10	7.6	7.1
11	3'	-1.6
12	3'	0.7
13	3'	2.6
14	5.7	4.8
	h64	
1	16.7	15.6
2	14.6	-14.8
3	17.8	-16.5
4	18.8	-18.6
5	14.7	-16.6
6	8.0	-4.6
7	3'	-0.4
8	7.6	-7.1
9	3'	0.8
10	7.5	-5.8
11	3'	0.7
12	11.4	13.6
13	3'	1.5
14	2'	4.2
	h74	
1	9.4	9.0
2	6.8	-4.9
3	3'	2.0
4	29.1	-33.2
5	10.8	-10.9
6	13.0	-13.3
7	26.1	-28.1
8	14.3	15.2
9	15.8	-15.8
10	8.0	5.4
11	9.2	-8.3
12	3'	1.6
13	2'	0.3
	h84	
1	38.7	45.2
2	3'	1.2
3	21.6	23.4
4	26.1	24.9
5	8.3	7.6
6	8.3	5.9
7	16.0	13.1
8	13.9	-11.7
9	10.9	12.2
10	5'	4.0
11	9.1	9.3
12	19.7	21.7
13	14.1	13.1
	h94	
1	18.2	20.1
2	13.0	-12.2
3	10.7	10.3
4	30.2	-29.2
5	7.6	-5.0
6	13.2	-14.1
7	3'	3.8
8	3'	-1.7
9	7.7	-9.2
10	3'	0.8
11	3'	-3.9
12	2'	1.8
	h10,4	
1	25.5	26.0
2	10.8	-9.3
3	3'	7.1
4	21.1	21.9
5	3'	-2.2
6	12.1	12.1
7	10.8	10.1
8	8.9	-9.2
9	3'	4.9
10	7.6	-7.0
11	7.4	7.3
	h11,4	
1	3'	-0.3
2	3'	-0.7
3	3'	2.7
4	9.5	-8.3
5	3'	-0.3
6	7.1	3.8
7	11.1	10.6
8	13.9	15.2
9	5'	-5.8
10	14.1	13.6
	h12,4	
1	16.1	14.5
2	9.8	7.2
3	11.2	-8.9
4	10.5	11.1
5	13.0	-13.7
6	3'	1.8
7	5'	-1.5
8	14.1	-14.6
9	6.8	-6.2
	h13,4	
1	7.5	-7.7
2	3'	2.1
3	3'	1.3
4	3'	-3.4
5	3'	2.1
6	3'	-0.9
7	2'	-0.4
8	10.5	10.0
	h14,4	
1	12.8	12.0
2	5'	-3.8
3	5'	-4.7
4	2'	-1.6
5	7.8	-7.5
6	9.0	9.3
	h15,4	
1	2'	-0.2
2	9.8	-8.6
3	6.6	7.4
4	12.8	-14.3

The crystals have tetragonal symmetry with:

$a=b=14{\cdot}2\pm0{\cdot}1,\ c=6{\cdot}44\pm0{\cdot}01$ Å

$\varrho_{\text{obs}}=1{\cdot}18,\ \varrho_{\text{calc}}=1{\cdot}25$ g.cm^{-3}, $Z=8$ monomers or 4 dimers

Absences in the $hk0$ zone for $h+k$ odd gave two possible space groups $P4/n$ or $P4_2/n$. Since no (001) observations were available, Patterson sections at $z=0$ and $z=\frac{1}{2}$ were calculated and these indicated $P4_2/n$ as the correct space group.

Structural work

Packing considerations strongly favoured the dimeric form, and models of this form based on the dimeric molecules previously studied (Hazell, 1966; Hess, 1963) were constructed. They could adopt a molecular symmetry of 222, *mmm* or 2/*m*, depending on the positions of the second ethyl carbon atoms, but the only point group compatible with the short *c* axis and the space group, $P4_2/n$, was 2/*m* with the molecules on centres of symmetry.

The two independent groups of centres in the unit cell differ only in the choice of origin, so that the molecular centre was fixed at 0,0,0.

The structure was solved from Patterson syntheses, calculated using the Glasgow Fourier program on the University KDF9 computer. The F–F vectors were identified in the ($hk0$) projection of the Patterson function.

Comparison of the above mentioned molecular model with the fluorine positions so obtained indicated the orientation of the molecule. This was confirmed by the identification of fluorine to light atom peaks in the 3-D Patterson synthesis and gave a trial structure.

This structure was refined using the Glasgow *SFLS* program. With all observed reflexions included and refining anisotropic temperature factors a residual of 11·3% was reached.[*] Structure factors calculated for the unobserved reflexions were below the minimum observed values, (primed in Table 2).

The structure viewed along the *c* axis is shown in Fig. 1 and the atomic parameters are listed in Table 1. A comparison of the observed and calculated structure factors is given in Table 2.

Table 3. *Bond lengths and angles*

Estimated maximum errors are in brackets.

Bond	Et_2NBF_2	Me_2NBF	Me_2NBCl_2
B–N	1·638 (±0·03) Å	1·601 Å	1·591 Å
B–F	1·40 (±0·03)	1·350	1·83 (Cl)
N–C	1·54 (±0·03)	1·469	1·505
C–C	1·55 (±0·03)		
B–N–B	87·03 (±0·3)°	88·3°	86·9°
N–B–N	92·97 (±0·3)	91·7	93·1
C–N–C	113·41 (±0·5)	107·9	108·5
F–B–F	112·50 (±0·5)	111·8	107·2
B–N–C	113·45 (±1·0)	115·2	
N–B–F	112·49 (±1·0)	113·0	
N–C–C	113·01 (±1·0)		

Discussion

Diethylaminoborondifluoride does exist as a dimer in the solid state. The four membered boron–nitrogen ring is planar with the B–N–B angle 87·0±0·3° and the B–N bond length is 1·638±0·03 Å. All the bond lengths and angles are listed in Table 3 together with those of $(Me_2NBF_2)_2$ and $(Me_2NBCl_2)_2$ for comparison. The bond lengths between the ring and the adjacent atoms are slightly longer than those of the methyl compounds. This is probably due to the larger space required by the ethyl groups. The bonding in the ring is almost certainly the same for all three compounds but whether it is completely covalent or some form of three-centre bond is not yet certain. Theoretical calculations being carried out by Armstrong (1968), using LCAO–MO–SCF theory with Gaussian atomic orbitals as the starting point on the dimer $(BH_2NH_2)_2$ have given a B–N bond length of 1·63 Å and a B–N–B angle of 86°. These calculations also suggest that there is considerable σ-charge transfer from the boron to the nitrogen atoms leading to a charge distribution which is opposite to that expected on the simple three-centre or bent-bond theories. The values for the calculated bond lengths and angles are in reasonable agreement with those found experimentally, for the substituted compounds. It therefore seems likely that the charge distribution will be at least qualitatively what is suggested (*i.e.* $B\delta+$ and $N\delta-$). The X-ray data are unfortunately not sufficiently accurate to be able to detect the transfer of the 0·2–0·4 electron involved.

The authors wish to thank Professor D. W. J. Cruickshank and Dr M. R. Truter and their respective crystallographic groups at Glasgow and Leeds Universities for the use of their computer programs. One of us (IASE) also acknowledges maintenance grants from S.R.C. and Procter & Gamble.

References

Armstrong, D. (1968). Private communication.

Bannister, A. J., Greenwood, N. N., Straughan, B. P. & Walker, J. (1964). *J. Chem. Soc.* p. 994.

Edwards, I. A. S. (1968). Ph. D. Thesis, Newcastle.

Gerrard, W., Lappert, M. F. & Pearce, C. A. (1957). *J. Chem. Soc.* 381.

Greenwood, N. N. & Walker, J. (1967). *J. Chem. Soc.* (*A*), p. 959.

Hazell, A. C. (1966). *J. Chem. Soc.* (A), p. 1392.

Hess, H. (1963). *Z. Kristallogr.* **118**, 361.

Ostoff, R. C. & Brown, C. A. (1952). *J. Amer. Chem. Soc.* **74**, 2378.

Stadler, H. P. (1950). *Acta Cryst.* **3**, 262.

---

[*] H atoms were included in their expected positions, but not refined.