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The Disordered Structures of 1,4-Dibromo-2,5-diethyl-3,6-dimethylbenzene (BEMB1) and 1,3-Dibromo-2,5-diethyl-4,6-dimethylbenzene (BEMB2), $C_{12}H_{16}Br_2$

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Abstract. $M_r = 320{\cdot}1$, $F(000) = 316$, monoclinic, $P2_1$, room temperature, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 9{\cdot}01\ \mathrm{mm}^{-1}$. BEMB1: $a = 9{\cdot}084\ (5)$, $b = 4{\cdot}459\ (8)$, $c = 17{\cdot}940\ (11)$ Å, $\beta = 122{\cdot}82\ (3)°$, $V = 610{\cdot}7$ Å^3, $Z = 2$, $D_x = 1{\cdot}74\ \mathrm{Mg\ m}^{-3}$. BEMB2: $a = 9{\cdot}086\ (1)$, $b = 4{\cdot}442\ (1)$, $c = 17{\cdot}969\ (2)$ Å, $\beta = 122{\cdot}69\ (1)°$, $V = 610{\cdot}4$ Å^3, $Z = 2$, $D_x = 1{\cdot}74\ \mathrm{Mg\ m}^{-3}$. Constrained least-squares refinements resulted in $R = 0{\cdot}064$, $R_w = 0{\cdot}094$ for 661 reflections with $|F_o| > 6\sigma(|F_o|)$ for BEMB1 and $R = 0{\cdot}063$, $R_w = 0{\cdot}089$ for 933 reflections with $|F_o| > 6\sigma(|F_o|)$ for BEMB2. In both isomers the 1,3,4,6 substituents show disorder of Br and CH_3. For BEMB1 the 1,4 sites are occupied on average by 0·563 (2) Br and 0·437 (2) C and *vice versa* for 3,6, while for BEMB2 the 1,3 sites are occupied on average by 0·506 (1) Br and 0·494 (1) C and *vice versa* for the 4,6 sites.

Introduction. In previous publications (Welberry, Jones & Epstein, 1982; Epstein, Welberry & Jones, 1982; Epstein & Welberry, 1983) we have described our interest in disordered molecular crystals, in which the disorder occurs between the halogen and methyl substituents of aromatic molecules. The reasons for selecting these halogen,methyl-substituted aromatics have been detailed by Jones & Welberry (1980). A common feature of these earlier studies was that all the molecules possessed quite large molecular dipole moments as a result of the disposition of the halogen and methyl substituents. Furthermore, diffuse X-ray scattering studies of these systems, which revealed the short-range order between the orientations of neighbouring molecules, suggested that dipole effects were important in determining the details of the disorder.

In the present study we have selected a pair of isomeric aromatic compounds, see Fig. 1, in which one isomer, BEMB1, does not have a molecular dipole, while the other, BEMB2, does. Preliminary Weissenberg photographs of these two isomers showed them to be almost isostructural, thus making them an ideal system for a comparative study of their disorder properties. Although the dipole moment for BEMB2 has not been measured, by comparison with *m*-dichlorobenzene, a value somewhat in excess of 1·7 debye (1 debye ≡ $3{\cdot}336 \times 10^{-30}$ C m) (*Handbook of Chemistry and Physics,* 1982) would be anticipated.

A prerequisite for a study of the diffuse scattering is a conventional determination of the 'average' crystal structure using Bragg data, and in this paper we report on this part of the current project. Results of diffuse-scattering experiments, which are still in progress, will be reported in a separate paper.

In previous determinations of this type of disordered structure we have represented the 'average' structure by placing at the disordered atomic sites a composite atom consisting of a fraction δ of halogen and $(1-\delta)$ of methyl carbon and refining only one set of positional and thermal parameters for such a site. Although one of the primary aims was a determination of the site occupancy δ, other aspects of this method are not completely satisfactory, and in the present study we use constrained-refinement techniques to allow a determination of two complete molecular fragments at each molecular site.

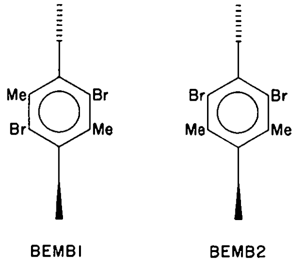

Fig. 1. Structural formulae for BEMB1 and BEMB2.

Experimental. *Preparation of BEMB*1. 1,4-Dimethylbenzene was acylated with acetyl chloride/$AlCl_3$ in carbon disulphide and the carbonyl group in the resultant acetyl substituent reduced with hydrogen over a 10% C/Pd catalyst in ether to form 1-ethyl-2,5-dimethylbenzene. The Friedel–Crafts acylation and catalytic hydrogenation was then repeated on this product to yield 1,4-diethyl-2,5-dimethylbenzene. In the absence of light and at 273 K reaction with bromine in a solution of acetic acid/CCl_4 containing a catalytic amount of iron produced BEMB1, m.p. 361–362 K. Elemental analysis, PMR and mass-spectrometer measurements gave results consistent with the expected molecular structure. BEMB1 was separated and recrystallized from acetic acid to form clear, prismatic crystals.

*Preparation of BEMB*2. 3,5-Dimethylbenzoyl chloride was treated with dimethylcadmium yielding 3,5-dimethylacetophenone. Friedel–Crafts acetylation and catalytic hydrogenation of this product produced a mixture of 4-ethyl-2,6-dimethylacetophenone and 2-ethyl-4,6-dimethylacetophenone. These products were reduced by B_2H_6 in diglyme to give their corresponding vinyl derivatives and these were further reduced to 1,4-diethyl-2,6-dimethylbenzene and 1,2-diethyl-3,5-dimethylbenzene by refluxing with an excess of metallic sodium in absolute ethanol. The mixture was brominated as for BEMB1 and the two isomers BEMB2, m.p. 360–361 K, and 1,3-dibromo-4,5-diethyl-2,6-dimethylbenzene, m.p. 304–306 K, were separated by fractional crystallization from ethanol to produce clear, prismatic crystals.

*Data collection, BEMB*1. Unit-cell dimensions from a least squares analysis of the Cu $K\alpha_1$ θ values of 15 reflections recorded by the Weissenberg method ($58° < \theta < 84°$); camera radius 57·3 mm, film loaded in the Straumanis mode. Intensity data recorded on film, equi-inclination Weissenberg method, graphite-monochromated Cu $K\alpha$ radiation. Two crystals used in the data collection: one to record the layers $h0l$–$h3l$, and the other $hk0$–$hk2$. hkl ranges −11 to 9, 0 to 5, and 0 to 21, respectively; $(\sin\theta/\lambda)_{\max} < 0{\cdot}7$ Å^{-1}. The crystal mounted about **b** had faces (010), (0$\bar{1}$0), (101), ($\bar{1}$0$\bar{1}$), (10$\bar{2}$) and ($\bar{1}$02) developed, their respective distances from a common internal origin being 0·184, 0·184, 0·118, 0·118, 0·061 and 0·061 mm. The crystal mounted about **c** had the same faces developed, their respective distances from a common internal origin being 0·199, 0·199, 0·118, 0·118, 0·055 and 0·055 mm. Films scanned with an Optronics P1700. Reflection indices and intensities determined using software made available by Dr M. Elder (Daresbury Laboratory, Science Research Council, Daresbury, Warrington, England). Lorentz, polarization (Levy & Ellison, 1960) and absorption corrections applied; the different layers were placed on a common scale (Rae & Blake, 1966). 720 unique reflections; $R_{\rm int}$, obtained by merging equivalent reflections after scaling, was 0·044.

*Data collection, BEMB*2. Unit-cell dimensions from a least-squares analysis of the Cu $K\alpha_1$ θ values of 11 high-angle reflections ($76° < \theta < 84°$) obtained in the same manner as described for BEMB1. Crystal selected for data collection had faces (100), ($\bar{1}$00), (010), (0$\bar{1}$0), (10$\bar{2}$) and ($\bar{1}$02) developed, their respective distances from a common internal origin being 0·05, 0·05, 0·16, 0·16, 0·03 and 0·03 mm. The resulting maximum-absorption-weighted mean-free-path length, $\bar{T}$, in the crystal was 0·13 mm ($\mu\bar{T} = 0{\cdot}81$). 933 independent reflections with $|F_o| > 6\sigma(|F_o|)$ and $\theta < 63{\cdot}5°$, 293 K, Picker FACS-1 diffractometer, graphite-monochromated Cu $K\alpha$ radiation, θ–2θ scan. $R_{\rm int}$ from merging 126 multiple/equivalent reflections was 0·011. Estimated standard deviations from counting statistics. Three standard reflections (600, 020 and 0,0,12): max. deviation 6·6%. Lorentz, polarization and absorption corrections applied.

It should be noted that use of photographic data for BEMB1 and diffractometer data for BEMB2 was dictated only by the availability of instrumentation at different times during the course of this work.

Structure determination and refinement

*BEMB*1. Structure determination was by means of *MULTAN*77 (Main, Lessinger, Woolfson, Germain & Declercq, 1977) using 135 structure amplitudes with $E > 1{\cdot}30$ and a planar fragment of an 'idealized' BEMB1 molecule having unknown orientation and position. The fragment consisted of the benzene ring and the atoms forming exocyclic bonds. Fragment geometry was obtained by extracting an average geometry from the relevant coordinates of 61 hexa-substituted benzenes listed in the Cambridge Crystallographic Database (CCD, last accession date November, 1982) (Allen, Bellard, Brice, Cartwright, Doubleday, Higgs, Hummelink, Hummelink-Peters, Kennard, Motherwell, Rodgers & Watson, 1979)* and constraining the fragment to planarity using the vector-addition method of Craven (1982). All non-hydrogen atoms appeared in the E map produced from the set of phases having the highest overall figure of merit. A Fourier difference synthesis suggested the presence of Br atoms at the sites of the methyl groups attached to the benzene ring (hereafter referred to as ring methyls), a situation that can only arise from orientational disorder of the BEMB1 molecules given that the crystal is chemically pure. Accordingly, a second molecule was introduced into the asymmetric unit by rotating the first 180° about an axis passing through the centre of mass of the molecule and the aromatic 3–4, 1–6 bonds.

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* A list of REFCODES has been deposited. See deposition footnote.

Least-squares refinement was carried out using the constrained-refinement program *RAELS*83 (Rae, 1983). With this program it is possible to refine two molecules of fractional occupancy and different orientations at the same molecular site, using a single molecular geometry. This single molecular geometry is defined relative to a local orthonormal axial system and refineable transformations from this axial system to the crystal axes are used (Rae, 1976). For space group $P2_1$, origin definition is effected by not refining the y translational component of one of the axial system transformations. The same molecular geometry can also be used for different symmetry-unrelated sites in the asymmetric unit. In addition it is possible to constrain fragments of molecules to have the same geometry using either strict or slack constraints. In this way, allowance can be made for orientational variations between otherwise identical fragments, for example between methyl-group orientations.

For BEMB1 two fragments were used. The major planar fragment consisted of the benzene ring, the Br atoms, the ring methyl C atoms and the methylene C atoms. Also included in this fragment (but out of the plane) were the methylene H atoms. No H-atom positions were specified for the ring-methyl C atoms. The second fragment was a rigid methyl group for the terminal C atoms of the ethyl moieties.

The local coordinates of the ring fragment, but not those of the methyl fragment, together with the axial-system transformations placing the local coordinates into the asymmetric unit were refined using full-matrix least-squares refinement: $\sum w(|F_o| - |F_c|)^2$ minimized, $w^{-1} = \sigma^2(|F_o|)$; σ determined using the method of Einstein & Jones (1971) with $A = 3{\cdot}5$, $B = 9{\cdot}0$, $C = 16{\cdot}0$. Reflections with $|F_o| < 6\sigma(|F_o|)$ were absent from the data set. Standard atomic scattering factors were used for the Br and C atoms (*International Tables for X-ray Crystallography*, 1962) and spherically bonded scattering factors were used for the H atoms (Stewart, Davidson & Simpson, 1965). Anomalous-dispersion corrections (*International Tables for X-ray Crystallography*, 1974) were applied to the Br and C scattering factors. Throughout the refinement: planarity of the benzene ring and exocyclic bonds was strictly maintained; the bond lengths of the aromatic bonds were slack constrained to 1·395 Å; the C(aromatic)—C(methyl) bonds were slack constrained to 1·51 Å; the C—Br bonds were slack constrained to be equal as were the C(aromatic)—C(methylene) bonds; the C(methylene)—C(methyl) bonds were slack constrained to 1·54 Å; the $\angle 612$ and $\angle 345$ ring angles were slack constrained to 120·0°; the geometries of the methylene H atoms were slack constrained to tetrahedral geometry with a C—H bond length of 1·0 Å; the bond angles having a methyl C as the central atom were slack constrained to the tetrahedral angle; and the occupancies of the two molecules were strictly constrained to add to unity. All slack constraints were given equal weights of 10 on the weight scale used by *RAELS*83 (Rae, 1978). Identical rigid-body thermal motion was ascribed to the two molecules using a 15-parameter rigid-body *TLX* model which had the principal axes of the **L** tensor as reference axes (Rae, 1975*b*). These axes approximately coincide with the principal axes of inertia of the rigid group. The final discrepancy factors for 661 observed reflections were $R = 0{\cdot}064$, $R_w = 0{\cdot}094$, $S = 1{\cdot}27$ for 88 refineable parameters. Note that S is not a true goodness-of-fit since w was not based on counting statistics. All $\Delta/\sigma < 0{\cdot}3$, average $\Delta/\sigma < 0{\cdot}1$. Reflection $\bar{7}$,2,15 had $|F_c| << |F_o|$ ($\Delta/\sigma \sim 15$) and was given zero weight in the refinement, but included in the calculation of discrepancy factors and direct-space syntheses. Residual density on final Fourier difference map *ca* $\pm 0{\cdot}6$ e Å^{-3} with the max. residual density in the regions of the Br atoms. There was no unusual thermal motion and no librations about the principal librational axes were greater than 5°. The site occupancies of the two molecules refined to 0·563 (2) and 0·437 (2).

The atomic parameters for the non-hydrogen atoms in the two molecules are given in Table 1.[*] The atomic notation and an *ORTEP* thermal-ellipsoid plot of molecule (I) at the 50% probability level (Johnson, 1976) is shown in Fig. 2(*a*).

*BEMB*2. Since BEMB1 and BEMB2 are virtually isostructural, interchange of the 3,4 ring substituents of BEMB1 and adjustment of their bond lengths to match

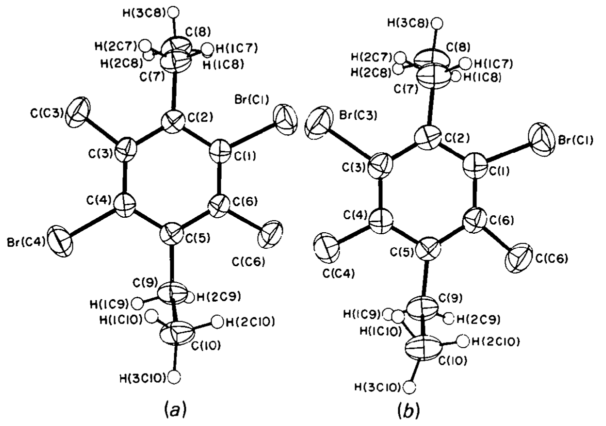

Fig. 2. The atomic notation and thermal-ellipsoid plot of molecule (I) for (*a*) BEMB1 and (*b*) BEMB2.

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[*] Even though the H-atom geometries in each isomer have been constrained, the H-atom coordinates are of doubtful reliability because of the disorder and room-temperature data collection. H-atom parameters and geometry for BEMB1 and BEMB2, together with lists of structure factors, anisotropic thermal parameters and REFCODES have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39346 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

those of the 1,6 substituents gave initial parameters for least-squares refinement of BEMB2. The refinement procedure was identical to that of BEMB1. With all $\Delta/\sigma < 0{\cdot}4$ (average $\Delta/\sigma < 0{\cdot}1$) refinement converged to $R = 0{\cdot}063$, $R_w = 0{\cdot}089$, $S = 3{\cdot}55$ (88 refineable parameters). It was noted during the refinement that the three reflections with $\sin\theta/\lambda < 0{\cdot}1$ Å^{-1} had R ~0·37 ($\Delta/\sigma > 20$) and, consequently, these reflections were given zero weight in the refinement but included in the calculation of discrepancy factors and direct-space syntheses. Residual density on the final Fourier difference map *ca* ±0·8 e Å^{-3}. As for BEMB1, there was no unusual thermal motion and again all librations about the principal librational axes were less than 5°. The final site occupancies of the two molecules were 0·506 (1) and 0·494 (1).

The atomic parameters for the non-hydrogen atoms in the two molecules are given in Table 2. An *ORTEP* thermal-ellipsoid plot of molecule (I) is shown in Fig. 2(*b*).

Table 1. *Atomic parameters* (×10³) *for the non-hydrogen atoms of molecules* (I) *and* (II) *in BEMB*1

Molecule (I) has site occupancy 0·563 (2); molecule (II), 0·437 (2).
U_{eq}(Å^2) = $\frac{1}{3}\sum U_{ij}$ where the U_{ij} are defined relative to an orthonormal axial system (Rae, 1975*a*).

	Molecule (I)				Molecule (II)			
	x	y	z	U_{eq}	x	y	z	U_{eq}
Br(C1)	275 (1)	740 (2)	201 (1)	58 (1)	416 (1)	395 (1)	388 (1)	59 (1)
Br(C4)	−281 (1)	237 (2)	294 (1)	62 (1)	−422 (1)	626 (1)	121 (1)	63 (1)
C(C3)	−374 (2)	645 (5)	122 (1)	56 (1)	−232 (4)	232 (3)	304 (2)	56 (1)
C(C6)	364 (2)	369 (4)	358 (1)	52 (1)	248 (3)	755 (3)	222 (2)	52 (1)
C(1)	108 (2)	604 (3)	223 (1)	34 (1)	175 (1)	451 (2)	315 (1)	34 (1)
C(2)	−72 (2)	669 (3)	167 (1)	33 (1)	56 (2)	325 (2)	334 (1)	34 (1)
C(3)	−185 (2)	556 (3)	190 (1)	36 (1)	−122 (2)	382 (2)	275 (1)	36 (1)
C(4)	−125 (2)	384 (3)	266 (1)	36 (1)	−183 (1)	556 (3)	199 (1)	36 (1)
C(5)	54 (3)	320 (3)	322 (1)	33 (1)	−65 (3)	681 (2)	180 (1)	33 (1)
C(6)	169 (2)	432 (3)	300 (1)	34 (1)	114 (2)	626 (3)	239 (1)	34 (1)
C(7)	−134 (7)	857 (3)	84 (1)	46 (1)	126 (7)	137 (3)	417 (1)	47 (1)
C(8)	−166 (6)	654 (10)	9 (2)	52 (1)	181 (8)	341 (11)	497 (3)	53 (1)
C(9)	126 (7)	134 (3)	405 (1)	45 (1)	−124 (7)	871 (3)	99 (1)	45 (1)
C(10)	183 (6)	313 (10)	492 (3)	52 (1)	−175 (7)	697 (12)	14 (2)	52 (1)

Table 2. *Atomic parameters* (×10⁴) *for the non-hydrogen atoms of molecules* (I) *and* (II) *in BEMB*2

Molecule (I) has site occupancy 0·506 (1); molecule (II), 0·494 (1).
U_{eq}(Å^2) = $\frac{1}{3}\sum U_{ij}$ as for BEMB1.

	Molecule (I)				Molecule (II)			
	x	y	z	U_{eq}	x	y	z	U_{eq}
Br(C1)	2806 (2)	7371 (7)	2031 (3)	698 (5)	4125 (2)	3809 (6)	3821 (1)	685 (5)
Br(C3)	−4134 (2)	6147 (7)	1190 (1)	697 (5)	−2819 (2)	2362 (6)	2956 (1)	659 (5)
C(C4)	−2327 (13)	2496 (15)	2952 (7)	573 (4)	−3704 (8)	6360 (16)	1338 (6)	631 (4)
C(C6)	3697 (8)	3591 (16)	3670 (5)	621 (4)	2345 (14)	7587 (13)	2103 (7)	611 (5)
C(1)	1094 (6)	6073 (9)	2211 (4)	414 (4)	1735 (4)	4360 (8)	3145 (3)	401 (4)
C(2)	−712 (7)	6554 (8)	1681 (3)	392 (4)	471 (7)	3255 (7)	3291 (3)	369 (4)
C(3)	−1781 (4)	5351 (10)	1946 (4)	409 (4)	−1286 (6)	3957 (8)	2687 (4)	400 (4)
C(4)	−1047 (7)	3695 (10)	2729 (4)	388 (4)	−1763 (6)	5739 (9)	1949 (4)	410 (4)
C(5)	754 (8)	3201 (10)	3262 (4)	370 (4)	−512 (8)	6855 (8)	1797 (3)	390 (4)
C(6)	1811 (6)	4409 (10)	2993 (3)	411 (4)	1238 (7)	6143 (8)	2403 (4)	410 (4)
C(7)	−1321 (16)	8398 (10)	849 (4)	526 (6)	1185 (16)	1347 (11)	4122 (4)	480 (5)
C(8)	−1668 (24)	6325 (48)	83 (8)	622 (9)	1796 (25)	3130 (41)	4976 (7)	571 (7)
C(9)	1360 (17)	1360 (13)	4093 (4)	477 (5)	−1227 (17)	8758 (11)	968 (4)	523 (6)
C(10)	1775 (27)	3001 (50)	4893 (9)	556 (7)	−1671 (26)	6796 (40)	166 (8)	608 (8)

Table 3. *Bond lengths* (Å) *and valence angles* (°) *for the non-hydrogen atoms of BEMB*1 *and BEMB*2

	BEMB1	BEMB2		BEMB1	BEMB2		BEMB1	BEMB2
C(1)—C(2)	1·408 (10) (*c*)	1·398 (3) (*c*)	C(1)—Br(C1)	1·864 (7) (*d*)	1·844 (3) (*d*)	C(2)—C(7)	1·517 (11) (*f*)	1·523 (5) (*f*)
C(2)—C(3)	1·394 (10)	1·397 (3)	C(3)—*X* (*a*)	1·518 (9) (*e*)	1·845 (3) (*d*)	C(5)—C(9)	1·513 (11) (*f*)	1·520 (5) (*f*)
C(3)—C(4)	1·396 (8)	1·397 (3)	C(4)—*Y* (*b*)	1·866 (7) (*d*)	1·517 (4) (*e*)	C(7)—C(8)	1·540 (12) (*g*)	1·541 (4) (*g*)
C(4)—C(5)	1·399 (11)	1·396 (3)	C(6)—C(C6)	1·521 (9) (*e*)	1·515 (4) (*e*)	C(9)—C(10)	1·540 (11) (*g*)	1·539 (4) (*g*)
C(5)—C(6)	1·396 (11)	1·394 (3)						
C(6)—C(1)—C(2)	120·6 (5) (*h*)	120·2 (2) (*h*)	Br(C1)—C(1)—C(6)	117·0 (12)	111·2 (4)	C(9)—C(5)—C(4)	122·4 (26)	115·3 (7)
C(1)—C(2)—C(3)	117·7 (8)	119·1 (2)	C(7)—C(2)—C(1)	119·3 (26)	114·9 (6)	C(9)—C(5)—C(6)	119·2 (26)	126·5 (7)
C(2)—C(3)—C(4)	121·9 (8)	120·1 (2) (*h*)	C(7)—C(2)—C(3)	123·0 (27)	126·0 (6)	C(C6)—C(6)—C(5)	120·9 (18)	108·8 (6)
C(3)—C(4)—C(5)	120·2 (5) (*h*)	121·3 (3)	*X*—C(3)—C(2)	111·5 (20)	114·8 (4)	C(C6)—C(6)—C(1)	117·9 (17)	130·0 (6)
C(4)—C(5)—C(6)	118·4 (8)	118·2 (4)	*X*—C(3)—C(4)	126·6 (19)	125·1 (4)	C(2)—C(7)—C(8)	110·0 (23)	115·1 (8)
C(5)—C(6)—C(1)	121·2 (8)	121·2 (3)	*Y*—C(4)—C(3)	120·6 (14)	115·7 (6)	C(5)—C(9)—C(10)	115·5 (23)	111·1 (8)
Br(C1)—C(1)—C(2)	122·5 (12)	128·6 (4)	*Y*—C(4)—C(5)	119·2 (14)	123·0 (7)			

Notes: (*a*) *X* = C(C3) for BEMB1 and Br(C3) for BEMB2. (*b*) *Y* = Br(C4) for BEMB1 and C(C4) for BEMB2. (*c*) Ring bonds slack constrained to 1·395 Å. (*d*) For each structure, slack constrained to be equal. (*e*) Slack constrained to 1·51 Å. (*f*) For each structure, slack constrained to be equal. (*g*) Slack constrained to 1·54 Å. (*h*) Slack constrained to 120·0°.

Discussion. Table 3 lists the bond lengths and valence angles for the non-hydrogen atoms of BEMB1 and BEMB2. Since molecules (I) and (II) in each isomer have the same geometry, the geometrical parameters of only one molecule have been included in the table. The BEMB1 parameters have significantly greater e.s.d.'s compared to those of BEMB2. This lack of resolution is a direct consequence of there being appreciably fewer high-angle reflections – 380 reflections with $\sin\theta/\lambda > 0{\cdot}4$ Å^{-1} for BEMB1 compared with 595 for BEMB2. For both isomers the least-squares minimum seemed to be broad – the removal of constraints had negligible effect on the discrepancy factors but resulted in significant, and sometimes physically unreasonable, changes in geometrical parameters.

The CCD (November, 1982) contains structural coordinates of five hexasubstituted benzenes having at least one Br substituent. Without these structures being screened for accuracy of results, the C—Br bond lengths range between 1·717 and 1·927 Å with mean value 1·86 (6) Å. The C—Br bond lengths for BEMB1 and BEMB2 are well within one standard deviation of this value. For 30 hexasubstituted benzenes having at least one C(aromatic)—C(exocyclic) bond the C_{ar}—C_{exo} bond lengths range between 1·396 and 1·585 Å with mean 1·51 (4) Å. With the C_{ar}—CH_3 bonds slack constrained to 1·51 Å and the C_{ar}—CH_2 bonds slack constrained to be equal, the average C_{ar}—C_{exo} bond length for BEMB1 and BEMB2 is 1·518 (3) Å. Examination of the ring bond lengths and angles of 61 hexasubstituted benzenes showed that there were no significant changes from those of benzene and it was for this reason that the ring geometries of BEMB1 and BEMB2 were slack constrained to that of benzene in the least-squares refinements.

The strict-planarity constraint applied to the benzene ring and exocyclic bonds is reasonably consistent with the majority of hexasubstituted benzenes taken from the database. Only perchloro-*p*-xylene (Solans, Galí, Miravitlles & Font-Altaba, 1978) has a benzene ring differing grossly from planarity but this is attributable to severe steric strain.

The ethyl-group conformations are the same as those adopted in hexaethylbenzene (Iverson, Hunter, Blount, Damewood & Mislow, 1981) where the C_{ar}—CH_2—CH_3 planes are essentially perpendicular to the plane of the benzene ring. In that structure the average dihedral angle between the C_{ar}—CH_2—CH_3 planes and the benzene ring is 89·5°. For BEMB1 and BEMB2 the corresponding value is 87 (1)°.

Fig. 3 shows the positioning of molecules (I) and (II) in the asymmetric units of BEMB1 and BEMB2. In both structures the planes of the types (I) and (II) molecules are almost parallel, the dihedral angle being 3·3° for BEMB1 and 2·0° for BEMB2. The planes are displaced by *ca* 0·2 Å. The symmetry of both structures is close to $P2_1/c$. If such symmetry were strictly adhered to, the molecular site would be required on average to contain an inversion centre. For BEMB1 this could be achieved for any value of the site occupancy but for BEMB2 50/50 occupancy would be required. It is interesting to note that conventional refinement of an average molecule in $P2_1/c$ converged for both isomers with R values of *ca* 0·07. As expected, unacceptably large thermal displacements were obtained, particularly in the direction perpendicular to the plane of the molecule.

The orientational disorder in both isomers introduces four types of intermolecular contact for a given pair of neighbouring molecules depending upon which molecular orientations are present. A detailed analysis of these contacts and their relation to the short-range-order effects observed in the diffuse-scattering experiments will be given in a subsequent paper. In Fig. 4 we show the molecular packing with all molecules in orientation (I). All molecules surrounding the central molecule (55501) which have a contact involving Br and ring methyl groups are included, and the relevant contacts indicated by dashed lines. With all the molecules in orientation (I) these contact distances are within the range 3·43–4·84 Å for BEMB1 and 3·57–4·79 Å for BEMB2.

It is significant that, despite very different dipole moments, the two isomers form practically identical structures. Moreover, preliminary diffuse-scattering studies have also revealed substantial short-range-ordering effects, even for BEMB1 which has no net dipole. It thus seems likely that in considering the effects of intermolecular interactions, a more localized description should be taken in which the dipole effects are associated with Br—ring bonds, for example, rather than as molecular dipoles. We have found in previous studies that, as a general rule, short-range ordering occurs in such a way as to try to minimize the number of Br—Br and methyl—methyl intermolecular contacts

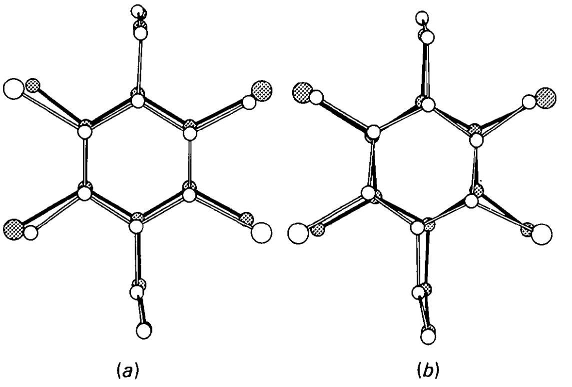

Fig. 3. The asymmetric units of (*a*) BEMB1 and (*b*) BEMB2 with molecule (I) indicated by the open bonds and unshaded atoms.

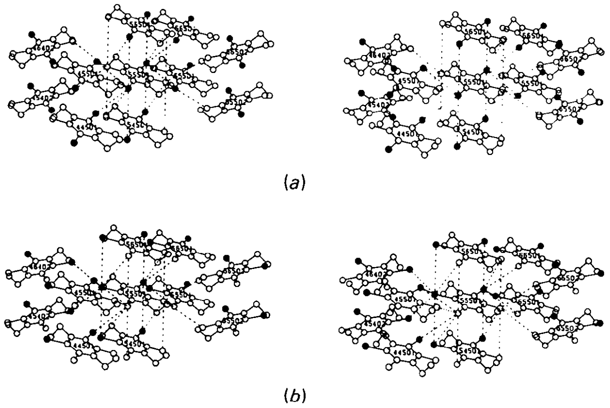

Fig. 4. Stereoviews of the molecular packing in (*a*) BEMB1 and (*b*) BEMB2 with all molecules in orientation (I). Shaded circles represent Br atoms.

in favour of Br—methyl contacts. Such an observation is in general agreement with the notion of localized dipoles and a detailed analysis along these lines is in progress. Since previous studies were only carried out with 'average' or 'idealized' Br and methyl positions it was not possible to correlate the degree of order with the precise details of each intermolecular contact. In the present study, the use of constrained refinements has allowed determination of positions for both the Br and the methyl at each disordered site. It is therefore hoped that a more quantitative description of the causes of the short-range ordering can be made.

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Structure of Difluoro(methylamino)phosphine, CH_4F_2NP, at 97 K

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Abstract. $M_r = 99{\cdot}02$, triclinic, $P\bar{1}$, $a = 4{\cdot}9969\ (18)$, $b = 5{\cdot}4618\ (18)$, $c = 8{\cdot}2231\ (25)$ Å, $\alpha = 106{\cdot}435\ (26)$, $\beta = 108{\cdot}088\ (29)$, $\gamma = 76{\cdot}780\ (29)^\circ$, $U = 202{\cdot}2\ (4)$ Å^3, $Z = 2$, $D_x = 1{\cdot}641$ Mg m^{-3}, $\bar{\lambda}$(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}531$ mm^{-1}, $F(000) = 100$. Final $R = 0{\cdot}0397$ for 1055 observed reflections. Molecules are linked by hydrogen bonding into chains which run alternately parallel and antiparallel to the crystallographic *b* axis.