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The crystal structure of 4-difluoromethoxybenzylidene-4'-(1",1",2",2",3",3",4",4"-octafluorobutyl)aniline and modelling of the 4-methoxybenzylidene-4'-*n*-butylaniline crystal structure

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The crystal structure of 4-difluoromethoxybenzylidene-4′-(1″,1″,2″,2″,3″,3″,4″,4″-octafluorobutyl)aniline and modelling of the 4-methoxybenzylidene-4′-*n*-butylaniline crystal structure

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The crystal and molecular structure of a non-mesogenic member of the series of mesogenic fluorinated 4-methoxybenzylidene-4′-*n*-butylaniline (MBBA) derivatives is described. Calculations based on atom–atom potentials were carried out to test the variability of the hypothetical crystal structures based on the MBBA derivatives studied by the authors and to build the variable crystal structures for the classical nematogen MBBA.

1. Introduction

It is well known that much information about liquid-crystalline phases can be obtained from crystal data of their solid-crystalline precursors. Supramolecular fragments (molecular associates formed by strong intermolecular van der Waals interactions) such as stacks and layers are often retained in the mesophases [1]. The principle method for determining the structure of single crystals is X-ray diffraction. However, when single crystals of sufficient quality for X-ray analysis cannot be obtained the modelling of packing arrangements by means of atom–atom potential energy calculations can often provide very useful information [2–4]. Such a computational approach can be useful in attempting to build models of hypothetical crystal packing (or packing in polymorphs) which can provide us with information about different molecular packings which can probably be realized in liquid crystals.

This paper is part of a systematic study of the mesogenic properties and structure of 4-methoxybenzylidene-4′-*n*-butylaniline (MBBA) and its fluorinated derivatives. The molecules studied here are defined in table 1 which also summarizes results from earlier studies of MBBA derivatives. We have carried out the X-ray structure determination of 4-difluoromethoxybenzylidene-4′-(1″,1″,2″,2″,3″,3″,4″,4″-octafluorobutyl)aniline (I) and the calculation of a number of hypothetical packing modes in various space groups. The structural and computational studies on the fluorinated MBBA derivatives [5–7] served as a basis for testing structural models for unfluorinated MBBA whose structure has yet to be determined.

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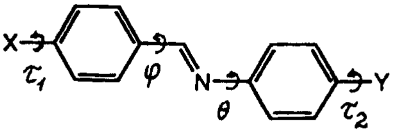
Table 1. Mesogenic properties and structural characteristics of MBBA and its fluorinated analogues.



Compounds references	Substituents *X*	Substituents *Y*	Phase transition temperatures†	Packing type	Torsion angles $\varphi/°$	Torsion angles $\theta/°$
MBBA	H_3CO	C_4H_9	C 21°C N47°C I	Parallel‡	—	—
I§	F_2H_8CO	C_4F_8H	C 52°C I	Layered	6·6 −1·5	48·6 52·1
II [3]	H_3CO	C_4F_9	C 78°C S 98°C I	Layered	−15·2	43·8
III [3]	F_2HCO	C_4H_9	C 31°C S 39°C I	Layered	14·8	22·1
IV [4]	F_3CO	C_4F_9	C 28°C I	Stacked	1·3	32·6
V [5]	H_3CO	C_4F_8H	C1 60°C I- ↑ ↓ 33°C C2 51°C	Parallel	14·5	44·9
EBBA [8]	H_5C_2O	C_4H_9	C 38°C N 77°C I	Parallel	12·2	45·8

† C, C1, crystal; N, nematic phase; I, isotropic liquid.
‡ Suggested packing type.
§ Torsion angles are given for molecules I and I′.

2. Experimental

Single crystals of **I** were prepared by evaporation from ethanol solution. Crystals of **I** are monoclinic, at −120°C: $a = 10·387(4)$, $b = 9·245(3)$, $c = 37·38(1)$ Å, $\beta = 93·47(2)°$, $V = 3621(1)$ Å^3, $\rho_{calc} = 1·66$ g cm^{-3}, $Z = 8$, space group $P2_1/n$ (two independent molecules). The unit cell parameters and intensities of 5583 independent reflections were measured at −120°C with an automatic diffractor Syntex $P2_1$ (Mo–K_α radiation, graphite monochromator, $\theta/2\theta$ scan, $2\theta < 60°$). The structure was solved by direct methods with the MULTAN program and refined by block diagonal least squares with anisotropic thermal parameters for the 2720 reflections with $F^2 > 3\sigma$. All of the hydrogen atoms were included in the final stages of refinement with fixed positional and thermal parameters $B_{iso} = 5$ Å^2. The final values of the discrepancy factors are $R = 0·107$ and $R_w = 0·131$. The molecular geometry of the two molecules (**I** and **I′**) with the atom numbering is shown in figure 1. The atomic coordinates and temperature factors are given in table 2.

3. Method of calculations and computational details

The method used for a search of optimal crystal structure first suggested by Kitaigorodsky [2] is based on the minimization of the intermolecular van der Waals energy calculated with the atom–atom approximation. We have employed this method for comparison of the relative energetic preference of molecular packing of **I** and MBBA in the space groups found experimentally for crystals of compounds **II–IV**.

The lattice energy was calculated with the 6-exp potential functions using parameters proposed by Kitaigorodsky (see [9]) and Williams [10]. A program written by A. J. Pertsin (Institute of Organoelement Compounds, Moscow, U.S.S.R.) for the Soviet BESM 6 computer was used for the energy minimization. The program written

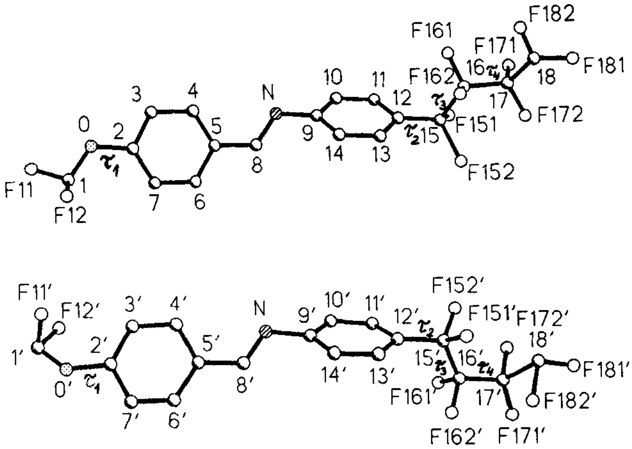


Figure 1. Molecules I and I′ in the crystal. The conformational difference is clearly described by torsion angles for molecules I and I′ τ_1, −175·0, 20·4; τ_2, 95·7, 86·1; τ_3, 174·0, 173·5; τ_4, −167·1, 29·7, respectively.

by the authors was used for the energy calculation of structures with several crystallographically independent molecules without energy minimization. The parameter sets by Kitaigorodsky and Williams were tested by the calculation of experimentally studied structures II–IV and 4-ethyloxybenzylidene-4′-*n*-butylaniline (EBBA). According to the criterion proposed in [11] the parameter set is considered reliable when the differences between the experimental and calculated values are as follows: cell edges are less than 1 per cent, unit cell angles less that 1°, positions of molecular centroids less than 0·1 Å and angles which characterize the molecular orientation less than 2°. Experimental and calculated data for the crystal structures of II–IV are given in table 3. It is evident that both parameter sets tested satisfactorily describe the calculated structures. However, for structures II and IV the agreement between calculated and experimental values is better for the Williams' parameters and therefore these parameters were used for all subsequent calculations.

In all of the calculations on model systems we have made the following assumptions.

(i) To build the hypothetical crystal structures of related compounds we have used the crystal structures of the compounds investigated with substitution of hydrogen for fluorine atoms and vice versa in the desired positions. The standard bond lengths for C-F were used (1·36 Å in CF_2 and 1·33 Å in CF_3 groups).

(ii) Calculations of the optimal crystal structures of EBBA, II and V were performed without variation of the molecular conformations, because these conformations are close to the conformation of the isolated benzylidene aniline (BA) molecule whose energetics have been studied earlier [12].

(iii) In other structures the possibility of conformational variation was taken into account. In these cases the total crystal lattice energy was calculated as a sum of intermolecular van der Waals and intramolecular conformation energy. The conformational energy was calculated with Allinger's force field with the

Table 2. Coordinates of non-hydrogen atoms and their equivalent isotropic temperature factors B_{equ}iso in structure **I**.

Atom	x/Å	y/Å	z/Å	B_{equ}iso/Å^2
F11	1·4902(7)	−0·541 (1)	0·7728(2)	9·5(2)
F12	1·3020(7)	−0·5799(9)	0·7516(2)	9·7(2)
F151	1·0143(7)	0·0078(6)	0·4239(2)	7·2(2)
F152	0·8108(5)	−0·0920(8)	0·4427(2)	7·1(2)
F161	1·0874(5)	−0·2598(8)	0·4004(2)	7·1(2)
F162	0·9117(7)	−0·3171(7)	0·4155(2)	8·5(2)
F171	0·997 (1)	−0·089 (1)	0·3550(3)	15·4(3)
F172	0·8153(9)	−0·081 (1)	0·3711(3)	20·1(3)
F181	0·8249(9)	−0·226 (1)	0·3136(2)	11·1(3)
F182	0·957 (1)	−0·372 (1)	0·3413(2)	12·0(3)
O	1·4509(6)	−0·5065(8)	0·7177(2)	5·7(2)
N	1·2525(7)	−0·3043(8)	0·5613(2)	4·2(2)
C1	1·401 (1)	−0·496 (1)	0·7497(3)	6·7(3)
C2	1·3847(9)	−0·447 (1)	0·6880(3)	4·7(2)
C3	1·4415(9)	−0·476 (1)	0·6569(3)	5·0(2)
C4	1·3819(9)	−0·424 (1)	0·6244(2)	4·1(2)
C5	1·2675(8)	−0·346 (1)	0·6244(2)	3·5(2)
C6	1·2117(9)	−0·320 (1)	0·6560(3)	4·6(2)
C7	1·271 (1)	−0·368 (1)	0·6875(3)	5·5(3)
C8	1·2036(9)	−0·294 (1)	0·5919(3)	4·1(2)
C9	1·1782(8)	−0·2597(9)	0·5310(2)	3·4(2)
C10	1·2367(9)	−0·169 (1)	0·5066(3)	1·2(2)
C11	1·1707(9)	−0·124 (1)	0·4770(3)	4·3(2)
C12	1·0391(8)	−0·167 (1)	0·1693(3)	3·8(2)
C13	0·9835(9)	−0·256 (1)	0·4935(2)	4·2(2)
C14	1·0504(8)	−0·302 (1)	0·5235(3)	4·3(2)
C15	0·9660(9)	−0·117 (1)	0·4372(3)	4·9(2)
C16	0·9660(8)	−0·225 (1)	0·4056(3)	4·0(2)
C17	0·906 (1)	−0·180 (2)	0·3705(4)	7·6(4)
C18	0·881 (2)	−0·282 (2)	0·3438(4)	11·8(5)
F11′	0·128 (1)	0·251 (1)	0·3822(3)	19·2(4)
F12′	0·270 (1)	0·307 (2)	0·3674(3)	19·9(5)
F151′	0·7569(6)	0·035 (1)	0·6957(2)	9·9(2)
F152′	0·6356(8)	−0·1487(7)	0·69174(2)	9·2(2)
F161′	0·4332(6)	0·018 (1)	0·7103(2)	9·3(2)
F162′	0·5617(8)	0·1966(7)	0·7164(2)	8·0(2)
F171′	0·5166(7)	0·0715(9)	0·7773(2)	9·3(2)
F172′	0·5433(9)	−0·161 (1)	0·7572(2)	11·2(3)
F181′	0·7162(7)	−0·0764(9)	0·8023(2)	8·7(2)
F182′	0·719 (1)	0·1293(8)	0·7690(2)	12·0(3)
O′	0·232 (1)	0·440 (1)	0·4036(3)	11·9(3)
N′	0·4694(6)	0·1430(8)	0·5462(2)	3·5(2)
C1′	0·185 (1)	0·381 (2)	0·3744(5)	11·5(5)
C2′	0·283 (1)	0·385 (1)	0·4358(3)	4·9(2)
C3′	0·330 (1)	0·249 (1)	0·4408(3)	5·4(3)
C4′	0·3818(9)	0·205 (1)	0·1742(3)	1·2(2)
C5′	0·3852(8)	0·3063(9)	0·5023(2)	3·3(2)
C6′	0·3352(9)	0·444 (1)	0·4953(3)	1·6(2)
C7′	0·2853(9)	0·485 (1)	0·4629(3)	4·9(2)
C8′	0·4297(7)	0·2651(9)	0·5380(3)	3·3(2)
C9′	0·5101(8)	0·1131(9)	0·5821(2)	3·5(2)
C10′	0·4609(9)	−0·010 (1)	0·5979(2)	4·3(2)
C11′	0·498 (1)	−0·045 (1)	0·6318(3)	5·0(2)
C12′	0·5886(9)	0·036 (1)	0·6512(2)	4·3(2)
C13′	0·6415(9)	0·160 (1)	0·6346(3)	5·4(3)
C14′	0·5993(8)	0·198 (1)	0·6013(3)	4·3(2)
C15′	0·6335(9)	−0·003 (1)	0·6881(3)	5·1(2)
C16′	0·5546(9)	0·052 (1)	0·7173(3)	4·8(2)
C17′	0·585 (1)	0·005 (2)	0·7545(3)	8·0(3)
C18′	0·712 (1)	−0·034 (2)	0·7689(3)	10·5(4)

parameter set from the MM2 program [13]. For calculation of the torsional energy the parameter V_2 (two fold torsional constant) was fitted for torsion angles τ_1, φ and θ were taken as 14·6, 25·1 and 9·2 kJ mol^{-1}, respectively, and for the angle τ_2 $V_2=0$. Parameter V_2 was fitted according to quantum chemical calculations for anisole [14] and benzylidene aniline [12].

(iv) In calculations of the hypothetical structures the initial unit cell parameters were increased by *c.* 20 per cent, to prevent the structure from falling into a local minimum.

(v) The radius of the summation sphere was taken to be 7 Å for all atomic types.

Minimization of the energy of structures **III** and **IV** including the conformational energy led to good agreement between calculated and experimental values of the torsion angles (maximum deviation 3°). These results show that the initial torsion parameters are quite satisfactory.

4. Results and discussion

4.1. *Structure* I

Compound **I** is an analogue of compounds **II–V** but it does not exhibit mesogenic properties (see table 1). The compounds of these series differ by the number of F and H atoms in the substituents *X* and *Y*. The different volume and polarity of substituents *X* and *Y* can lead to changes in the type of molecular packing in the mesophase and the crystal; it is the relationship between these molecular parameters and the structural properties that we wish to understand.

There are two crystallographically independent and conformationally distinct molecules (**I** and **I**′) in crystal **I**; this peculiarity is quite usual for crystals of mesogens [15–17]. The shape of the BA core characterized by the angles φ and θ (see table 1), is very similar in both molecules and close to the calculated shape of the BA molecule ($\varphi=0°$ and $\theta=45°$) [12]. The molecules **I** and **I**′ differ by the orientation of the *X* and *Y* groups and the conformation of the *Y* substituent (see figure 1).

Figure 2 represents the structural arrangement of molecules **I** and **I**′ in the crystalline state seen along the crystallographic *b* axis. Some short intermolecular distances of the C–H…F–C type are observed: H1…F181 ($1/2+x$, $-1/2$-y, $1/2+z$) 2·49 Å and H18′…F182′ ($1/2$-x, $-1/2+y$, $3/2-z$) 2·43 Å (the sum of the F and H van der Waals radii is equal to 2·67 Å [18]). In this connection it is worth noting that the atoms H1 and H18′ have acidic characters because they belong to $-CF_2HO$ and $-C_4F_8H$ groups which makes them potential candidates for this interaction, reminiscent of hydrogen bonds.

It is clear from figure 2 that molecules in the crystal are arranged in layers normal to the *c* axis. To confirm the layer type of this crystal packing the calculation of the intermolecular van der Waals interactions in this structure were performed and the results are given in table 4. The intermolecular interactions were analyzed following the method of Zorkii [19]. It turned out that the intermolecular interactions within the layer is about 4·8 times larger than that between the layers, so that the calculations provide an energetic rationale for the existence of the layered structure. Forces between layers are weak and thus most likely of the van der Waals type or at most the weak hydrogen bonds noted previously. However, these interlayer interactions can be sufficiently strong to prevent the formation of the layer mesophase structure at the first stages of mesophase formation.

Table 3. Comparison of the parameters for the experimental and calculated structures†.

Parameters	a/Å	b/Å	c/Å	β/°	X/Å	Y/Å	Z/Å	φ_x/°	φ_y/°	φ_z/°	$-U$/kJ mol^{-1}
EBBA											
Exp.	7·943	5·623	37·376	92·2	0·522	0·397	0·162	120·3	131·6	103·5	
Calc.‡	7·930	5·560	37·590	93·7	0·529	0·412	0·163	119·1	130·7	101·9	124·7
	7·547	5.313	37·182	92·7	0·527	0·429	0·164	119·2	130·1	101·6	131·0
	0·1	1·1	0·5	1·5	0·006	0·014	0·001	1·2	0·9	1·6	
	4·9	5·5	0·5	0·5	0·005	0·032	0·002	1·1	1·5	1·9	
II											
Exp.	5·6584	39·992	7·8788	91·5	0·343	−0·012	0·751	9·9†	−26·1	150·4	
Calc.‡	5·6814	40·407	7·9626	90·5	0·349	−0·013	0·747	6·1	−25·1	151·8	139·7
	5·4234	39·910	7·6591	90·7	0·351	−0·011	0·746	6·1	−27·2	148·6	133·9
	0·4	1·0	1·0	1·0	0·005	0·001	0·003	3·8	1·0	1·4	
	4·2	0·2	2·7	0·8	0·007	0·001	0·004	3·8	1·1	1·8	
III											
Exp.	5·5803	7·4224	37·542	90·0	−0·361	0·809	0·774	98·6	−46·1	5·1	
Calc.‡	5·7491	7·5191	37·213	90·0	−0·368	−0·786	0·772	99·1	−45·0	2·7	137·7
	5·4812	7·2241	36·632	90·0	−0·375	0·777	0·772	98·9	−44·9	2·9	141·8
	3·0	1·3	0·9	—	0·007	0·022	0·002	0·5	1·1	2·4	
	1·7	2·6	2·4	—	0·014	0·632	0·002	0·3	1·2	2·2	
IV											
Exp.	18·394	5·0743	20·000	102·6	0·075	0·052	−0·092	114·8	−143·5	−37·4	
Calc.‡	18·556	5·0095	20·117	103·3	0·074	0·053	−0·093	114·1	−143·1	−37·1	152·7
	18·485	4·8251	19·045	102·9	0·073	0·064	−0·093	114·9	−143·0	−36·6	146·4
	0·8	1·2	0·6	0·7	0·001	0·001	0·018	0·7	0·4	0·3	
	0·5	4·5	4·7	0·3	0·002	0·012	0·011	0·1	0·5	0·8	
V											
Exp.	15·792	5·6872	19·584	91·9	0·616	−0·166	0·038	48·8	118·3	99·2	
Calc.‡	15·853	5·9061	19·606	90·9	0·617	−0·164	0·045	48·6	119·0	98·3	130·1
	15·620	5·6204	18·993	92·2	0·616	−0·157	0·040	47·7	118·6	98·1	129·3
	0·3	3·8	0·1	0·1	0·001	0·002	0·007	0·2	0·7	0·9	
	1·1	1·2	3·0	0·3	0·000	0·009	0·002	1·1	1·6	1·1	

† Differences between calculated and experimental unit cell parameters are given in per cent, monoclinic angle and angles of molecular orientation—in degrees and displacement of molecular centroids (X, Y, Z) in Å.

‡ The first row of values was calculated with Williams' parameters and the second with Kitaigorodsky's parameters.

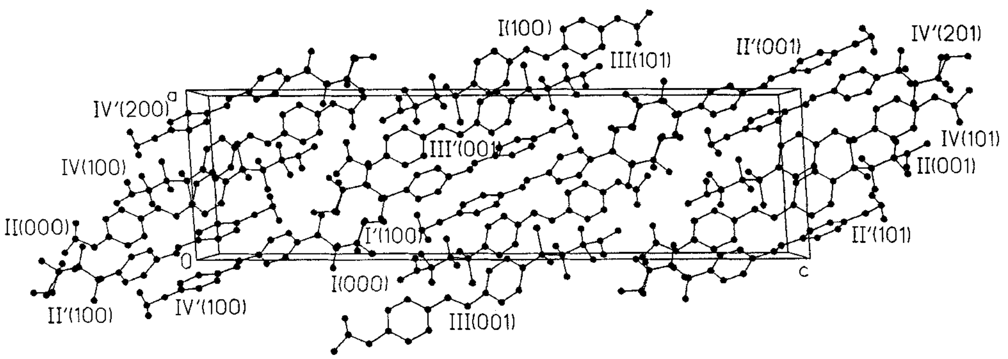


Figure 2. Molecular packing in crystal I along the *b* axis. Specification of the molecules corresponds to table 4.

Table 4. Intermolecular interaction energy in structure I.

Interacting molecules†	$-U/\mathrm{kJ\,mol^{-1}}$	Interacting molecules†	$-U/\mathrm{kJ\,mol^{-1}}$
In the layer		Between the layers	
I(000)–III(011)	20·33	I(000)–II'(011)	4·44
I(000)–III(001)	20·08	I(000)–II'(111)	3·89
I(000)–III'(101)	16·69	I(000)–IV'(100)	3·14
I(000)–I'(100)	15·65	I'(000)–II'(111)	3·43
I(000)–III'(001)	15·36	I'(000)–II'(101)	3·43
I'(000)–III'(101)	14·56	I'(000)–IV'(010)	2·22
I(000)–I(110)	14·43	I'(000)–IV'(111)	2·22
I'(000)–III'(101)	13·68	I(000)–II(011)	2·13
I(000)–I'(000)	1·13	I(000)–II(001)	2·13
$-U_{\mathrm{layer}} = -54{\cdot}72\,\mathrm{kJ\,mol^{-1}}$		$-U_{\mathrm{interlayer}} = -27{\cdot}02\,\mathrm{kJ\,mol^{-1}}$	

† Molecules specified as suggested in [29].

Table 5. Lattice energy ($-U/\mathrm{kJ\,mol^{-1}}$) of hypothetical structures in different space groups.

Space group and packing type	$P2_1/c$ parallel	$P2_1/n$ layered	$P2_12_12_1$ layered	$P2_1/n$ stacked	$P2_1/c$ parallel
	Structure				
Molecule	EBBA	II	III	IV	V
I	129·3	128·9	142·3	139·7	126·4
MBBA	124·7	122·6	127·2	120·9	117·6

To find the other possible packing types for molecule **I** the calculations of hypothetical structures (analogues of **II**–**IV**) were performed. The results of these calculations can be used to suggest models for the structures with the energetically preferable molecular packing which are similar to the molecular organization in the mesophase. The results of the calculations are given in table 5. The intermolecular energy was not minimized in structure **I** because the program employed does not handle structures with several independent molecules in the asymmetric unit. The structures **III** and **IV** with layer and chain type of packing, respectively, were found to be the most favourable for molecule **I**. If the hypothetical structure **III** is also a precursor of a layered smectic mesophase, structure **IV** (as that of the MBBA analogue [20]) is, on the other hand, the precursor of a non-mesogenic phase, since it has been shown earlier [4] that the most energetically favourable modes of molecular association in the latter structure are chains (stacks). We assume that at a phase transition such stacks are the last element of order to be destroyed and thus hinder the formation of a liquid-crystalline structure.

It is clear that there is no simple analogy between the observed solid crystal structure of **I** and structures of the other solid phases of **I**, if they exist, because the conformation of one of the independent molecules is not optimal energetically (the Y substituent is non-transoid). If the conformations of **I** and **I′** are considered to be similar, packing of molecules **I** is probably like the packing of molecules **IV** (which differ from molecules **I** only by one atom) and do not display liquid-crystalline properties.

3.2. *Crystal structure of MBBA*

MBBA is a typical nematogenic compound, with a nematic mesophase in the temperature range 22–28°C. We have noted that a complete X-ray structure analysis of MBBA single crystals has not yet been performed due to the failure to obtain suitable crystals. Our own extensive efforts in this regard include both solution and zone refining experiments [21].

Ten phases of MBBA (including nematic and isotropic) have been identified by neutron scattering results, X-ray, DSC and Raman scattering data [22–25]. The pattern of MBBA phase transitions is rather complicated and in particular two different routes of such transitions are N→C0→C1→C2→C3→C4→N and N↔C6↔C5. A significant feature of these transitions is the existence of at least two solid modifications at one temperature. Briefly the structural characteristics of some of these phases are as follows [19]: C0, the phase is very similar to a nematic phase; C1 and C2, smectic layered phases; C3 and C4, crystalline phases different from C5 and C6 crystalline phases. In [26] this type of polymorphism has been named isothermic polyphase polymorphism, because cooling the mesophase leads to at least two solid phases. Nevertheless, the similarity of nematic EBBA and MBBA properties provides support for the assumption that the crystal packing of at least one MBBA modification is similar to the EBBA structure. This similarity also seems likely for the C6 or C4 solid phases which directly transform into the nematic mesophase. Therefore, for the modelling of possible types of MBBA structure we have used the structures of EBBA and fluorinated derivatives **II**–**IV** of MBBA studied earlier [5–7]. The results of energy minimization of these structures are shown in table 5. It is clear that there are two energetically preferable structures of MBBA: one structure with parallel molecular organization (an analogue of EBBA) and a second structure with a layer type of packing (an analogue of **III**) with and without a conformational degree of freedom. The lattice parameters corresponding to the model at convergence are

	MBBA (EBBA)	MBBA (III)
a/Å	8·21	5·79
b/Å	5·41	7·44
c/Å	36·39	36·28
β/°	96·9	90·0
V/Å^3	1604	1563
Space group	$P2_1/c$	$P2_12_12_1$
Z	4	4

The calculated coordinates of non-hydrogen atoms are given in table 6 and the molecular packings are shown in figures 3 and 4.

From the experimental data [17] some variants of the monoclinic unit cell for the C5 and C6 phases were found. The two variants involving the smallest perturbation from the structures calculated previously are

	C5	C6
a/Å	7·7	7·8
b/Å	5·3	5·7
c/Å	34·8	33·5
β/°	94·6	94·2

These are in satisfactory agreement with the results of our calculations. The layer type of MBBA packing (an analogue of III) agrees with the neutron [18] and X-ray investigations [17, 19] of frozen liquid-crystalline MBBA phases which show a smectic

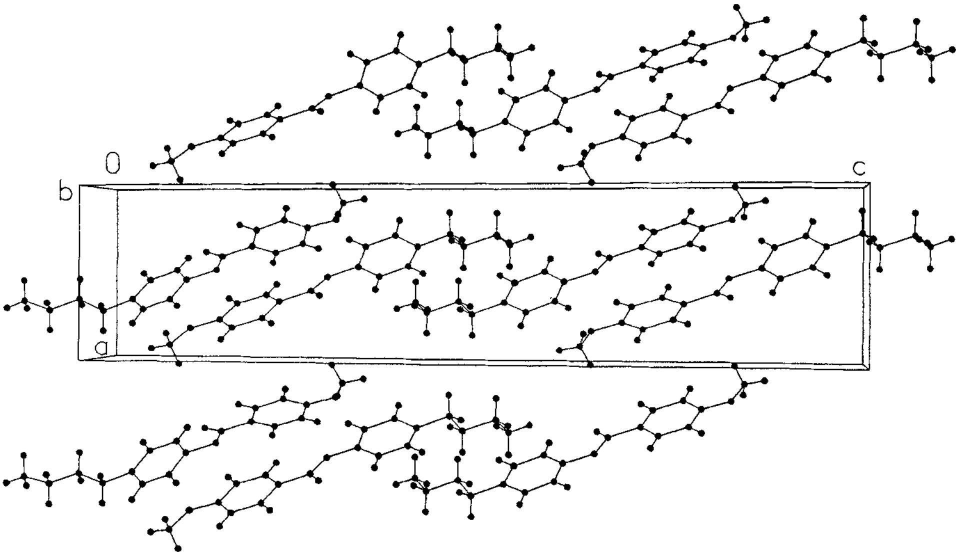


Figure 3. Molecular packing in an MBBA crystal (an analogue of EBBA) along the *b* axis.

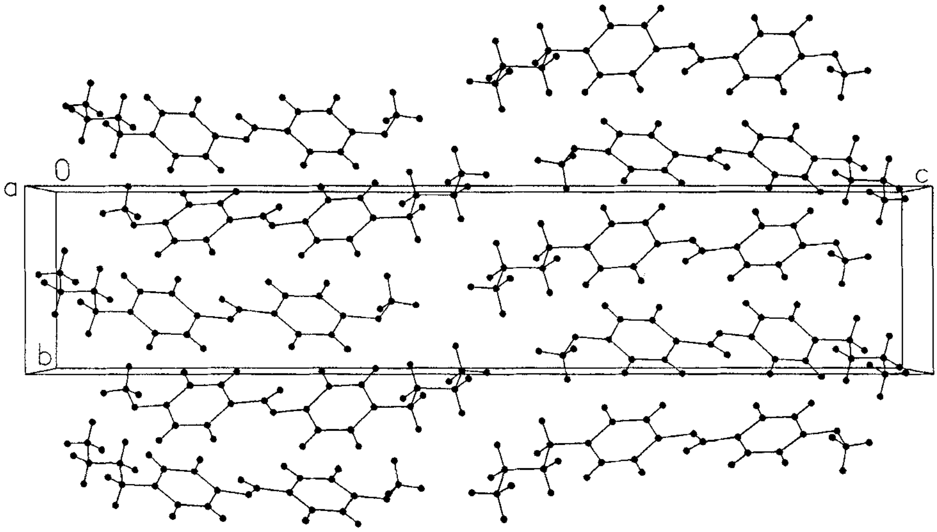


Figure 4. Molecular packing in an MBBA crystal (an analogue of III) along the *a* axis.

Table 6. Calculated coordinates of non-hydrogen atoms of the MBBA molecule in structures of III and EBBA.

III				EBBA			
Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
C1	−0·0200	0·8159	0·6437	C1	0·7583	0·1525	0·2972
C2	−0·1994	0·7140	0·6581	C2	0·6705	0·3625	0·2831
C3	−0·2527	0·7187	0·6947	C3	0·6201	0·3819	0·2461
C4	−0·1200	0·8269	0·7188	C4	0·6559	0·1917	0·2223
C5	0·0665	0·9210	0·7041	C5	0·7439	−0·0129	0·2361
C6	0·1199	0·9180	0·6672	C6	0·7981	−0·0366	0·2733
O	0·0135	0·8019	0·6062	O	0·8052	0·1591	0·3346
C8	0·1900	0·8947	0·5912	C8	0·8930	−0·0496	0·3508
C9	−0·1754	0·8459	0·7577	C9	0·5971	0·2087	0·1818
N	−0·3699	0·7924	0·7710	N	0·5182	0·3906	0·1670
C11	−0·4184	0·8132	0·8088	C11	0·4612	0·3787	0·1275
C12	−0·5940	0·7089	0·8237	C12	0·3495	0·2039	0·1133
C13	−0·6453	0·7148	0·8602	C13	0·2895	0·2194	0·0761
C14	−0·5304	0·8300	0·8846	C14	0·3457	0·4027	0·0528
C15	−0·3576	0·9396	0·8691	C15	0·4555	0·5689	0·0690
C16	−0·3026	0·9296	0·8329	C16	0·5157	0·5672	0·1062
C17	−0·5877	0·8346	0·9254	C17	0·2779	0·4089	0·0119
C18	−0·8024	0·9402	0·9337	C18	0·3467	0·2019	−0·0099
C19	−0·8754	0·9380	0·9739	C19	0·2837	0·2051	−0·0510
C20	−1·0944	1·0408	0·9823	C20	0·3391	−0·0182	−0·0715

character. The atomic coordinates of MBBA in the different proposed space groups can be used, in principle, as a basis for a trial crystal structure of MBBA and computer modelling of its mesophase by means of molecular dynamics [27, 28].

In this paper we consider the models with one system of independent molecules. It is obvious that among the solid phases of MBBA the phases with conformationally distinct molecules (conformational polymorphs) and phases with several independent molecules which can have similar of distinct conformations may exist. The crystal structures of the latter type are quite usual for mesogenic compounds [16, 17, 30]. For example, one of the fluorinated EBBA derivatives forms the crystals built of three systems of confomationally distinct molecules [30]. We intend to consider these structures in the future.

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