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Crystal structure and packing analysis of the liquid crystal dimer alpha,omega-bis(4-cyanobiphenyl-4-yloxy)octane

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Crystal structure and packing analysis of the liquid crystal dimer α,ω -bis(4-cyanobiphenyl-4'-yloxy)octane

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The crystal structure of the liquid crystal dimer α,ω -bis(4-cyanobiphenyl-4'-yloxy)octane has been determined from diffraction data obtained with synchrotron radiation. The structure is triclinic, with the space group $P-1$ with $Z = 2$ and the unit cell parameters are $a = 7.135(5) \text{ \AA}$, $b = 12.811(5) \text{ \AA}$, $c = 15.639(5) \text{ \AA}$, $\alpha = 75.800(5)^\circ$, $\beta = 84.690(5)^\circ$, $\gamma = 77.930(5)^\circ$. The flexible spacer linking the mesogenic groups is in the all-*trans*-conformation. Although the molecule has a potential centre of symmetry, it occupies a general position in the cell; this unusual behaviour has been investigated with the aid of a theoretical evaluation of the packing energy.

1. Introduction

Liquid crystal dimers consist of two mesogenic groups linked by a flexible spacer [1]. These materials are of interest because they mimic certain aspects of the behaviour of semi-flexible main chain liquid crystal polymers. In addition the dimers exhibit quite fascinating properties which include an unusually strong alternation in such transitional properties as the nematic–isotropic transition temperature, the entropy change and the orientational order parameters of the mesogenic groups. At a superficial level these odd–even effects have been attributed to the difference in the shape of dimers with odd and even numbers of atoms in the flexible spacers. However, other factors that include the synergy between the conformational and orientational order are equally important [2]. These can be understood either with the aid of molecular field theory [3] or via computer

simulation [4]. In either case, some knowledge of the molecular geometry is important if a realistic model of the liquid crystal dimer is to be developed. For example, molecular field calculations have revealed just how sensitive the predictions of the model are to the angle between the long axis of the mesogenic group and the link to the alkyl chain [5]. There is, therefore, a clear need for structural studies of liquid crystal dimers, but few of these have been reported [6–10] presumably because of the difficulty of growing single crystals suitable for X-ray analysis. One of the first such investigations was for the odd-membered α,ω -bis(4-cyanobiphenyl-4'-yloxy)heptane (BCBO7) [6] which revealed the bent shape of the dimer, at least when the chain was in its all-*trans*-conformation. Clearly it would be advantageous to have the corresponding structure for an even member of the same series. However, although a sample of α,ω -bis(4-cyanobiphenyl-4'-yloxy)octane (BCBO8) was available, we were unable to grow single crystals suitable for conventional X-ray analysis. Now, several years later,

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we have been successful by using analysis with synchrotron radiation. Here we report results of this study, thus making available the molecular structures of an odd and an even liquid crystal dimer based on the symmetric cyanobiphenyl mesogenic groups.

2. Experimental and structure determination

The largest crystal of BCBO8 (*c.* $0.08 \times 0.10 \times 0.02 \text{ mm}^3$) was obtained by recrystallization from a solution in boiling ethyl acetate. It was mounted on a Siemens P4 diffractometer with a conventional X-ray source ($\lambda = 1.54179 \text{ \AA}$, current = 34 mA, voltage = 44 kV) with which it was possible to centre just 21 reflections in the range $8^\circ < \theta < 22^\circ$. These preliminary results allowed us only to determine the unit cell parameters, reported in table 1, but no structural analysis could be undertaken. After this we decided to use synchrotron radiation, available at the X-ray diffraction beamline of ELETTRA (Trieste, Italy). Data with a resolution of 0.850 \AA were recorded on a MAR Research 345 image plate using radiation with $\lambda = 0.81069 \text{ \AA}$, an oscillation angle of 2° and a sample to detector distance of 100 mm. Images were processed and scaled using the programs DENZO and SCALEPACK [11]. A total of 4281 unique reflections

were collected, of which 3295 were considered observed, having intensity I greater than twice the standard deviation of the noise, $\sigma(I)$.

The structure was solved by direct methods using the program SIR97 [12] which revealed all non-H atoms. All the H atoms were located from successive difference electron density maps and freely refined. Refinement was completed using a full-matrix least-squares minimization of F^2 with the program SHELX97 [13] employing anisotropic temperature factors for all non-H atoms. Details of the data collection and structure refinement are reported in table 1.

3. Results and discussion

3.1. Molecular geometry

A perspective view of the molecule, with the atomic numbering scheme, is shown in figure 1 and selected geometric parameters are reported in table 2.

As already observed in the odd dimer BCBO7, the ether linked alkane chain has an extended all-*trans*-conformation, with a mean torsion angle on the ten chain atoms of $180.8(1)^\circ$; all of the atoms are coplanar with the maximum deviation from the least-squares plane passing through the ten chain atoms being just $0.054(1) \text{ \AA}$ at the C7 atom. Along the alkane chain, the bond lengths are all equal within experimental error, while the bond angles show a slight alternation; that is those centred on even numbered carbon atoms are significantly smaller (mean values $112.8(1)^\circ$) than those centred on odd numbered carbon atoms (mean values $114.1(4)^\circ$). As a consequence the chain is slightly arched, a feature that has already been observed in other long chain aliphatic compounds [14]. In the two biphenyl units, bond lengths are in the expected range (from $1.371(2)$ to $1.394(2) \text{ \AA}$), whereas the slight narrowing found in the endo angles centred on C12 and C15 and, symmetrically, on C25 and C28, is in agreement with the geometry of other biphenyl moieties reported in the Cambridge Structural Database [15] and also for BCBO7. In particular, the geometry of the 4-cyanobiphenyl fragment of BCBO8 compares well with that of the equivalent fragment present in α -hydroxy- ω -(4-cyanobiphenyl-4'-yloxy)octane and in related compounds with nonane, decane and undecane chains [16] and in 4'-octyloxy-4-cyanobiphenyl [17]. The relative positions of the phenyl rings within each biphenyl unit are given by the torsion angles reported in table 2. The two external phenyl rings are nearly parallel to each other (the dihedral angle between them is just $4.0(1)^\circ$) and the two internal phenyl rings are nearly coplanar with the non-H atoms of the spacer. The long axes, O1 ... C21 and O2 ... C34, of the mesogenic groups are coplanar with the plane of the chain, and make an angle

Table 1. Crystal data and structure refinement for BCBO8.

Empirical formula	$\text{C}_{34}\text{H}_{32}\text{N}_2\text{O}_2$
Formula weight	500.62
Temperature	293(2) K
Wavelength	0.81069 \AA
Crystal system, space group	Triclinic, <i>P</i> -1
Unit cell dimensions	$a = 7.135(5) \text{ \AA}$ $\alpha = 75.800(5)^\circ$ $b = 12.811(5) \text{ \AA}$ $\beta = 84.690(5)^\circ$ $c = 15.639(5) \text{ \AA}$ $\gamma = 77.930(5)^\circ$
Volume	$1353.9(12) \text{ \AA}^3$
Z, Calculated density	2, 1.228 Mg m^{-3}
Absorption coefficient	0.076 mm^{-1}
$F(000)$	532
Crystal size	$0.08 \times 0.10 \times 0.02 \text{ mm}^3$
Theta range for data collection	2.15° to 28.50°
Index ranges	$0 \leq h \leq 8$, $-14 \leq k \leq 15$, $-17 \leq l \leq 18$
Reflections collected/unique	4281/4281
Completeness to $\theta = 28.50^\circ$	92.4%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4281/0/440
Goodness-of-fit on F^2	1.026
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0414$, $wR2 = 0.1091$
R indices (all data)	$R1 = 0.0549$, $wR2 = 0.1200$
Extinction coefficient	0.000(7)
Largest peak and hole in the difference map	0.127 and $-0.124 \text{ e. \AA}^{-3}$

Table 2. Selected geometric parameters (Å, °) for BCBO8.

O(1)–C(1)	1.428(2)	C(3)–C(4)	1.515(2)	
O(1)–C(9)	1.364(2)	C(4)–C(5)	1.504(2)	
O(2)–C(8)	1.429(2)	C(5)–C(6)	1.514(2)	
O(2)–C(22)	1.361(2)	C(6)–C(7)	1.505(2)	
N(1)–C(21)	1.141(2)	C(7)–C(8)	1.498(2)	
N(2)–C(34)	1.140(2)	C(12)–C(15)	1.475(2)	
C(1)–C(2)	1.496(2)	C(18)–C(21)	1.438(2)	
C(2)–C(3)	1.507(2)	C(25)–C(28)	1.476(2)	
C(31)–C(34)	1.433(2)			
C(1)–O(1)–C(9)	118.62(12)	C(20)–C(15)–C(12)	121.07(14)	
C(8)–O(2)–C(22)	119.05(12)	C(16)–C(15)–C(12)	121.51(14)	
O(1)–C(1)–C(2)	107.90(14)	C(17)–C(18)–C(21)	121.07(15)	
C(1)–C(2)–C(3)	112.59(14)	N(1)–C(21)–C(18)	176.84(17)	
C(2)–C(3)–C(4)	114.88(14)	O(2)–C(22)–C(27)	125.06(14)	
C(5)–C(4)–C(3)	112.75(14)	O(2)–C(22)–C(23)	115.85(12)	
C(4)–C(5)–C(6)	115.31(14)	C(26)–C(25)–C(28)	121.07(13)	
C(7)–C(6)–C(5)	112.29(14)	C(24)–C(25)–C(28)	121.78(14)	
C(8)–C(7)–C(6)	114.11(14)	C(29)–C(28)–C(25)	121.84(13)	
O(2)–C(8)–C(7)	107.34(13)	C(33)–C(28)–C(25)	120.39(13)	
O(1)–C(9)–C(10)	115.55(14)	C(32)–C(31)–C(34)	119.89(14)	
O(1)–C(9)–C(14)	125.26(14)	C(30)–C(31)–C(34)	120.10(15)	
C(13)–C(12)–C(15)	121.64(14)	N(2)–C(34)–C(31)	178.91(17)	
C(11)–C(12)–C(15)	121.41(14)	C(19)–C(18)–C(21)	119.46(15)	
C(9)–O(1)–C(1)–C(2)	177.20(13)			
C(1)–O(1)–C(9)–C(10)	176.87(14)			
C(22)–O(2)–C(8)–C(7)	175.98(13)			
C(8)–O(2)–C(22)–C(23)	173.80(14)			
O(1)–C(1)–C(2)–C(3)	179.68(15)			
C(1)–C(2)–C(3)–C(4)	178.19(15)			
C(2)–C(3)–C(4)–C(5)	176.84(15)			
C(3)–C(4)–C(5)–C(6)	178.24(15)			
C(4)–C(5)–C(6)–C(7)	179.75(16)			
C(5)–C(6)–C(7)–C(8)	178.41(15)			
C(6)–C(7)–C(8)–O(2)	175.66(15)			
C(13)–C(12)–C(15)–C(20)	38.7(2)			
C(24)–C(25)–C(28)–C(29)	38.4(2)			
D–H ... A ^a	d(D–H)	d(H ... A)	d(D ... A)	< (DHA)
C(17)–H(17) ... N(2)#1	1.006(17)	2.597(17)	3.410(3)	137.8(12)
C(32)–H(32) ... N(2)#2	0.931(16)	2.557(16)	3.396(2)	150.1(13)

^a Symmetry transformations used to generate equivalent atoms: #1 $x - 4, y + 1, z - 1$ #2 $-x + 4, -y - 1, -z + 3$.

of 6.9° with each other. This is the main difference between the overall geometry of odd dimer BCBO7 and that of the even dimer BCBO8 (in BCBO7 this angle is 34.2°); the reason is obviously the different parity of the spacer. It is this major difference in the molecular geometry that, together with the conformational freedom resulting from the flexible spacer, is responsible for the dramatic odd–even effects of the liquid crystalline properties. In this respect we acknowledge that such a correlation between all-*trans*-geometry and odd–even effects was not observed in [7], where a similar comparison between the structures of α,ω -bis(4-*n*-alkylanilinebenzylidene-4'-oxy)alkanes containing terminal alkyl chains (*m.O.n.O.m*) was drawn. The four membered

spacer in 5.O.4.O.5 contains a '*gauche*' torsional rotation whereas an all-*trans*-conformation is present in the odd-membered spacer in 5.O.5.O.5.

Defining the long chain axis as the line connecting the midpoints of the O1–C9 and O2–C22 bonds, the angles between the long chain axis and each of the long axes of the mesogenic groups are 155.6° and 162.4° for O1 ... N1 and O2 ... N2, respectively (for the odd dimer BCBO7, a mean value of 162.6° was found). These angles depend on how the flexible spacer is connected to the two cyanobiphenyl groups. Since the mean chain plane and the planes of the internal phenyl rings are coplanar, there is a short distance between atoms C1 and C14 and, equivalently, between atoms C8 and C27.

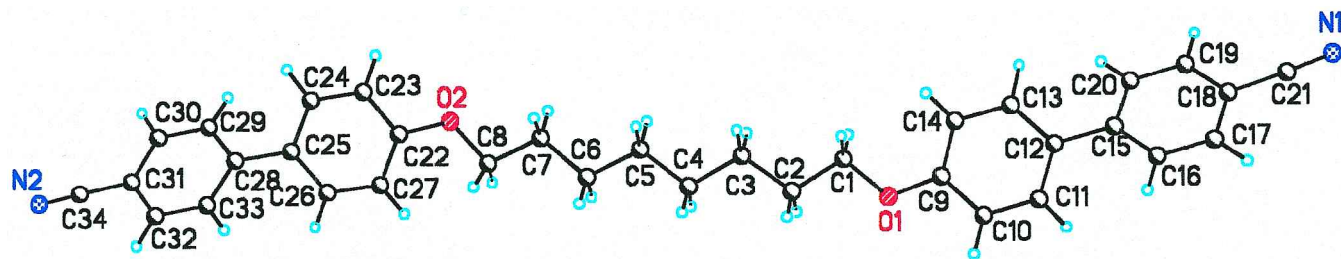


Figure 1. A view of α,ω -bis(4-cyanobiphenyl-4'-yloxy)octane showing the atomic numbering scheme.

This close proximity may result in the opening of the C1-O1-C9 angle to 118° and of the O1-C9-C14 angle to 125° and in the reduction of the O1-C9-C10 angle to 115° , on one side and similarly for the other mesogenic group. These distortions tend to increase the linearity of the overall molecular skeleton in molecules with both even- and odd-membered spacers. The detailed geometrical information now available for both odd and even cyanobiphenyl dimers will be of considerable value in the computer modelling of the behaviour of liquid crystal dimers.

3.2. Crystal packing

The crystal packing for BCBO8 shows a rather unusual feature that merits detailed discussion. In spite of the potential centre of symmetry located between atoms C4 and C5 and of the centrosymmetric space group, the molecule is not centrosymmetric itself and occupies a general position in the unit cell. Deviations from centrosymmetry are shown in figure 2, where the real molecule is compared with the two hypothetical centrosymmetric halves generated by inversion from the respective halves of the real molecule. It may be seen that the difference between the actual position of one extreme N atom and the position generated by imposing a centre of symmetry is 1.78 \AA . This lack of symmetry is rather unusual since α,ω -disubstituted long chain alkanes with an even number of carbon atoms are normally rigorously centrosymmetric with few exceptions. A

deviation from centrosymmetry was observed in α,ω -bis(1-cyanophenyl-4-oxy)pentane [3] and in sodium 1,12-dodecylene disulphate hydrate [4]; in the former compound, however, structural differences between the two halves of the molecule appear negligible and in the latter case the asymmetry concerns only one of the two independent molecules in the unit cell. Another deviation from centrosymmetry has been observed in the above-cited α,ω -bis(4-*n*-pentylanilinebenzylidene-4'-oxy)butane (5.O4O.5) [7] where a strong intramolecular effect is present. Indeed one of the torsion angles in the spacer is in a *gauche*-state, all others being *trans*; this *gauche*-bond breaks the molecular symmetry but increases the linearity of the molecule.

In the crystal, see figure 3, the molecules of BCBO8 are aligned head-to-tail to form infinite chains via C17-H...N2 interactions between one molecule and the following one; adjacent chains are arranged in an antiparallel way. Every chain is connected to one of its antiparallel neighbours by means of weak C32-H...N2 interchain contacts. The crystal is built up of sheets of interdigitated pairs of chains displaced along the chain direction by half a molecule. It is interesting to note that a similar interdigitated arrangement was also found in 5.O5O.5, where no polar terminal groups are present. Focusing attention on close contacts involving the polar $\text{-C}\equiv\text{N}$ groups of BCBO8, it appears that the $\text{-C}\equiv\text{N}$ moieties are completely surrounded by polar groups and are involved in bifurcated interactions, whereas the

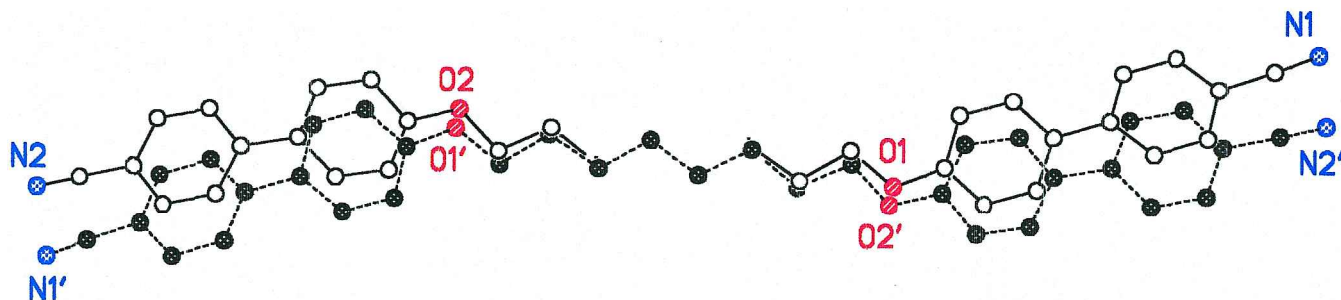


Figure 2. The real molecule (with atoms drawn as open circles linked by full lines) and two hypothetical centrosymmetric halves of the molecule generated via a centre of symmetry located between C4 and C5 (atoms generated by this symmetry operation are labelled with a prime). Distances: $\text{O1} \cdots \text{O2}' = \text{O2} \cdots \text{O1}' = 0.468 \text{ \AA}$; $\text{N1} \cdots \text{N2}' = \text{N2} \cdots \text{N1}' = 1.782 \text{ \AA}$.

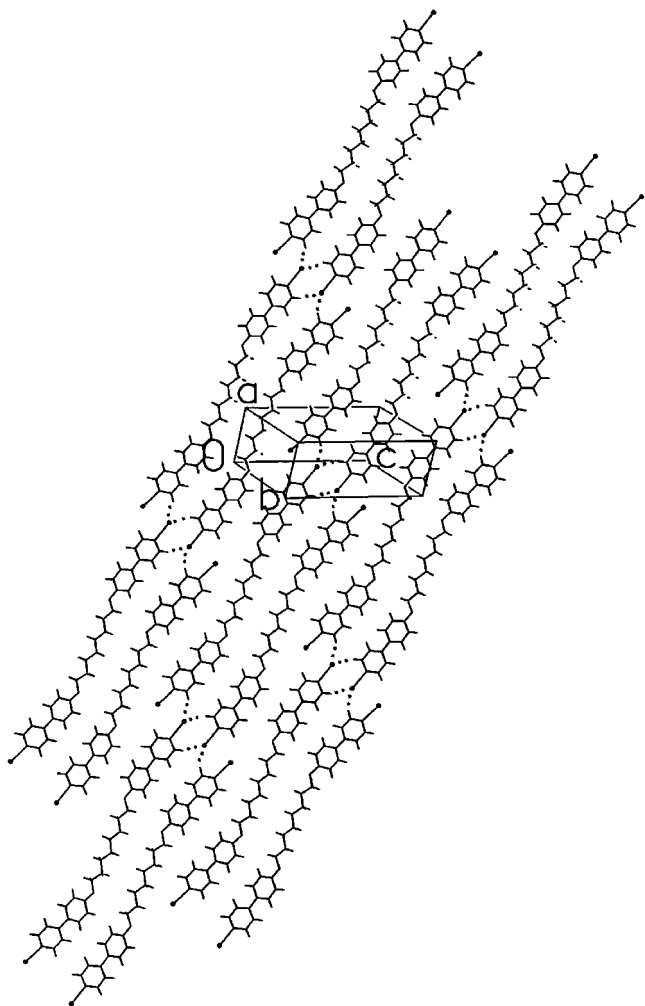


Figure 3. Parallel projection of the crystal structure of BCBO8. Dotted lines indicate the unusually short N...H distances which may be regarded as weak hydrogen bonds.

$\text{-C}\equiv\text{N1}$ moieties are only partially surrounded by polar groups, being also close to the hydrocarbon spacers, and have no intermolecular contacts shorter than the sum of the van der Waals radii. This feature may account for the asymmetry of the molecule.

We have tried to find an explanation for this unusual behaviour with the aid of theoretical packing energy calculations, as described in the next section.

Figure 4 shows the crystal packing viewed along the molecular long axis. As found also in 5.O4O.5 [7], a pseudo-hexagonal close packed arrangement is clearly visible; in BCBO8 this however appears more flattened than that found in 5.O4O.5.

3.3. Crystal packing calculations

Calculations were carried out with the program CHAMP [18], which was designed for modelling crystalline polymers [19, 20] and oligomers [21, 22]

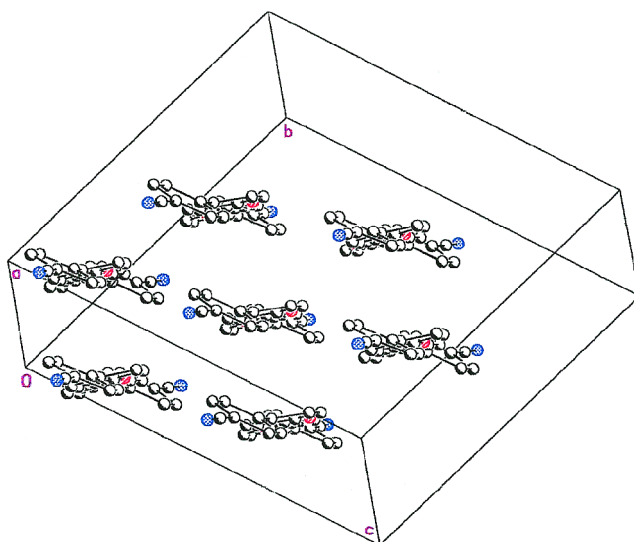


Figure 4. Flattened pseudo-hexagonal close packed arrangement of BCBO8 viewed along the molecular long axis.

and allows for simultaneous optimization of intra- and inter-molecular interactions. The force field employed in these calculations is taken from MM2 [23]; this includes repulsive, attractive and electrostatic interactions, together with torsional, bond bending and bond stretching potentials.

As we would expect, calculations for the isolated molecule indicate that the asymmetry cannot be ascribed to the intramolecular interactions, but, in agreement with the analysis based on experiment, it is due to the crystal packing. The crystallographic model (Model A) was the starting point of an intra- and inter-molecular energy minimization, and the resulting model (Model B) is very similar to the starting one with a mean displacement of 0.21 \AA for non-hydrogen atoms. This deviation could be reduced to 0.08 \AA which caused an increase of only 1.63 kJ mol^{-1} ; this is achieved by adding quadratic terms to the force field which restrict the atoms to their starting positions. This means that our packing analysis is likely to give a good description of the forces acting within the crystal.

To investigate the nature of the forces that favour the asymmetric molecular structure, we decided to calculate the packing energy for two structural models that may be derived from the experimental one by forcing the molecule to have a centre of symmetry. Figure 5(a) shows the minimum energy structure obtained under the constraint that the molecule is centrosymmetric. In this structure, which maintains the experimental unit cell, all of the molecules are parallel, so that molecules 5, 1, 2 and molecules 7, 1, 2, respectively, can provide the b, c base of the cell for the two new models (hereafter Model C and Model D) having the a -axis in common

Table 3. Relative lattice energies and r.m.s. deviations of non-hydrogen atoms from experimental positions for various minimum energy models of BCBO8.

Model	Cell	Z	Molecular symmetry	$\Delta E_{\text{tot}}/\text{kJ mol}^{-1}$	$\Delta E_{\text{Coul}}/\text{kJ mol}^{-1}$	r.m.s.d./Å
Free Min. B	Exptl	2	NO	0.0	0.0	0.206
Constr. Min.	Exptl	2	NO	1.63	3.72	0.081
Symm. Min.	Exptl	2	P-1	10.38	-3.05	0.342
Model C	A	1	P-1	-7.91	-12.26	0.593
Model D	B	1	P-1	14.35	4.10	0.576

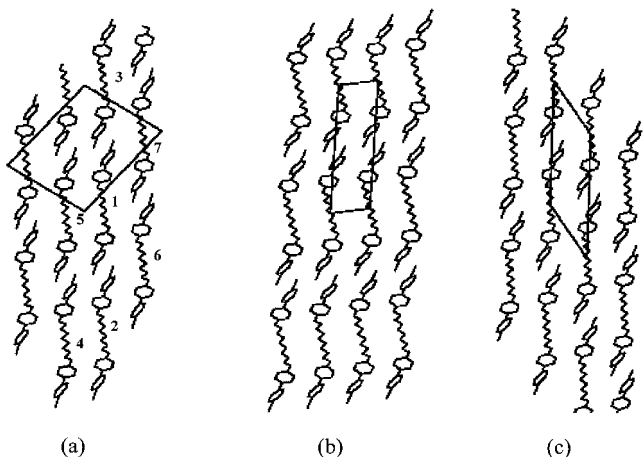


Figure 5. Symmetric crystallographic models of BCBO8: (a) Experimental unit cell, symmetrical molecule; (b) Model C: $b = 6.03 \text{ \AA}$, $c = 17.62 \text{ \AA}$, $\alpha = 79.1^\circ$; (c) Model D: $b = 15.32 \text{ \AA}$, $c = 17.62 \text{ \AA}$, $\alpha = 122.2^\circ$.

with model A and volumes equal to one half that of the crystallographic cell. As we can see from figures 5(b) and 5(c), the two models repeat one of the two motifs that characterize model A along the $b+c$ direction. Model C is characterized by an uninterrupted propagation of polar contacts between the two extremes of the molecules, whereas model D is characterized, along the same direction, by an alternate sequence of polar interactions and hydrocarbon moieties.

Relative packing energy data are reported in table 3. It may be seen that model C has an energy lower than that of model B by 7.9 kJ mol^{-1} , whereas model D has an energy higher than that of model B by 14.2 kJ mol^{-1} . This was somehow surprising to us since we did not expect to find a structural model that is more stable than that observed. A possible explanation may be found in the imperfect parametrization of the electrostatic interactions adopted in our force field. These interactions are surely very important in determining the actual value of the packing energy and even small uncertainties may be responsible for the calculated differences. Nevertheless, some conclusion may be drawn from our calculations and we point out the existence of alternative, more symmetric models that involve packing energies close to

that of the observed model. A definite explanation for the preference for model B is at present beyond our approach, since it probably involves a much more accurate evaluation of the electrostatic interactions.

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