X-ray Structure at 150 K of the Polar Alkyl Mesogenic Compound 7CBB: 4-Cyanobiphenyl-4′-Heptylbiphenyl Carboxylate

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ABSTRACT

The compound under study 7CBB consists of two biphenyl moieties A-B and C-D linked by a carboxylate group. Ring A terminates in a 4-cyano group and C-D is linked to the terminal alkyl chain. A previously reported room temperature determination of the crystal structure employing MoKα X-radiation was thought to contain serious errors in describing the alkyl chain as being disordered. The X-ray structure factors were not deposited with this published structure and as a consequence two new X-ray data sets have been collected: (1) using MoKα radiation at room temperature 295K (a repeat of the previous study) and (2) using CuKα radiation at 150K in an attempt, which proved successful, to improve the overall quality of the structure determination. The corrected MoKα structure and the CuKα structure both reported here have enabled the previous errors to be identified, concluding that there is no disorder in the alkyl chain. The alkyl chain in the MoKα structure at 295K was found to have anisotropic thermal factors slightly exaggerated with respect to the remainder of the structure. However, this effect is not observed in the CuKα structure at 150K, all anisotropic thermal factors including those in the alkyl chain being reduced to cover a much smaller overall range of values. Consequently, it can be concluded that the effect observed in the alkyl chain at 295K is merely one of a thermal nature, not one of disorder. There are no unusual bond lengths or angles present. The biphenyl moieties are planar within 0.035Å and 0.020Å respectively. The dihedral angles of all ring pairs have been calculated. Calculation of intermolecular distances between molecules related by a centre of symmetry reveals the existence of a number of van-der Waals interactions. The H-bonding motif typical of crystal structures of cyanobiphenyl compounds is observed. The molecular packing mode corresponds to that of a precursor of the smectic phase.
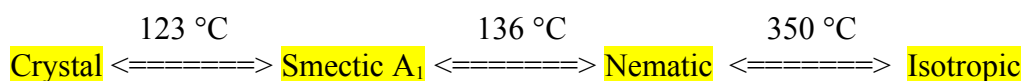
1. Introduction

The liquid crystalline compound, a member of the nCBB series with $n = 7,4$–cyanobiphenyl–4′–heptylbiphenyl carboxylate (7CBB) was prepared at the Institute of Chemistry, Military University of Technology, Warsaw, Poland [1]. The structural formula of the compound is given below in Scheme 1.
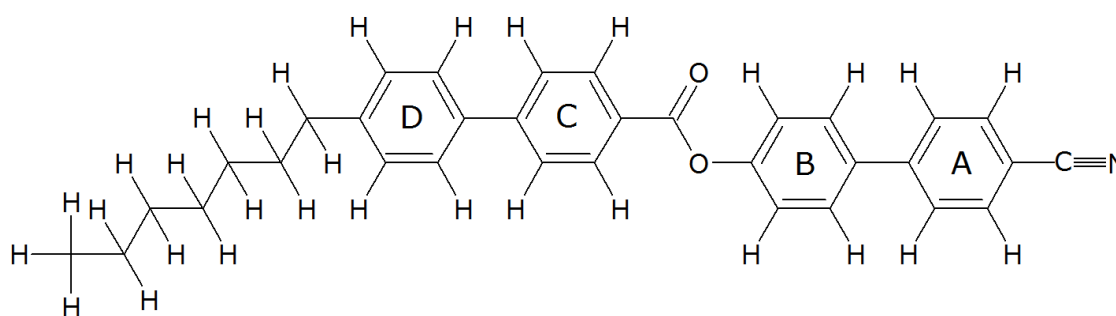
Scheme 1. Chemical structure of 7CBB.

The phase transitions and analysis of the phase diagrams of mesogenic compound 7CBB were studied by using optical microscopy, scanning calorimetry and X-ray diffraction methods by Dabrowski *et al*. [1]. The reported transition temperatures are given below:

$$\text{Crystal} \xleftrightarrow{\;123\,°C\;} \text{Smectic A}_1 \xleftrightarrow{\;136\,°C\;} \text{Nematic} \xleftrightarrow{\;350\,°C\;} \text{Isotropic}$$

A previously reported room temperature determination of the crystal structure of 7CBB employing MoKα radiation was thought to contain serious errors in describing the alkyl chain as being disordered as described by Haldar *et al.* [2]. In this connection we have undertaken a new study of the crystal structure of 7CBB in order to improve the overall quality of the structure determination as well as to identify the errors made by Haldar *et al.* [2].

2. Experimental

2.1 *Crystallization*

7CBB was prepared as described by Dabrowski *et al.* [1]. Transparent plate-shaped crystals were obtained by slow evaporation at 296 K from acetone solution.

2.2 *X-ray Data Collection*

(a) *MoKα data at Room Temperature 295 K*

A suitable crystal with dimensions $0.270×0.233×0.161$ mm^3 was selected and an Agilent Oxford Diffraction SuperNova equipped with microfocus Cu and MoKα X-ray sources and an Atlas CCD detector. The crystal was kept at 295 K during data collection. A full sphere of data was collected with MoKα X-rays and the data were processed with the program CrysAlisPro, Agilent Technologies Version 1.171.36.28. The crystal showed excellent diffraction quality and no variation in intensity during the course of data collection. A total of 40,781 integrated reflections were collected, reducing to a data set of 6355 [R(int) = 0.0341], and completeness of data to θ = 29.485° of 99.4%. Further details of the crystal data are in Table 1(a). The lattice parameters are compared with Haldar *et al.* [2] and found that they are almost same for both study. The chemical formulae and atom numbering scheme are given in Figure 1. The crystals are monoclinic, space group $P2_1/c$.

(b) *CuKα data at Temperature 150 K*

A second suitable crystal with dimensions $0.784×0.105×0.058$ mm^3 was selected and mounted on the diffractometer and was cooled to 150 K. A full sphere of data was collected with CuKα radiation and processed as described above. The crystal showed excellent diffraction quality and no variation in intensity during the course of data collection. A total of 36,185 integrated reflections were collected, reducing to a data set of 5025 [R(int) = 0.0444], and completeness of data to theta = 67.684° of 99.9%. Further details of the crystal data are in Table 1(b). The chemical formulae and atom numbering scheme are given in Figure 1 (drawn with Ortep/Raster [3,4]). Note: rings A, B, C and D are designated 1, 2, 3 and 4

respectively in Haldar *et al.* [2]. The crystal structure remains monoclinic, space group $P2_1/c$ at 150 K.

2.3 *X-ray Structure Solution and Refinement*

Initially using the program Olex2 [5] each 7CBB structure was solved with the SHELXS [6] structure solution program using direct methods and refined with the SHELXL [7] refinement package using full matrix least squares minimization. H atoms were placed geometrically and refined in riding mode with isotropic thermal parameters. Further refinement was subsequently carried out as follows for both data sets. The non-H atoms were first renumbered to comply with the chemical numbering scheme shown in Figure 1. All H atoms were deleted and after further cycles of anisotropic refinement involving the non-H atoms a SHELXL [7] difference electron density plot was examined. The strongest peaks were found to be located in geometrically acceptable positions as H atoms and were subsequently refined in position with isotropic thermal parameters. All H atoms in the two structures were located during this procedure. Final X-ray refinement was carried out using SHELXL-97 [7] implemented in the WinGX system of programs [8]. This technique resulted in slight improvements to both structures as can be seen with reference to Tables 1(a) and (b). Least squares planes were calculated, possible H-bonds were recorded and complete sets of crystal tables were produced in WinGX [8]. Geometrical calculations were made with the programs PARST [9, 10] and PLATON [11] as implemented in WinGX.

3. Results and Discussions

3.1 *Results*

(a) *MoKα Data at Room Temperature 295 K*

In the final refinement cycle there were 6459 data to 449 parameters, resulting in a final goodness-of-fit on F^2 of 1.023. Final R indices for [I>2σ(I)] were $R_1 = 0.0518$, $wR_2 = 0.1339$ and R indices (all data) $R_1 = 0.0687$, $wR_2 = 0.1476$. The largest and smallest difference electron density regions were +0.305 and -0.220 e.$Å^{-3}$ respectively. Full crystal data are available in the Table 1(a).

(b) *CuKα Data at Temperature 150 K*

In the final refinement cycle there were 4975 data to 449 parameters, resulting in a final goodness-of-fit on F^2 of 0.928. Final R indices for [I>2σ(I)] were R_1 = 0.0405, wR_2 = 0.1216 and R indices (all data) R_1 = 0.0451, wR_2 = 0.1285. The largest and smallest difference electron density regions were +0.198 and -0.191 e.Å^{-3} respectively. Full crystal data are available in the Table 1(b).

3.2 *Reported Disorder in the structure of 7CBB of Haldar et al.* [2]

Haldar *et al.* [2] reported a crystal structure for 7CBB derived from MoKα X-ray data at room temperature (RT) in which they describe the alkyl chain attached to C24 as being disordered. The data deposited for this structure, CCDC 689871, does not include the X-ray structure factors required for a direct inspection of the reasoning behind the conclusion that the alkyl chain is disordered. Consequently, as described above, a fresh set of diffraction data was collected under the same conditions as used by Haldar *et al.* in order to reproduce, as near as possible the conditions that led Haldar *et al.* to this conclusion. The diffraction data of Haldar *et al.* is derived from a crystal having the same crystallographic parameters as that used in the present study and also exposed to MoKα radiation at room temperature. The two analyses were therefore expected to be directly comparable. The atom numbering, shown in Figure 1 and used throughout, is that of Haldar *et al.* who had concluded that the alkyl chain attached to C24 was disordered, with atoms C28 and C29 occupying alternate minor sites designated C28A and C29A (Figure 2). There is no description in Haldar *et al.* of how or why the existence of C28A and C29A was identified. Haldar *et al.* did not report the initial positions or relative occupancies of the atoms in the major and minor sites of their model but the parameters for C28 and C29 indicate refined site occupancy factors of 0.78 and 0.66 respectively. The refined coordinated of atoms C28A and C28B in the deposited .cif file are remarkably similar to the coordinates of the two highest difference peaks in the present study.

Haldar *et al.* did not provide any details of how the proposed disordering was refined. However, based on the reported atomic positions it is clear, as described below, that the model of the minor alkyl chain has totally unacceptable molecular geometry, although Haldar *et al.* failed to report this. It can be shown from calculations based on the data in the deposited .cif file that bond lengths C27-C28A = 1.277Å and C29A-C30 = 1.316Å, both of which are much shorter than standard values [12] and are therefore unacceptable. This observation is discussed further below.

3.3 *Examination of Possible Disorder in 7CBB in the Present MoKα Study*

In order to clarify this situation, difference electron density difference maps from the present analysis of the room temperature MoKα structure were examined. When N1 was omitted from the analysis the largest difference electron density peak (for N1) had a relative value of 4.43. With reference to the refinement of the complete structure the two largest difference peaks Q1 and Q2 appeared graphically to be located close to peaks C28A and C29A (Figure 2) respectively in Figure 1 of Haldar *et al.* [2] analysis. In our present study Q1 with a relative difference electron density value of 0.92 and Q2 a value of 0.52 has been found. The coordinates of these difference peaks are listed in Table 2(b). It is clear from the coordinates listed here (Table 2(a)) that Haldar *et al.'s* C28A has remarkably similar coordinates to Q1 in the present analysis and C29A has remarkably similar values to Q2.

3.4 *Comments on the Minor Alkyl Chain Investigation*

Selected molecular geometry for the minor alkyl chain conformation for both Haldar *et al.'s* published structure and that of the present study are given in Table 3 which clearly indicates that the bond lengths C27-Q1(C28A) and Q2(C29A)-C30 are very short and that these values are unacceptable [12]. Since C28A and C29A in Haldar *et al.'s* structure have very similar fractional coordinates to Q1 and Q2 in the present structure (Table 2(b)) the corresponding

bond lengths in the disordered alkyl chain of Haldar *et al.* are very similar to those in the present structure as has been shown by calculations based on Haldar *et al.*'s deposited .cif file. It may therefore be concluded that the minor alkyl chain in Haldar *et al.*'s published structure does not constitute a model with acceptable geometry.

3.5 *Attempt to refine the alkyl chain in the present study*

The program SHELXL [7] linked to the WinGX suite [8] was employed in the refinement of the 7CCB structure. An attempt to refine the assumed disordered alkyl chain followed the facilities in SHELX which allows selected atoms to belong to PART 0 (the ordered part not involving the alkyl chain), PART 1 (the major disordered alkyl chain) and PART 2 (the minor disordered alkyl chain) and SAME instructions were used in an attempt to control the geometry of corresponding bonds and angles in the major and minor alkyl chains. The occupancy factors of the corresponding atoms in the two chains were linked by a free variable as recommended in the SHELX Instruction Manual. This refinement became unstable and was stopped by the program, a result which confirms the incorrect assignment of disorder in the alkyl chain of both Haldar *et al.*'s published structure and the present follow up study. Consequently, the present study was continued assuming that the alkyl chain has a single conformation drawn with Biovia [13] as shown in Figure 2.

It has been noted that in the initial model shown here, the major alkyl chain corresponds to that resulting from the direct methods program SHELXS. C28A and C29A correspond to difference peaks Q1 and Q2 respectively and have very similar coordinates to the reportedly refined disordered model of Haldar *et al.* (Table 3). When included in the least squares refinement, the disordered model including the major and minor alkyl chains as shown here, failed to refine. This model was therefore abandoned for a single alkyl chain model based on the original SHELXS model which refined successfully as described above. We observed

that (i) In the starting models atoms 27, 30, 31, 32 and 33 have the same coordinates in both Major and Minor chains; (ii) The starting occupancies are Chain A = 0.8 and Chain B it is 0.2; (iii) Atom C24 marks the beginning of the rest of the structure which shows no disorder.

3.6 Final Comments on the State of the Alkyl Chain

Figure 3 shows Ortep/Raster [3, 4] 60% probability thermal ellipsoids for (a) the RT structure and (b) the LT structure. The alkyl chain thermal ellipsoids for the RT structure are noticeably exaggerated compared to those for the remainder of the structure, an effect which is not present in the LT structure. It may be concluded therefore that in the Mo RT structure this is a thermal effect and as we have determined in the above study cannot be explained in terms of static disorder.

3.7 Discussion: Structure of 7CBB from CuKα data at Temperature 150 K

(a) Molecular geometry and conformation

Figure 1 shows the chemical formula and atom numbering scheme. Figures 4 and 5 are Ortep/ Raster [3,4] views of the molecule looking approximately perpendicular to rings C-D and A-B respectively. Figure 5 shows the unusual step formation comprising (i) the alkyl chain and rings C-D and (ii) rings A-B and the 4-cyano moiety.

There are no unusual bond lengths or angles in the 7CBB structure. In the alkyl chain involving atoms C24 to C33 the mean C-C bond length is 1.532(8)Å and the mean bond angle is 113.2(1.2)°. In phenyl rings A, B, C and D the mean bond lengths are 1.391(6)Å, 1.386(8)Å, 1.393(7)Å and 1.392(4)Å respectively and the mean bond angles are 120.0(1.7)°, 120.0(2.0)°, 120.0(1.7)° and 120.0(2.3)° respectively. The mean planes of the phenyl moieties A, B, C and D are planar within 0.004(8)Å, 0.007(8)Å, 0.004(7)Å and 0.004(8)Å. The combined least squares plane for rings A and B are planar within 0.035(9)Å and C and D

within 0.020(9)Å. The C atoms of the alkyl chain are planar within 0.054(9)Å and this plane makes an angle of 5.18(9)° with the combined C+D plane. The C atoms of the alkyl chain and the C and D rings are planar within 0.371(10)Å. The combined A and B rings make an angle of 58.48(2)° with the combined C and D plane. C14=O1 = 1.197(1)Å is a typical double bond, the single C-O bonds are C11-O2 = 1.404(1)Å and C14-O2=1.363(1) Å. In the 4-cyano moiety N1≡C1 =1.149(1)Å and C1-C2=1.437(1)Å have typical values. The bond angle N1≡C1-C2 =178.6(1)°.

(b) *Crystal Packing and Intermolecular Interactions*

The molecular packing in the crystal is illustrated in Figures 6, 7 and 8, drawn with MERCURY [14]. There is a possible intermolecular H-bond involving N1 and a symmetry related C3 atom as shown in Figure 9 drawn with MERCURY [14]. The packing of the compound in the crystalline state is driven by the formation of weak H-bonds involving the strong cyano acceptor and weak aromatic C-H or aliphatic C-H donors. It has also been observed that weak H-bonds of the type C-H····O are present in the crystal packing. Some of these are actually established between the cyano acceptor of a molecule and the ortho C_{ar}-H donor of a centrosymmetrically related molecule leading to the formation of H-bonded dimers as shown in Figures 6 and 9. Figure 9 depicts possible H-bond between C3-H3 ...N1 with geometry N1-C3 = 3.371(2) Å, C3-H3 ...N1 = 157.3(125)°. The symmetry operation −x+2, +y-1/2, -z+1/2+1 has been applied. Table 4 lists the intermolecular hydrogen bonds in the structure.

The H-bonding motif is typical of the crystal structures of cyanophenyl compounds [15,16]. The calculations of intermolecular distances between molecules related by a centre of symmetry reveals the existence of numerous van der Waals interactions between the carboxylate and cyano group. Selected contact distances less than 3.65Å are shown in Table

5. Pairs of molecules related through the centre of symmetry are bound together by dipole induced dipole interaction between the chain part and polar cyano groups.

Molecules of the pair overlap almost completely so that the cyano groups lie at opposite ends (related by inversion centre of symmetry) as shown in Figure 7 with molecular packing coefficient 0.676 (including H atoms) following the formula given by Kitaigorodsky [17].

(c) Smectic A_1 phase of 7CBB

Previous studies of 7CCB by Dabrowski *et al.* [1] have shown that in the liquid crystalline state the compound exhibits a smectic A_1 (SmA$_1$) phase when it melts at 123 ^{o}C. Smectic A (SmA) phase has a layered structure with layer planes perpendicular to the preferred direction of molecular long axes; within the layers the centers of mass of the molecules are randomly distributed [18]. Figure 7 clearly depicts that the pairs of molecules are packed in interpenetrating layers - precursor to the SmA phase. Crystal to SmA transition should therefore be of the 'displacive' nature [19]. The calculated molecular length (L) for the most stretched all *trans*-configuration is found to be 28.002 Å. From the X-ray study in liquid crystalline phase of 7CBB [1, 20, 21] the smectic layer thickness (d) was found to be 30.2 Å at 130 ^{0}C . Here the layer thickness is close to the molecular length in the crystalline state. The main factor which allows one to distinguish the particular subtypes of the SmA phases is the ratio of the smectic layer spacing d to the molecular length L in its most extended form. The SmA$_1$ liquid crystal has a layer spacing d ≈ L [22]. Here for 7CBB the value of d/L is found to be 1.08 and it may give rise to a smectic A_1 structure [23].

Supplementary Material:

Crystallographic data for the structure at 150 K determined with CuKα radiation and reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC−1920388. CCDC−1920389 contains the supplementary crystallographic data for the structure at 295 K measured with MoKα radiation. Copies of available material can be obtained free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax +44-(0)-1223336033 or email: teched@chemcrys.cam.ac.uk).

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List of Tables

Table 1(a). Crystal data and structure refinement: 7CBB MoKα data at 295 K.

Identification code	exp_1351_shelx
Empirical formula	$C_{33} H_{31} N O_2$
Formula weight	473.59
Temperature	295 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P\ 2_1/c$
Unit cell dimensions	a = 16.3999(7) Å, α= 90°.
	b = 5.5964(2) Å, β= 92.368(4)°.
	c = 27.2446(13) Å, γ = 90°.
Volume	2498.39(18) Å^3
Z	4
Density (calculated)	1.259 Mg/m^3
Absorption coefficient	0.077 mm^{-1}
F(000)	1008
Crystal size	0.270x0.233 x0.161 mm^3
Theta range for data collection	3.717 to 29.485°
Index ranges	-22<=h<=22, -7<=k<=7, -37<=l<=34
Reflections collected	36446
Independent reflections	6459 [R(int) = 0.0341]
Completeness to theta = 25.242°	99.4 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6459 / 0 / 449
Goodness-of-fit on F^2	1.023
Final R indices [I>2sigma(I)]	R1 = 0.0518, wR2 = 0.1339
R indices (all data)	R1 = 0.0687, wR2 = 0.1476
Extinction coefficient	n/a
Largest diff. peak and hole	0.835 and -0.399 e.Å^{-3}

Table 1(b). Crystal data and structure refinement: 7CBB CuKα data at 150 K.

Identification code	exp_1072_shelx
Empirical formula	$C_{33} H_{31} N O_2$
Formula weight	473.59
Temperature	150 K
Wavelength	1.54184 Å
Crystal system	Monoclinic
Space group	$P 2_1/c$
Unit cell dimensions	a = 16.4276(2) Å $\alpha = 90°$.
	b = 5.60520(10) Å $\beta = 92.3550(10)°$.
	c = 27.2964(3) Å $\gamma = 90°$.
Volume	2511.33(6) $Å^3$
Z	4
Density (calculated)	1.253 Mg/m^3
Absorption coefficient	0.600 mm^{-1}
F(000)	1008
Crystal size	0.784 x 0.105 x 0.058 mm^3
Theta range for data collection	4.129 to 73.573°
Index ranges	-20<=h<=20, -6<=k<=6, -33<=l<=33
Reflections collected	35832
Independent reflections	4975 [R(int) = 0.0444]
Completeness to theta = 67.684°	99.0 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4975 / 0 / 449
Goodness-of-fit on F^2	0.928
Final R indices [I>2sigma(I)]	R1 = 0.0405, wR2 = 0.1216
R indices (all data)	R1 = 0.0451, wR2 = 0.1285
Extinction coefficient	n/a
Largest diff. peak and hole	0.198 and -0.191 e.$Å^{-3}$

Table 2. Selected atomic coordinates in the alkyl chains of (a) Haldar *et al.* [2] and (b) the present study.

(a) From Haldar *et al.'s* Table 2 and .cif file

Atom	x	y	z	difference density
C28A	0.1219(6)	0.826(4)	0.1291(4)	Not given
C29A	0.0647(10)	0.894(7)	0.0854(5)	Not given

(b) Present study from difference density

Atom	x	y	z	difference density
Q1	0.1240	0.7933	0.1296	0.92
Q2	0.0682	0.88252	0.0835	0.52

Table 3. The Alkyl Chain in the Present Study:
Molecular geometry associated with the sequence C24-C27-Q1(C28A)-Q2(C29A)-C30

Atoms	Bond length Å
C24-C27	1.513
C27-Q1(C28A)	1.292*
Q1(C28A)-Q2(C29A)	1.536
Q2(C29A)-C(30)	1.180*
Atoms	Bond angle º
C24-C27-Q1(C28A)	120.59
C27-Q1(C28A)-Q2(C29A)	113.99
Q1(C28A)-Q2(C29A)-C30	110.81

Table 4. Hydrogen bonding geometry with e.s.d.s in parenthesis (Å, º).

D-H…A	D-H	D…A	H…A	D-H…A
C20-H20…O2^i	0.983(15)	2.735(1)	2.404(14)	98.94(95)
C16-H16…O1^i	0.957(14)	2.859(1)	2.573(14)	97.40(91)
C12-H12…O1^i	0.951(16)	3.058(1)	2.989(15)	85.07(91)
C10-H10…O1^{ii}	0.942(17)	3.446(1)	2.521(17)	167.61(41)
C3-H3…N1^{iii}	0.936(15)	3.371(2)	2.488(15)	157.33(125)
C12-H12…O2^{iv}	0.951(16)	3.738(1)	2.841(16)	157.55(124)
C28-H28B…N1^{iv}	1.015(16)	3.567(2)	2.976(16)	117.97(108)

Symmetry codes: ^{i} x, y, z; ^{ii} x, +y-1, +z; ^{iii} –x+2, +y-1/2, -z+1/2+1; -x+1, -y+1, -z+1.

D: Donor; A: Acceptor.

Table 5. Selected intermolecular short contact distances less than 3.65 Å (with e.s.d.s in parenthesis).

Atoms		Distance/Å	Atoms		Distance/Å
C19	C21[i]	3.5897(15)	C2	C22[iv]	3.6080(15)
C12	O1[ii]	3.4480(14)	C1	C23[iv]	3.5809(16)
C10	C15[iii]	3.6010(16)	N1	C28[iii]	3.5681(17)
C2	C23[iv]	3.5483(16)			

Atom at: [i] –x+1, y+1/2, -z+1/2; [ii] x, y-1, z; [iii] –x+1, -y+1, -z+1; [iv] –x+1, -y, -z+1.

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Figure 1. Atom numbering scheme of 7CBB for the CuKα 150 K structure is shown. Drawn with Ortep/Raster [3,4].

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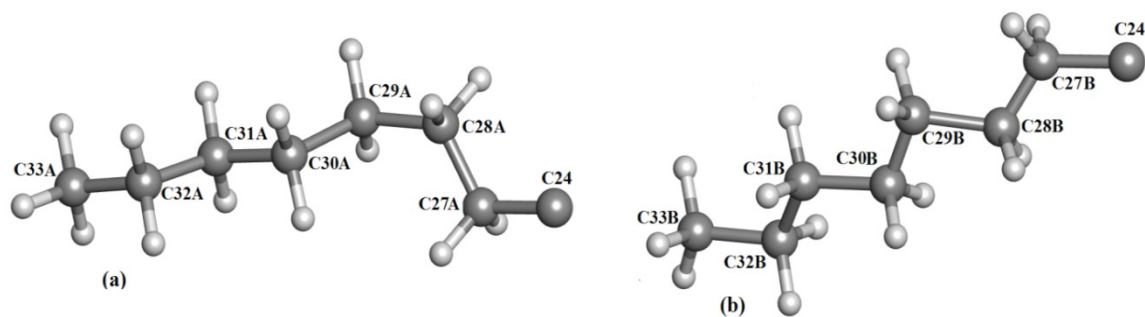
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(a) 7CBB Mo 295K

(b) 7CBB Cu 150K
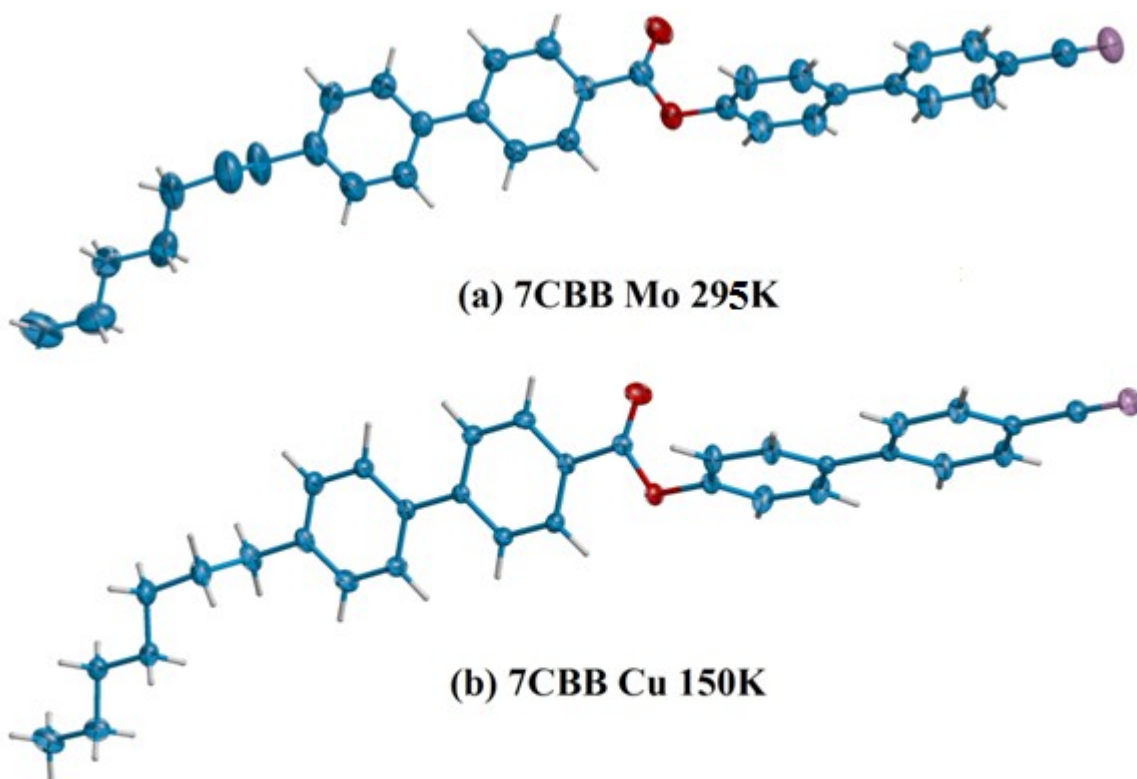
Figure 3. Ortep/Raster 60% probability thermal ellipsoids for 7CBB (a) the Mo RT structure and (b) the Cu LT structure. The alkyl chain thermal ellipsoids for the RT structure are

noticeably exaggerated compared to those for the remainder of the structure, an effect which is not present in the LT structure. It may be concluded therefore that in the Mo RT structure this is a thermal effect and cannot be explained in terms of static disorder.
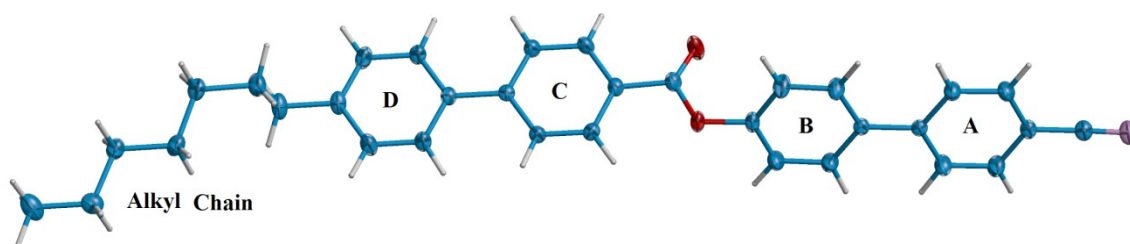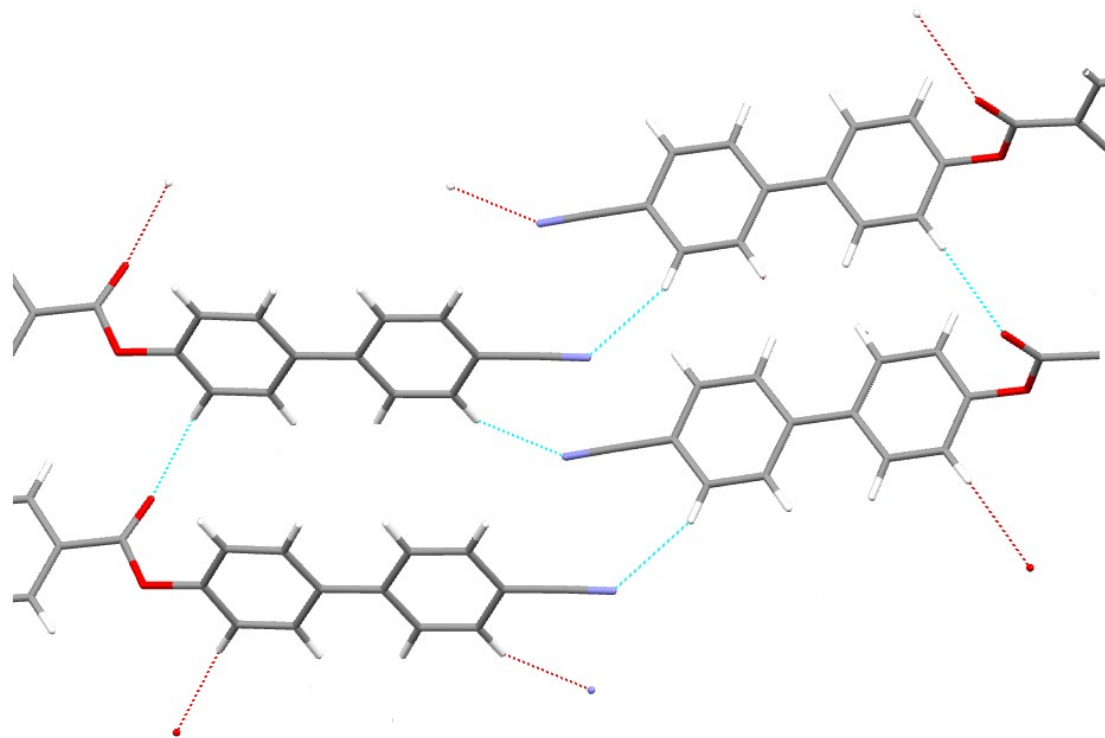

Figure 4. 7CBB : The 150 K Cu structure viewed perpendicular to the D-C plane. Thermal ellipsoids are shown at 60% probability. Drawn with Ortep/Raster [3,4].
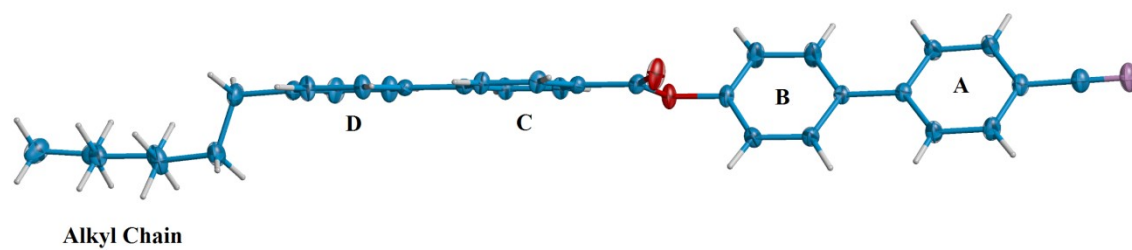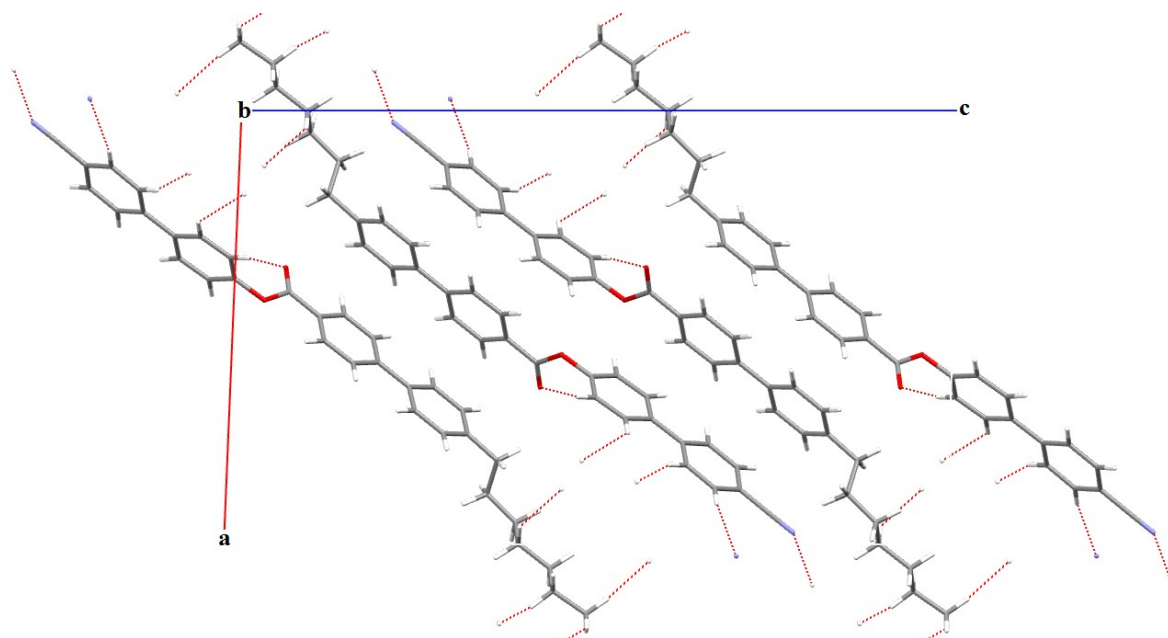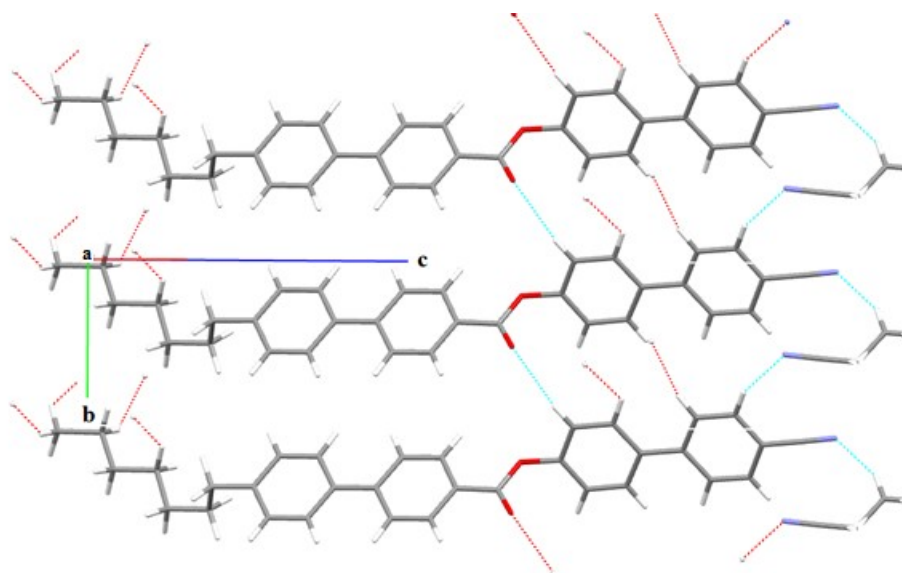
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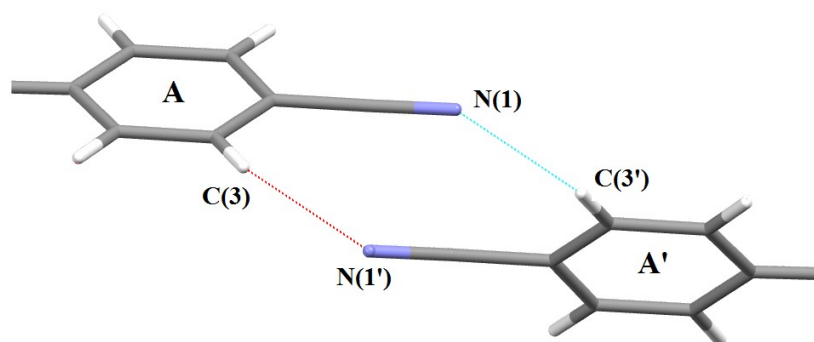
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