Effects of the lateral substituent on the cubic phase formation of two analogous compounds, 4′-n-hexadecyloxy-3′-cyanobiphenyl-4-carboxylic acid (ACBC-16) and its 3′-nitro compound (ANBC-16)

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(Received 27 July 2014; accepted 22 September 2014)

Two cubic (Cub) phase forming compounds, 4′-n-hexadecyloxy-3′-cyanobiphenyl-4-carboxylic acid (ACBC-16) and its 3′-nitro analogue (ANBC-16) were studied by infrared (IR) spectroscopy. In the temperature region of the Cub phase, the molar fraction of hydrogen-bonded COOH groups estimated for ACBC-16 was by 0.05 at maximum larger than that for ANBC-16 and the aromatic ring C═C stretching (ν(C═C)\textsubscript{ring}) band frequency of ACBC-16 was by 3 cm\textsuperscript{-1} lower than that of ANBC-16. The quantum chemical calculation at DFT/B3LYP level, on the one hand, showed no meaningful difference in the stabilisation energy for dimerisation and the ν(C═C)\textsubscript{ring} band frequency between the respective model compounds. These results can be ascribed to the different steric effects of the side groups; the CN group would make possible the close contact of neighbouring phenyl rings while the bulky NO\textsubscript{2} group would not, giving slightly more stabilised dimerisation of ACBC-16 in the Cub phase than in ANBC-16.

\textbf{Keywords:} cubic mesophase; infrared spectroscopy; quantum chemical calculation; steric effect; hydrogen bonding

1. Introduction

Thermotropic cubic (Cub) phases, especially bicontinuous types, are very fascinating because they have three-dimensional long-range periodicity and optically isotropy in contrast with other conventional liquid crystals (LCs).[1–7] Although synthetic efforts have exploited many new types of compounds that exhibit those phases, the following two series are a prototype in this field: 4′-n-alkoxy-3′-nitrobenzenophenyl-4-carboxylic acids [8] (X = NO\textsubscript{2} in Figure 1 and designated as ANBC-n, where n is the number of carbon atoms in the alkoy tail) and 4′-n-alkoxy-3′-cyanobiphenyl-4-carboxylic acids [9,10] (X = CN in Figure 1, ACBC-n). The chemical structures of the two series are quite similar; they are rodlike, having two chemically incompatible parts, flexible alkyl chains and a rigid aromatic core. X-ray diffraction (XRD) studies revealed that the Cub phases of their n = 16 homologues (ANBC-16 [11] and ACBC-16 [12]) have the same symmetry Ia\textsubscript{3}d. The structure consists of two pairs of interpenetrating networks of channel segments with junctions where three segments join (3-by-3 networks) [13,14]; the space is divided into two regions, both of which are three-dimensionally continuous, and thus called bicontinuous. The characteristic structure is not only one of the most complicated in the LC systems but also has potential to be used for many attractive applications such as nano-porous templates, catalytic bases, separation membrane films, and three-dimensional ionic/electroconductive and so on.[6]

The Ia\textsubscript{3}d structure is also seen in lyotropic [15,16] and block copolymer systems.[17,18] In both the systems, particular chemical bonds and groups are too small to fill the lattice dimension and thus could be smeared into two chemically incompatible regions. The way how the two continuous regions fill the space was directly displayed by transmission electron microtomography.[18] In low-molecular-mass one-component systems such as ANBC-n or ACBC-n series examined in this article, however, it is not easy to imagine how constituent molecules are packed in the cubic lattice and which part of the molecules, for example, alkyl chain or aromatic core, forms the channel segments; one-unit volume contains hundreds or thousands of molecules, and information on the crystallographic space group and lattice dimension given by XRD does not directly lead to the final answer. Information at the molecular level is also necessary to consider the molecular packing in the cubic lattice; NMR and infrared (IR) spectroscopic studies are demanded because they are expected to provide the diffusional motion of the constituent molecules and the vibrational state of each chemical bond. Such investigations are, nevertheless, scarcely carried out especially in thermotropic LC systems.[19–23]

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In the temperature scale, the Cub phase is most often neighboured by the smectic C (SmC) phase with a layered structure. In contrast with the drastic structural change between the two phases macroscopically, the transition entropy is comparatively small, which is even mysterious. To explain this, one of the authors revealed that by dividing the transition entropy into two contributions from the two incompatible parts of the constituent molecules (quasi binary picture), both the parts are competing; in the Cub phase the chain part is more disordered while the core part is more ordered than in the SmC phase.[24–29] To support this picture experimentally, it is crucial to know how the two parts change during the transition. This picture has also been applied to other LC phases.[30–34]

The present article compares and discusses the Cub phases of ACBC-16 and ANBC-16. Unlike the ANBC-n series,[8,9,11,19–22,24,25,27–29,35–47] publications for the ACBC-n series are unexpectedly rare,[9,10,12,48–50] but it is now known that both ACBC-n and ANBC-n series exhibit two types of Cub phases with Ia3d and Im3m symmetries, depending upon the alkoxy chain length, or the number of carbon atoms n in the chain. Considering the close similarity of molecular structures, the phase behaviours are expected to be similar at the same chain length n = 16. In reality, however, the temperature region of the Cub phase (440–478 K, interval 38 K) for ACBC-16 is wider than that (451–472 K, interval 21 K) for ANBC-16. An interesting point is that the SmC layer thickness (L_{SmC}) and lattice dimension (a) of ACBC-16 are about 4% and 2.5% larger than the corresponding values of ANBC-16, respectively, and rather close to the value of ANBC-17 or -18. The appearance of the Cub phase type as a function of n in the ACBC-n series is almost the same as in the ANBC-n series, but shifted towards shorter n by 1 or

2. Those slight differences in L_{SmC} a and the n dividing the two Cub phase regions between the two series should be ascribed to the different lateral substituents X because the other parts are completely identical.

In both ANBC-n and ACBC-n series, it is easily expected that the hydrogen bonding state of the terminal COOH groups largely influences the stability of the Cub phase. IR spectroscopy is one of the useful tools to obtain such information. For the ANBC-n system, our previous temperature-dependent IR studies revealed that about 80% of terminal COOH groups form hydrogen bonding and thus the hydrogen-bonded dimers are basic building units for the Cub phase structure; increased dissociation of COOHs at elevated temperatures destabilises the Cub phase.[20,22] The present article provides the IR spectral results for ACBC-16. The aim is to clarify the hydrogen bonding state of the terminal COOHs, to examine the effect of the replacement of the lateral substituent from X = NO₂ to CN on it, and to reveal the resultant aggregation state at the molecular level in the Cub phase.

2. Results and discussion

2.1 Band assignments

Figure 2 shows the IR spectrum of ACBC-16 at room temperature. Most of the absorption bands are common to ANBC-16. Table 1 compares the frequencies of major peaks of both the compounds, together with the assignments. The assignment of each band is based on the previous literature[20,51] and theoretical calculation carried out in this work for two model compounds (3'-cyanophenyl benzoic acid (cyano-PBA) and its 3'-nitro analogue (nitro-PBA), whose chemical structures are given in later Figure 5 and Figure S1 in Supplemental Material (SM). The comparison of the calculated spectrum with the observed one showed that the correspondence is evident in the region 3500–1300 cm⁻¹, although the former
Table 1. Comparison of the calculated and observed IR band frequencies of ACBC-16 and ANBC-16.

| Frequency (in cm\(^{-1}\)) and intensity\(^a\) | Assignment\(^c\) |
|-----------------------------------------------|------------------|
| Observed | Calculated\(^b\) | Observed | Calculated\(^b\) | Assignment\(^c\) |
| 3074 w,sh | 3072 | 43 | 3079 w,sh | 3073 | 33 | v(C–H)\(_{\text{ring}}\) |
| 3053 w | 3062 w | 43 | v(C–H)\(_{\text{ring}}\) |
| 2950 w | – | – | 2955 w | – | – | v(\(\nu\)_\((\text{C–H})\)\(_{\text{ring}}\)) |
| 2922 vs | – | – | 2922 vs | – | – | v(\(\nu\)_\((\text{C–H})\)\(_{\text{ring}}\)) |
| 2850 vs | – | – | 2850 s | – | – | v(\(\nu\)_\((\text{C–H})\)\(_{\text{ring}}\)) |
| 2666 w | | | 2662 w | Overtones and combinations of lower frequency bands |
| 2538 w | | | 2539 w | Enhanced by Fermi resonance with the broad OH stretching peak |
| 2226 m | 2254 | 18 | – | – | v(\(\nu\)_\((\text{C≡N})\)) |
| 1686 vs | 1693 | 1100 | 1687 vs | 1693 | 1100 | v(\(\nu\)_\((\text{C═O})\)\(_{\text{H-bonded}}\)) |
| 1650 0.05 | 1651 0.03 | v(\(\nu\)_\((\text{C═O})\)\(_{\text{H-bonded}}\)) |
| 1603 s | 1600 | 210 | 1607 s | 1600 | 210 | v(\(\nu\)_\((\text{C≡N})\)) |
| 1586 w | 1587 | 0.11 | 1572 13 | v(\(\nu\)_\((\text{C≡N})\)) |
| 1566 w | 1566 | 4.2 | 1537 s | 1561 | 170 | v(\(\nu\)_\((\text{C≡N})\)) |
| 1548 0.52 | 1546 1.9 | v(\(\nu\)_\((\text{C≡N})\)) |
| 1525 m | 1547 | 57 | 1558 w,sh | 1546 | 94 | v(\(\nu\)_\((\text{C≡N})\)) |
| 1496 m | 1498 | 23 | 1515 m | 1499 | 18 | v(\(\nu\)_\((\text{C≡N})\)) |
| 1497 0.07 | 1493? w | 1499 | 0.39 | v(\(\nu\)_\((\text{C≡N})\)) |
| 1467 m | – | – | 1466 m | – | – | \(\delta\)(CH\(_3\)), \(\delta\)(CH\(_2\)) |
| 1466 19 | 1463 | 1.1 | v(C\(_\equiv\text{ring}\)) |
| 1466 1.5 | 1463 | 9.0 | v(C\(_\equiv\text{ring}\)) |
| 1450 0.14 | 1453 w | 1449 | 0.10 | O–H ibp + ring C–H ibp |
| 1427 m | – | – | 1426 m | – | – | \(\delta\)(CH\(_3\)) |
| 1417 m | 1417 | 370 | | | | O–H ibp + ring C–H ibp |
| 1387 m | 1409 | 150 | 1422 | 140 | O–H ibp + ring C–H ibp |
| 1373 w | 1379 | 40 | 1387 | 0.03 | Ring C–H ibp + O–H ibp |
| 1379 1.0 | 1399 w,sh | 1387 | 25 | Ring C–H ibp + O–H ibp |
| – | – | – | 1342 | 140 | v(\(\nu\)_\((\text{NO}_2)\)) |
| – | – | 1349 m | 1342 | 520 | v(\(\nu\)_\((\text{NO}_2)\)) |
| 1327 m,sh | 1311 | 110 | 1310 | 1.8 | Ring C–H ibp |
| 1304 m,sh | 1304 | 220 | 1297 m,sh | 1305 | 260 | Ring C–H ibp + O–H ibp |
| 1286 vs | – | – | 1284 vs | – | – | v(\(\nu\)_\((\text{C–O–C})\)) |
| 1267 w,sh | – | – | 1258 w,sh | – | – | v(\(\nu\)_\((\text{C–O–C})\)) |
| 1289 42 | 1288 | 74 | 1288 | 0.01 | Ring C–H ibp + O–H ibp |
| 1273 0.01 | 1273 | 0.23 | Ring C–H ibp + ring C–H ibp |
| 1267 w,sh | 1267 | 5.8 | v(\(\nu\)_\((\text{C–CN})\) + ring C–H ibp + ring C–H ibp |
| 1267 w,sh | 1267 | 8.3 | v(\(\nu\)_\((\text{C–CN})\) + ring C–H ibp + ring C–H ibp |
| 1258 w,sh | 1262 | 49 | 1262 | 3.7 | O–H ibp + ring C–H ibp |
| 1267 w,sh | 1260 | 21 | 1248 | 7.6 | Ring C–H ibp |
| 1195 m | – | – | 1196 m | – | – | v(\(\nu\)_\((\text{C–O–C})\)) |
| 1172 0.003 | 1172 | 0.004 | Ring C–H ibp |

(Continued)
spectrum corresponds to the isolated state in vacuum. To improve the agreement in frequency between the calculated and the observed spectra, a scaling scheme [52] was used. The best scaling factor was 0.959, which was obtained from the least-squares fit in the region 1200–1700 cm\(^{-1}\) of 13 bands for ACBC-16 and 17 bands for ANBC-16 (see Figure S2 in SM). The scaled frequencies are listed as the calculated ones in Table 1.

We mainly analyse the following four bands: alkoxy CH\(_2\) asymmetric (\(\nu_{as}(C–H)\)) and symmetric (\(\nu_{s}(C–H)\)) stretching bands in the region 2800–3000 cm\(^{-1}\), C≡N stretching (\(\nu(C≡N)\)) band at around 2226 cm\(^{-1}\), carbonyl C=O stretching bands of hydrogen-bonded

| Assignment | ACBC-16 | ANBC-16 |
|------------|---------|---------|
|            | Observed | Calculated\(^b\) | Observed | Calculated\(^b\) |
| Ring C–H ipb | 1177 w,sh | 1171 110 | 1170 w | 1171 110 |
|            | 1134 m | ? | 1129 w | ? |
|            | 1040 w | 1085 w | ? |
|            | 1008 w | 1013 w,sh | P(CH\(_2\)) |
|            | 998 m | 995 m | \(\nu(C–C)\)inter-ring |
|            | 968 w | ? |
| O–H oopb | 945 w,br | 942 w,br | P(CH\(_2\)) |
|            | 916 w | ? |
|            | 862 w | ? |
|            | 817 m | 818 m | Ring C–H oopb |
|            | 774 m | 774 m | P(CH\(_2\)) |
|            | 710 w | ? |
|            | 681 w | ? |
|            | 667 w | 642 w | ? |
|            | 547 w | 547 w | Ring oop def |
|            | 490 w | 496 w | Ring def |
|            | 454 w | 454 w | ? |

Notes: \(^{a}\)vs, very strong; s, strong; m, medium; w, weak; sh, shoulder; br, broad. 
\(^{b}\)Calculated for cyano-PBA and nitro-PBA (see text); scaling factor of 0.959 is used, and the intensity is in arbitrary unit.

Notes:
\(\nu_{as}(C–H)\) asymmetric stretching of CH\(_3\) group
\(\nu_{as}(C–H)\) asymmetric stretching of CH\(_2\) groups
\(\nu_{s}(C–H)\) symmetric stretching of CH\(_2\) groups
\(\delta(CH_3), \delta(CH_3)\) CH\(_3\) bending, CH\(_3\) asymmetric deformation
P(CH\(_2\)) CH\(_2\) rocking progression
\(\nu(C–O–C)\) alkyl C–O-aromatic C stretching
\(\nu(C=O)_{\text{H bonded}}\) hydrogen-bonded C=O stretching
O–H ipb O–H in-plane bending
O–H oopb O–H out-of-plane bending
\(\nu(C=N)\) C≡N stretching
\(\nu(C–CN)\) C–CN stretching
NO\(_2\) ipb NO\(_2\) in-plane bending
\(\nu(CNO_2)\) NO\(_2\) symmetric stretching
\(\nu(C–NO_2)\) C–NO\(_2\) stretching
\(\nu(C–H)_{\text{ring}}\) ring C–H stretching
\(\nu(C=C)_{\text{ring}}\) ring C=C stretching
Ring C–H ipb ring C–H in-plane bending
Ring C–H oopb ring C–H out-of-plane bending
Ring oop def ring out-of-plane deformation
Ring def ring deformation
\(\nu(C–C)_{\text{inter-ring}}\) inter-ring C–C stretching

Table 1. (Continued.)

| Frequency (in cm\(^{-1}\)) and intensity\(^a\) | ACBC-16 | ANBC-16 |
|--------------------------------------------|---------|---------|
| Observed | Calculated\(^b\) | Observed | Calculated\(^b\) |
| 1177 w,sh | 1171 110 | 1170 w | 1171 110 |
| 1134 m | ? | ? | ? |
| 1040 w | 1085 w | ? |
| 1008 w | 1013 w,sh | P(CH\(_2\)) |
| 998 m | 995 m | \(\nu(C–C)\)inter-ring |
| 968 w | ? |
| 945 w,br | 942 w,br | P(CH\(_2\)) |
| 916 w | ? |
| 862 w | ? |
| 817 m | 818 m | Ring C–H oopb |
| 774 m | 774 m | P(CH\(_2\)) |
| 710 w | ? |
| 681 w | ? |
| 667 w | 642 w | ? |
| 547 w | 547 w | Ring oop def |
| 490 w | 496 w | Ring def |
| 454 w | 454 w | ? |
COOH groups (ν(C=O)$_{\text{H-bonded}}$) at 1680–1690 cm$^{-1}$, and aromatic ring C=C stretching (ν(C=C)$_{\text{ring}}$) band at 1604–1609 cm$^{-1}$. As described later, these four bands are faithful reporters of the molecular states when temperature is changed and ACBC-16 undergoes phase transitions. We discuss the temperature behaviours in ACBC-16 in comparison with those in ANBC-16.

2.2 Alkoxy CH$_2$ stretching regions

Figure 3 shows plots of (a) the peak frequencies and (b) peak widths (full-width at half-maximum) of the ν$_{\text{as}}$(C–H)$_{\text{CH}_2}$ and ν$_{\text{s}}$(C–H)$_{\text{CH}_2}$ bands versus temperature, determined by band-shape analyses. In (a), as temperature increases from 298 K, the frequencies of the two bands initially increase mildly but at around 400 K show a steep rise reflecting the crystal (Cr$_2$) to SmC phase transition. After that, both the frequencies again increase monotonously until reaching their constant values in the normal liquid (I$_2$) phase, and only the slopes of the frequency versus temperature curves slightly decrease at the SmC to Cub phase transition temperature. As well known, the shift towards higher frequency of those bands reflects the disordering of chain packing and the introduction of gauche conformers on the alkoxy chains (i.e., melting of alkyl tails).[20] The frequencies of the ν$_{\text{as}}$(C–H)$_{\text{CH}_2}$ and ν$_{\text{s}}$(C–H)$_{\text{CH}_2}$ bands are 2926.5 cm$^{-1}$ and 2855.0 cm$^{-1}$ at 460.7 K in the Cub phase, respectively, and they are 2926.9 cm$^{-1}$ and 2855.2 cm$^{-1}$, respectively, at 491.4 K in the I$_2$ phase; for each band, the difference between the two states is within 0.5 cm$^{-1}$. As pointed out for the Cub phase of the 3’-nitro analogue ANBC-16,[20] this result implies that in the Cub phase, the conformational structure of the alkoxy chains is fully liquid-like, almost identical with that in the I$_2$ phase, in accordance with the universal trend exhibited by liquid crystalline mesophases.[30–34] The slope change at the SmC to Cub phase transition suggests that irrespective of a marked change in the macroscopic periodicity and symmetry at the transition, the local molecular environments of the two phases are quite similar, and only the rate of increase of gauche bond density slightly decreases above that temperature.

In (b), another interesting point can be found: The bandwidth of the ν$_{\text{as}}$(C–H)$_{\text{CH}_2}$ band begins to increase at temperatures about 30 K below the Cr$_2$ to SmC phase transition temperature, although the corresponding change is not evident for the ν$_{\text{s}}$(C–H)$_{\text{CH}_2}$ band. Since the broadening corresponds to the widening of the distribution of the vibrational states, this implies that the alkyl chain melting proceeds well below the transition temperature (i.e., pre-melting effect) as observed in the calorimetric result.[50]

2.3 Side group C≡N and aromatic ring C=C stretching regions

Figure 4(a) shows the peak frequency of the ν(C≡N) band in ACBC-16, together with that of the ν$_{\text{as}}$(NO$_2$) band in ANBC-16 and (b) the ν(C=C)$_{\text{ring}}$ bands both in ACBC-16 and in ANBC-16, as a function of temperature. The solid and broken curves are to guide the readers’ eyes.

Figure 3. (a) Peak frequencies and (b) bandwidths (full-width at half-maximum) of the ν$_{\text{as}}$(C–H)$_{\text{CH}_2}$ (○) and ν$_{\text{s}}$(C–H)$_{\text{CH}_2}$ (◊) bands in ACBC-16 as a function of temperature.

Figure 4. Peak frequencies of (a) the ν(C≡N) band in ACBC-16 and the ν$_{\text{as}}$(NO$_2$) band in ANBC-16 and (b) the ν(C=C)$_{\text{ring}}$ bands both in ACBC-16 and in ANBC-16, as a function of temperature. The solid and broken curves are to guide the readers’ eyes.
band in ANBC-16 for comparison, as a function of temperature. Both the bands come from the side group at the 3′-position of the biphenyl core (according to our theoretical calculation, the $\nu_{as}(NO_2)$ band actually includes the aromatic ring $C=\!C$ vibration component, as shown as $\nu(C=\!C)_{ring} + NO_2$ in-plane bending (ipb) in Table 1, but we use here the usual notation $\nu_{as}(NO_2)$). The frequency of the $\nu(C=\!N)$ band in ACBC-16 initially shows a gradual decrease from ~2226 cm$^{-1}$ to 2223.7 cm$^{-1}$, and about 10 K below the Cr$_2$ to SmC phase transition temperature, it begins to increase. After the frequency reaches 2227.2 cm$^{-1}$ at the Cr$_2$ to SmC phase transition temperature, it again decreases almost linearly with temperature up to the true liquid I$_2$ phase. No noticeable change is visible both at the SmC to Cub and the Cub to I$_1$ and to I$_2$ phase transition temperatures. The frequency of the corresponding side-group band in ANBC-16 shows a similar temperature behaviour, although the value shows a constant of ~1536.5 cm$^{-1}$ above the Cr$_2$ to SmC phase transition temperature until the I$_2$ phase region.

**2.4 Carbonyl C=O stretching region**

Figure 6 shows the temperature variation of the $\nu(C=O)$ band in ACBC-16. A peak at around 1685 cm$^{-1}$ observed at around room temperature is assigned to the band of hydrogen-bonded COOH groups ($\nu(C=O)_{H-bonded}$). The height of this peak gradually decreases with increasing temperature from 323 K, and above the Cr$_2$ to SmC phase transition temperature another peak at around 1730 cm$^{-1}$ becomes prominent, which is assigned to the carbonyl stretching vibration of monomeric COOH groups ($\nu(C=O)_{free}$). The spectral change observed is typical of dissociation of hydrogen-bonded COOH dimers with increasing temperature.$[53–57]$ We resolved the spectra in the region 1625–1800 cm$^{-1}$ into two
Lorentz functions by using the procedures described in the Experimental section. Representative results for the deconvolution are shown in Figure 7.

Figure 8 plots (a) the peak frequencies and (b) bandwidths of two resolved components of the \(\nu(C=O)\) band versus temperature. The peak frequency of the \(\nu(C=O)_{\text{H-bonded}}\) component ranges between 1691 and 1699 cm\(^{-1}\) and that of the \(\nu(C=O)_{\text{free}}\) component between 1732.5 and 1736.5 cm\(^{-1}\); both exhibit very gradual changes against temperature. However, the temperature dependence of their bandwidths shows a marked difference: The bandwidth of the former component is 18.2 ± 0.8 cm\(^{-1}\), independent of temperature, whereas that of the latter begins to increase at around 400 K on heating, and after that, showing a constant value of 13.5 cm\(^{-1}\) in the Cub, I\(_1\) and I\(_2\) phase regions.

According to the procedure of Allen et al. \[54\] we plotted \(1/\Delta \nu(C=O)_{\text{free}}\) against \(\Delta \nu(C=O)_{\text{H-bonded}}/\Delta \nu(C=O)_{\text{free}}\) by using the above deconvolution results at various temperatures, where \(\Delta \nu(C=O)_{\text{free}}\) and \(\Delta \nu(C=O)_{\text{H-bonded}}\) are the integrated absorbances of \(\nu(C=O)_{\text{free}}\) and \(\nu(C=O)_{\text{H-bonded}}\) components, respectively. The result is shown in Figure 9, which gives a linear relation above the melting point. The relation is represented (with a correlation factor of 0.99998) by Equation (1):

\[
\frac{1}{\Delta \nu(C=O)_{\text{free}}} = 0.0682 + (0.0445)(\Delta \nu(C=O)_{\text{H-bonded}}/\Delta \nu(C=O)_{\text{free}})
\]

(1)

Above the clearing point, the relation slightly changes as:

\[
\frac{1}{\Delta \nu(C=O)_{\text{free}}} = 0.0746 + (0.0418)(\Delta \nu(C=O)_{\text{H-bonded}}/\Delta \nu(C=O)_{\text{free}})
\]

(2)

(with a correlation factor of 0.99993).
From these results, the ratios of two molar extinction coefficients ($\varepsilon_{\text{H-bonded}} / \varepsilon_{\text{free}}$) were estimated at 1.53 and 1.79 in the ranges above the melting to the clearing points and above the clearing point for ACBC-16. The $A(\nu(C=O))_{\text{free}}$ and $A(\nu(C=O))_{\text{H-bonded}}$ are the integrated absorbances of the $\nu(C=O)_{\text{free}}$ and $\nu(C=O)_{\text{H-bonded}}$ components, respectively.

The values of $f$ obtained in this way are plotted versus temperature and shown in Figure 10, together with the plot for ANBC-16 for comparison; the $f$ values obtained this time for ANBC-16 were ≈0.05 smaller than those previously published data in the temperature range from melting to clearing temperatures.[20]

In Figure 10, the molar fraction of hydrogen-bonded COOH groups in ACBC-16 is 0.95 at the beginning of the SmC phase. It gradually decreases with increasing temperature up to around 460 K in the Cub phase. The fraction shows no noticeable change in the SmC to Cub phase transition temperature. When temperature further increases, the molar fraction starts decreasing rapidly. The decrease lasts until entering into the normal liquid $I_2$ phase region, and after that slightly slows down, where ≈50% of COOH groups are still in the hydrogen-bonded dimeric state. The variation of the fraction with temperature for ANBC-16 coincides with that for ACBC-16 in the temperature ranges of the SmC and $I_2$ phases. A major difference between the two compounds is that in the Cub phase temperature region, the molar fraction of hydrogen-bonded COOH groups in ACBC-16 is slightly but definitely (by ≈0.05 at maximum) higher than that in ANBC-16. The fractions at the Cub-$I_1$ transition temperatures are almost the same (=0.68) for both compounds. This supports our previous conclusion that the breaking of hydrogen bonding leads to the destruction of the Cub phase and the appearance of the next $I_1$ phase.[20] In other words, in the Cub phases, the dimerisation of ACBC-16 molecules is slightly more stabilised compared to ANBC-16. On the other hand, as mentioned in the Alkoxy CH$_2$ stretching regions section, the conformational disorder of the alkoxy chains in the SmC phase is already as large as in the Cub phase in
ACBC-16. This may be related to the extension of the Cub phase of ACBC-16 to lower temperature side as compared to ANBC-16.

The above monomer–dimer equilibrium may be described in terms of the dissociation constant \( K_d \), with the following equation:

\[
K_d = \frac{[\text{-COOH}]}{[\text{-COOH}]^2} \quad \text{for} \quad [\text{-COOH}]^2 \Rightarrow 2[\text{-COOH}]
\]  

where \([\text{-COOH}]^2\) and \([\text{-COOH}]\) are the concentrations of hydrogen-bonded COOH dimers (not of hydrogen-bonded COOH groups) and monomeric COOH groups, respectively. The \( K_d \) is also expressed as:

\[
\ln(K_d) = \ln \left( \frac{c(1-f)^2}{c} \right) = \ln \left( \frac{(1-f)^2}{f} \right) + \ln(2c)
\]  

where \( c \) is the (total) concentration of the molecules in the sample, independent of temperature, but usually unknown. Thus, instead of \( \ln(K_d) \), \( \ln[(1-f)^2/f] \) was plotted versus the reciprocal of temperature (1/T) for both ACBC-16 and ANBC-16. The result is shown in Figure 11. For the two compounds, the plots are divided into three temperature regions, which correspond well to the SmC and Cub, \( I_1 \) (including SmA phase, in case of ANBC-16) and \( I_2 \) phase regions, respectively. This implies that the dissociation is governed by not only temperature but also the aggregation state itself. In general, the slope is connected to the heat of dissociation in each temperature range, \( \Delta H \), by the following well-known equation,

\[
\ln(K_d) = -\Delta H/RT + \Delta S/R
\]  

where the variables have their usual meaning in thermodynamics. The estimated values of \( \Delta H \) for the SmC and Cub, \( I_1 \) and \( I_2 \) phase regions for ACBC-16 are 68 ± 1, 320 ± 9, 68 ± 5 kJ mol\(^{-1}\), respectively, and the values for ANBC-16 are 85 ± 3, 186 ± 16, 79 ± 7 kJ mol\(^{-1}\), respectively; here, we re-investigated the monomer–dimer equilibrium for ANBC-16, and the slope in the \( I_2 \) phase region was different from, and about three times larger than, the previous data.[20] For each compound, the value in the second region, the \( I_1 \) phase, is the largest among the three regions but contains a relatively large error because the boundary of the region is not so distinct. It is, however, certain that the largest value reflects the \( I_1 \) (including SmA phase in case of ANBC-16) being the temperature region where monomeric COOH groups are largely favoured at equilibrium. This result also supports our idea that the dimerisation of ACBC/ANBC molecules is essential for the formation of the Cub phase. A marked difference between the two compounds is in the SmC and Cub phase region, where the value in ACBC-16 is ~20% smaller than the corresponding value in ANBC-16.

### 2.5 Calculations of stabilisation energy: Electronic effect of the lateral substituent

The above IR results revealed that in the Cub phases the dimerisation of ACBC-16 molecules is slightly more stabilised compared to ANBC-16. The difference should be attributed to the effect of the lateral substituent \( X \) (\( X = \text{CN or NO}_2 \)). Two origins, electronic and steric, are considered. First, we consider the electronic effect of the lateral substituent \( X \) on the stabilisation of hydrogen-bonded dimers. For this purpose, cyano-PBA and nitro-PBA were selected and the stabilisation energies of hydrogen-bonded dimers were calculated at DFT/B3LYP/6-31G* level. The results of the calculations are summarised in Table 2. If the energy of a single (hydrogen-bonded) dimer is lower than the energy of two molecules which are far apart and not hydrogen-bonded, the dimer is stabilised; the difference is the stabilisation energy. The stabilisation energies obtained in this way are 67.54 kJ (mol of dimer\(^{-1}\)) for cyano-PBA and 67.58 kJ (mol of dimer\(^{-1}\)) for nitro-PBA, with no meaningful difference. This result rules out the possibility that the replacement of the lateral substituent \( X \) from \( \text{NO}_2 \) to \( \text{CN} \) gives a substantial effect on the electronic state.

From the calculations in Table 2, we can also estimate the dipole moments of both \( \text{CN} \) and \( \text{NO}_2 \) groups. The estimated values were 5.08 D

![Figure 11. van’t Hoff plots for dimer–monomer equilibrium for ACBC-16 (○) and ANBC-16 (●). \( K_d = [\text{-COOH}]/[\text{-COOH}]^2 \). Linear least-squares fits are also shown as solid lines.](image-url)
Table 2. Results of the DFT/B3LYP/6-31G* calculation for cyano-PBA and nitro-PBA.

| State      | Cyano-PBA (kJ mol⁻¹) | Nitro-PBA (kJ mol⁻¹) |
|------------|----------------------|---------------------|
| Monomer    | -744.122091          | -856.3803826        |
| Dissociative limitation | -1488.144182 | -1712.7607650       |
| Dimer      | -1488.276151         | -1712.7927430       |
| Stabilisation energy | 83.935         | 83.958              |
| Dimer a,b  | -1488.269906         | -1712.7865042       |
| Stabilisation energy | 67.536         | 67.578              |

Notes: a In Hartree energy (Eₕ, 1 eₕ = 4.36 × 10⁻¹⁸ J). b Basis set superposition error (BSSE)-corrected energy.

(1 D = 3.33 × 10⁻³⁰ C m) for CN and 5.09 D for NO₂, which are almost the same. Thus, we cannot help concluding that the observed difference in the stability of dimers in the Cub phases between the two compounds is not due to the electronic origin.

2.6 Steric effect of the lateral substituent

Before discussing the steric effect of the lateral substituent, we first examine the molecular size in the dimeric structure for both ACBC-16 and ANBC-16. The optimisation of the structure was carried out at the semi-empirical AM1 level by using a CS Chem3D package (produced by Cambridge Soft Corporation, Inc.). As expected, it was found that the molecular structures of both the compounds have almost the same shape and length. As for the volume of the side group, however, the NO₂ group is composed of three atoms, whereas the CN group is of two atoms, and thus both groups have different volumes. According to Bondi,[58] the van der Waals volume of NO₂ group is 0.0279 nm³ and that of CN group is 0.0244 nm³; the former is 14% more voluminous than the latter. However, this fact does not lead to different molecular breadths. In fact, the estimated core breadths of ACBC-16 and ANBC-16 were found to be fortuitously the same and 0.83 nm.

As mentioned in the Introduction, the XRD studies for ACBC-16 [12] showed that the phase type of the Cub phase is the same as formed in ANBC-16 [11,45] but the lattice dimension is 2.5% larger than that of ANBC-16 when compared at the same temperature, and rather close to the value of ANBC-17 or -18 having alkoxy chains with 1 or 2 more repeat units. Comparison of their SmC layer spacings also gives a similar trend. The layer spacing of ACBC-16 is in between those of ANBC-17 and -18. Those two results imply that from the viewpoint of the self-organised structures, ACBC-16 behaves as if ‘ANBC-17.5’. In other words, the replacement of the NO₂ group with the CN group gives an apparent extension effect on the alkoxy chain length. This gave us a hint when considering the steric effect of the lateral substituent.

One plausible explanation is that the NO₂ group is more bulky in the direction parallel to the molecular long axis than the CN group, which would cause a slightly larger slippage along that direction. In other words, the smaller slippage in ACBC-16 as compared to ANBC-16 would result in the smaller tilt in the SmC layer and thus the larger thickness of the layer. Here, what is important is that the basic aggregations constructing the SmC and Cub phase structures are the layers. Thus, not the slippage length itself but the thickness of the layer should be related to the lattice dimension of the Cub phase as well as the SmC layer spacing.

2.7 Molecular-level aggregation state in the Ia₃d-Cub phases

The structure of the Ia₃d-Cub phases of both ACBC-16 and ANBC-16 is nowadays believed to be a result of nanosegregation between the slightly polar aromatic core and non-polar alkoxy chain moieties, and within their unit lattices the aromatic cores aggregate to form a pair of 3-by-3 networks of channels with the remaining space filled by alkoxy chains[11,13]; it is considered that layerlike aggregations of the molecules in the SmC phase are split into pieces and transformed into the channel segments of the Cub phase.[16,59–61] This picture was experimentally proved by the XRD intensity analyses for an analogous system 1,2-bis(4'-alkoxybenzoyl)hydrazines (BABH-n).[60,61] This work also stressed that core-core aggregation is essential for the thermotropic Cub phases.

In this section, we discuss how differently the steric effect of the CN and NO₂ side groups influence the molecular-level aggregation states in the Ia₃d-Cub phases and the thermal stability. The present IR studies can provide information about those. First, starting with the assignment of the smaller slippage along the molecular long axes in ACBC-16 than in ANBC-16, closer overlap of neighbouring aromatic cores would be expected in the former, leading to stronger interdimer π–π interactions, compared to the latter. This has been shown in the present IR studies by the lower frequency of the ν(C=C)₂ band observed for ACBC-16 than for ANBC-16 (Figure 4). Thus, the different steric effects give rise to a difference in the interdimer π–π interactions between the two. We are also considering that the enhanced interdimer π–π interactions reduces the dissociation of hydrogen-bonded molecules into monomeric ones, resulting in
slightly more stabilised dimerisation of ACBC-16 molecules in the Cub phase compared to ANBC-16 (Figure 10).

We can depict the following local picture. In ACBC-16, the lower frequency shift of the ν(C≡N) band with increasing temperature was parallel to the temperature variation of the ν(C=O)_{ring} band frequency (Figure 4). This can be explained on the same ground as mentioned earlier. That is, in ACBC-16, the overlap of neighbouring phenyl rings would also make possible the intermolecular interaction between the partially negatively charged nitrogen atom of the C≡N group and partially positively charged ether oxygen atom; the interaction certainly contributes to the weakening of the C≡N bond, causing the lower frequency shift of the ν(C≡N) band. Figure 12(a) is one possible overlap model of two molecules in the Cub phase. Here, it should be noted that the model only displays a snapshot because the state is essentially dynamic.

The overlap of neighbouring phenyl rings might be enhanced by the segregated structure in the Cub phase, especially compared to the SmC phase. In ANBC-16, however, the bulky NO₂ group would hinder the close contact of neighbouring phenyl rings, because the molecules more or less librate around each long axis, with the side group also being rotating or librating around the C-N axis. Thus, we can depict a possible overlap fashion of two ANBC-16 molecules in the Cub phase as in Figure 12(b). This reasonably explains little temperature variation of the ν(C=O)_{ring} band frequency for ANBC-16. The present studies have elucidated how the steric effect of the lateral substituent changes the molecular-level aggregation state in the Ia3d-Cub phase and its thermal stability.

3. Conclusions

In the present IR studies, first of all, the assignment of the observed IR bands was made in the range 3500–1300 cm⁻¹ for both ACBC-16 and ANBC-16 on the basis of the literature and by the aid of theoretical DFT/B3LYP/6-31G* level calculations for two model compounds having a CN or a NO₂ group at the 3’-position (cyano-PBA and nitro-PBA, respectively). Next, information about the molecular changes at the phase transitions was obtained by elevating temperature for ACBC-16. The tail melting was monitored through the temperature-dependent ν_{as}(C-H)_{CH2} and ν_{s}(C-H)_{CH2} band frequencies, and similarly to the ANBC-16, the result proved fully liquidlike alkoxy chains in the Cub phase. A difference between the two compounds was seen in their ν(C=O)_{ring} bands; the ν(C=O)_{ring} band frequency in ACBC-16 was by 3 cm⁻¹ lower than that in ANBC-16, suggesting slightly stronger intermolecular π–π interaction in ACBC-16. Another difference was obtained by the quantitative analysis of the ν(C=O) band; in the Cub phase temperature region, the molar fraction of hydrogen-bonded COOH groups for ACBC-16 is by ≈0.05 at maximum larger than that for ANBC-16. On the other hand, stabilisation energies for dimerisation calculated at the DFT/B3LYP/6-31G* level gave no significant difference between the two model compounds. These results derived a conclusion that the steric effect of the lateral substituent at the 3’-position of the biphenyl ring is crucial, giving a difference in the way to pack the molecules laterally; the smaller slippage between the two neighbouring molecules along the long molecular axis in ACBC-16 would result in the smaller tilt in the SmC layer and also provide the larger stability of the Cub phase, as compared to ANBC-16. This argument is consistent with the X-ray results previously published; the SmC layer thickness and lattice dimension in the Cub phase of ACBC-16 are larger compared to ANBC-16.[12] It is noted that IR and XRD techniques are complementary with each other and useful to get more detailed information about the self-organised structure of the Cub phases at the molecular level. It should be also stressed that the thermal stability of the Cub phase is quite sensitive to the very minute chemical part of the constituent molecule such as CN or NO₂ group.
4. Experimental details

4.1 Preparation of ACBC-16

ACBC-16 was synthesised at Technische Universität Darmstadt. The quality of the sample was checked by elemental analysis. The detail is described in Ref. [50].

4.2 Differential scanning calorimetry and polarised optical microscopy

The phase transitions were examined by differential scanning calorimetry (DSC: Seiko Denshi, DSC-210) interfaced to a data station (Seiko Denshi, SSC 5000 system). The measurements were performed under a dry nitrogen flow of ca. 40 mL min⁻¹ and the scanning rate was 5 K min⁻¹. The texture of each mesophase was observed using a polarising optical microscope (POM: Nikon Optiphot-pol XTP-11) equipped with a hot stage (Mettler FP-82) and a central processor (Mettler FP80) at a heating/cooling rate of 5 or 10 K min⁻¹.

4.3 Infrared spectroscopy

The IR measurements were performed for both ACBC-16 and ANBC-16 samples using a Perkin Elmer Spectrum 400 (MIR/FIR) Fourier transform spectrometer. Samples were measured in transmission as dispersed in KBr pellets, and more than 32 scans at 4-cm⁻¹ resolution were signal-averaged. Experiments at elevated temperatures were carried out using a heated cell (SPECAC P/N 21,525 series) equipped with a controller (SPECAC 4000 series), where the temperatures were calibrated using an external thermocouple. Care was taken by waiting for enough time to accomplish the thermal equilibrium between the sample and the cell after the temperature reached to the objective temperature.

Digital encoding of the spectral data was carried out at 1-cm⁻¹ intervals, transferred into a personal computer for further calculations described below. The baseline of each spectrum was assumed to be a line through three minimum points in the regions 500–1700, 1700–2000, and around 4000 cm⁻¹, although we do not know the baseline a priori. After the baseline subtraction, the spectrum in the ν(C=O) band region was resolved using an IGOR software, using Gauss, Lorentz, or Voigt functions to minimise the deviation in the region 1690–1800 cm⁻¹. After comparing the results using three functions, we concluded that the result based on Lorentz function is appropriate because the fitting around the tail region was reasonably good and that the ratios of two molar extinction coefficients (ε_H-bonded/ε_free) for two analogous compounds (ACNC-16 and ANBC-16) were identical within the experimental errors (see the Carbonyl C=O stretching region section). On the other hand, we found that the result based on Voigt function is very susceptible to the influence of experimental errors and uncertainty of the baseline. In this work, the data for ANBC-16 were also calculated on the same procedure for comparison.

4.4 Quantum chemical calculations

Cyano-PBA and nitro-PBA were selected as the model compounds for ACBC-16 and ANBC-16, respectively, and quantum chemical calculations were carried out for those compounds using a Gaussian 03 program package.[62] Stabilisation energy for dimerisation and vibrational spectra were computed in the framework of the density functional theory (DFT) with the 6-31G* basis set. In the DFT methods, the Becke’s three-parameter exchange functional [63,64] was utilised in combination with the Lee, Yang and Parr correlation functional [65] (DFT/B3LYP). The geometries of the model compounds in the monomer and cyclic dimer structures were optimised by minimising their energies, and their stabilities were confirmed through the vibrational analyses. With respect to the geometry between the cyano-/nitro-aromatic C bond and the C=O bond, the syn conformer was selected when constructing the initial structure of the dimer because the syn conformer is, although the difference is small (0.2–0.3 kJ mol⁻¹), more stable than the corresponding anti conformer (see Table S1 in SM). All geometric parameters (optimised Cartesian coordinates and selected bond lengths and angles) and calculated frequencies are compiled in Tables S2–S11 in SM. To evaluate the stabilisation energy from dissociation limitation (where two monomers exist without interaction) to the dimer, the energy difference was calculated. In this calculation, the counterpoise method was applied for the correction of the basis set superposition error (BSSE).

Acknowledgements

We first thank Prof. W. Haase at Technische Universität Darmstadt (Germany), Drs. Y. G. Galyametdinov and I. Galyametdinova at Kazan Physical-Technical Institute (Russia), Dr. R. Eidenschink at NEMATEL (Germany) for kindly permitting the use of the ACBC-16 sample. Prof. Emeritus Michio Sorai at Osaka University (Japan) gave us a chance to study the ACBC-16; in fact the present work started from the collaboration work with those five scientists.[12,50]
Funding
This work was partly supported by Grant-in-Aid for Scientific Research (C) [grant numbers 18550121 and 25410091] from Japan Society for the Promotion of Science (JSPS) and by Grant-in-Aid for Scientific Research on Priority Areas [grant number 446/1902012] from Ministry of Education, Culture, Sports, Science and Technology (MEXT) (both for S.K.) and by Grant-in-Aid for Scientific Research (B) [grant number 26288031] from JSPS (K.S.). [12,50]

Supplemental data
Supplemental data for this article can be accessed here.

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