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Re-evaluation of the Thermal Behavior of 2:1 Halogen-Bonded Complexes Formed between 4-Alkoxycyanobiphenyls and 1,4-Diiodotetrafluorobenzene

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ABSTRACT: Three representative examples of 2:1 complexes formed between 4-alkoxycyanobiphenyls and 1,4-diiodotetrafluorobenzene have been reprepared, and single crystal data were obtained for all (including one redetermination). Their thermal behavior has been examined in detail using polarized optical microscopy, differential scanning calorimetry, and small-angle X-ray scattering, with no evidence for liquid crystallinity being found.

INTRODUCTION

Since their first report in 2004,[1] liquid crystals formed from halogen-bonded complexes have attracted a good deal of interest.[2,3] In this vein, last year, Ingle et al. published an account in this Journal of the formation of 2:1 halogen-bonded complexes using a series of 4-alkoxycyanobiphenyls and 1,4-diiodotetrafluorobenzene.[4] Among the data reported was an evaluation of the thermal behavior of the complexes, given that the halogen acceptors in the complexes are known liquid crystals, and a proposal that they showed liquid crystallinity.

Three of the complexes—CAB 6 XB, CAB 9 XB, and CAB 10 XB (Chart 1)—have now been subject to detailed thermal re-examination using DSC, polarized optical microscopy, and small-angle X-ray scattering. Each sample was prepared as single crystals, and the structure was solved (redetermination for CAB 10 XB). A reinterpretation of the properties is proposed.

Preparation and Single Crystal Structure Determinations. All of the components, namely, 4-hexyloxycyanobiphenyl (CAB 6), 4-nonyloxycyanobiphenyl (CAB 9), 4-decyloxycyanobiphenyl (CAB 10), and 1,4-diiodotetrafluorobenzene, were obtained commercially and used as supplied. The thermal data for the cyanobiphenyls in the previous paper are not accurate and so the correct values are given here for the two homologues used in this study.[5,6] Accurate data for the others reported originally are given in the Supporting Information.

CAB 6 (°C): Cr • 58 • N • 76.5 • Iso

CAB 9 (°C): Cr • 65 • SmA • 76 • N • 79.5 • Iso

CAB 10 (°C): Cr • 61 • SmA • 84.5 • Iso

Single crystals were prepared by dissolving the components in a precise 2:1 molar ratio (cyanobiphenyl/diiodotetrafluorobenzene) in a mixture of ethyl acetate:hexane (8:2 v/v), placing it in a sample vial, covering the top with pierced parafilm, and allowing the solvent to evaporate. Large, slab-like crystals were obtained for CAB 6 XB and CAB 9 XB, while smaller needles were obtained for CAB 10 XB; the main data parameters are collected in Table 1.

All three complexes crystallize in a triclinic system in the $P\overline{1}$ space group with reasonably similar unit cell dimensions, although the unit cell angles in CAB 6 XB differ. In considering the data for the two determinations of CAB 10 XB, the rather minor differences are almost certainly due to the different temperatures used (293[4] vs 110 K), which would also account for the improved R factors in the new determination.

In terms of molecular parameters, the N···I distances for CAB 10 XB in the two structures are rather similar at 3.041(2) Å (this work) and 3.079(5) Å (previous work[4]), and differences in the angles associated with the halogen bond are negligible. However, the dispositions of the components for CAB 6 XB and CAB 9 XB are quite different, and so a brief description follows.

The three complexes are shown in Figure 1a (CAB 6 XB), b (CAB 9 XB), and c (CAB 10 XB: image derived from the new determination) and are viewed by looking perpendicular to the plane of the diiodotetrafluorophenyl ring. Thus, while the N···I distances are similar in the three structures (2.986(2) 2.955(2), and 3.041(2) Å for CAB 6 XB, CAB 9 XB, and CAB 10 XB, respectively), the angle at nitrogen is very different (158.3(2), 157.2(2), and 174.6(2)° for CAB 6 XB, CAB 9 XB, and CAB 10 XB, respectively). This suggests an appreciably weaker interaction in the former cases given the directionality associated with the halogen bond. However, the orientation in the solid state is, of course, not necessarily a guide to what may happen in the molten form.

Thermal Behavior. Having had our attention drawn to the reported thermal behavior, the three complexes were selected for detailed re-examination, and in each case, pristine crystals were used for the thermal analysis. In considering the discussion below, it is helpful to appreciate the different time scales of the

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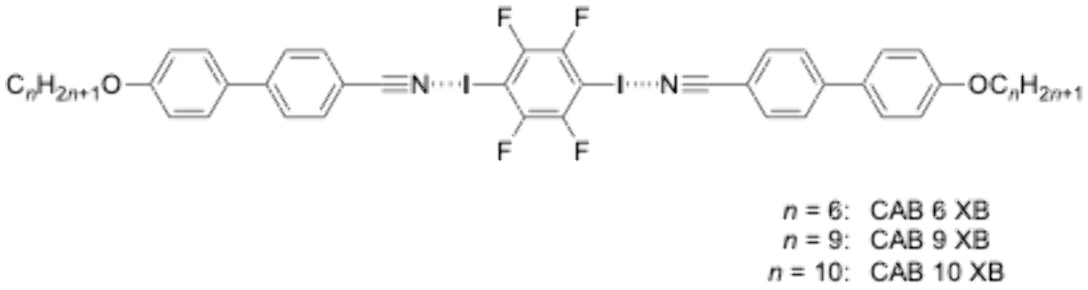
Chart 1. Structure of the Halogen-Bonded Complexes Studied in This Article[a]



[a] Other examples with $3 \leq n \leq 8$ were also reported in the previous publication.

Table 1. Principle Crystallographic Parameters for the New Structure Determinations with Data for CAB 10 XB Compared against the Published Structure

	CAB 6 XB	CAB 9 XB	CAB 10 XB	
	this work	this work	this work	previous paper
CCDC No.	2376244	2376243	2376242	2207664
T/K	110.00(10)	110.00(10)	110.00(10)	293(2)
crystal system	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	5.44290(10)	5.38612(13)	7.6721(2)	7.8495(9)
b/Å	13.8441(2)	13.7217(4)	11.4686(3)	11.5682(1)
c/Å	13.9596(2)	16.9711(4)	14.7400(4)	14.8276(2)
α/deg	103.353(2)	67.340(3)	68.211(3)	68.656(5)
β/deg	94.381(2)	83.497(2)	76.079(3)	75.214(5)
γ/deg	101.043(2)	79.377(2)	88.829(3)	87.999(5)
V/Å^3	996.45(3)	1136.39(6)	1165.49(6)	1209.81(3)
R_{all}, R_{obs}	0.0253, 0.0240	0.0269, 0.0250	0.0216, 0.0211	0.062, 0.047
wR_{all}, wR_{obs}	0.0649, 0.0639	0.0605, 0.0596	0.0513, 0.0510	0.127, 0.120
GOF on F^2	1.076	1.035	1.029	0.985

three experiments. Thus, heating a sample from, for example, 20 to 70 °C on the microscope hot stage would take 10 min, on top of which there will be occasions when the temperature is held while the sample is "poked and prodded" (see discussion below). Cooling takes a further 10 min, and so the whole experiment is completed in half an hour. The DSC data are recorded from 25 to 85 °C or 95 °C at 10 °C min^{-1} over three heating and three cooling ramps, thus taking around 40 min. SAXS in contrast requires that the sample be ramped from room temperature to 85 °C in *ca.* 3 °C steps. The heating takes a finite time, and then the sample must equilibrate thermally at each temperature before the data are collected. Thus, a complete heat−cool cycle takes on the order of 5 h.

Polarized Optical Microscopy. A sample of CAB 6 XB was heated at 5 K min^{-1} to 76 °C, at which temperature it melted to give an isotropic liquid. That the fluid was isotropic was confirmed by disturbing the sample with a metal needle, which has the effect of cooling the sample at the point of contact (which would reveal the presence of a phase at a slightly lower temperature) and also of causing macroscopic molecular reorientation and the appearance of a transient texture if a mesophase is present and aligned homeotropically. The needle had no effect whatsoever. The sample was then cooled at the same rate and was observed to crystallize sharply at 54.5 °C. During the cooling process, the sample was repeatedly disturbed with the metal needle, and no effects were seen. Explicitly, nothing was observed that would support the existence of any liquid crystal behavior.

A sample of CAB 9 XB was similarly heated at 5 K min^{-1} from ambient temperature to 72 °C, at which temperature a sharp melting event was observed to give an isotropic fluid (established as above). It was cooled at the same rate and was observed to crystallize sharply at 59.7 °C.

Studying CAB 10 XB in the same way was slightly different. The microscopy showed some evidence of thermal events as the temperature increased, and this time melting occurred over a few degrees until clearing was observed at 79 °C. It was evident that during the melting event there was both a liquid and a solid present, and the liquid was evidently isotropic. Such melting events do show birefringent crystallites suspended in the isotropic liquid, but this is distinctly different from what is observed when a liquid crystal clears. Interestingly, cooling the sample led to a very "clean" crystallization at 66 °C. Once more, nothing was observed that would support the existence of any liquid crystal behavior.

Differential Scanning Calorimetry. Samples of the complexes were heated from 25 to 85 °C (CAB 6 XB and CAB 9 XB) or 25 to 95 °C (CAB 10 XB) at 10 K min^{-1} for three heating and three cooling cycles; the traces are shown in Figure 2. Individual heat−cool cycles and onset temperatures and associated enthalpy changes for each complex are shown in the Supporting Information.

The traces for CAB 6 XB and CAB 9 XB are rather reproducible, showing melting at 74 and 76 °C, respectively, and supercooled crystallization. For CAB 6 XB, the onset temperatures of the first two crystallizations are all but identical at ~47.5 °C, whereas the third occurs at the higher temperature of 51.5 °C. This is not held to be significant as crystallization is happening below the thermodynamic melting point and so is in a kinetic regime. There is a very slight difference in the cooling onset on the first scan for CAB 9 XB. There is some suggestion of a small thermal event for CAB 9 XB at *ca.* 65 °C on heating whose intensity (and hence enthalpy change) increase with a scan number, with a concomitant reduction in the main melting enthalpy. This is seen also in the third heating scan of CAB 6 XB. In each case, the temperature coincides with the melting point of the free cyanobiphenyl, and so there may be some dissociation occurring, but the absence of any thermal events on cooling suggests ready reassociation. The melting enthalpies on the first scan are ~62 kJ mol^{-1} and ~68 kJ mol^{-1} for CAB 6 XB and CAB 9 XB, respectively, entirely consistent with a solid melting, while the significant hysteresis between melting and crystallization is also consistent with the behavior of a "simple" solid. For both complexes, there is, however, a small if steady reduction in the

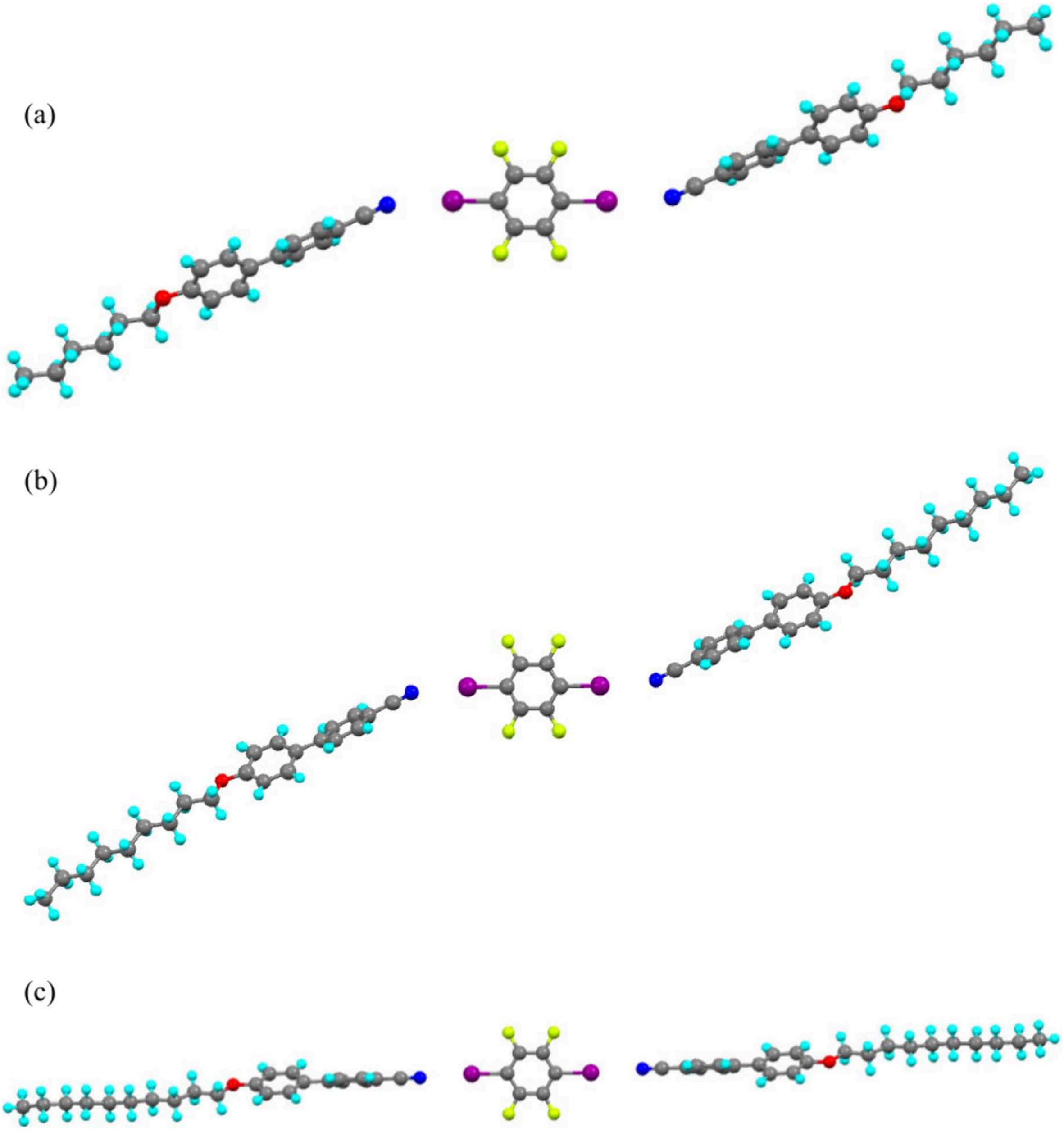


Figure 1. Structure of the 2:1 halogen-bonded complex for (a) CAB 6 XB, (b) CAB 9 XB, and (c) CAB 10 XB.

melting enthalpy change in successive scans, which would be consistent with dissociation in the melt, something that has been commented on previously.[3,7,8] Interestingly, the crystallization enthalpies nonetheless remain remarkably consistent.

The thermal behavior of CAB 10 XB is more involved, but as the point of this Comment is to address possible liquid crystal behavior, solid-state polymorphism has not been explored further. As such, and in common with the behavior of CAB 9 XB, a large melting event at around 77 °C is noted with an enthalpy change of 120 kJ mol^{-1} (calculated indicatively from the single event on the third heating cycle). Curiously, the crystallization enthalpy is around half of that observed for melting, but there are subsequent exotherms at lower temperatures as well as cold crystallization that could make up much or all of the difference. The hysteresis between melting and crystallization is again close to 30 °C, which along with the very large enthalpy of melting, does not support liquid crystal behavior.

Small-Angle X-ray Scattering. Data were collected at *ca.* 3 °C intervals on both heating and cooling for all samples over the ranges shown in the legend (Figure 3).

The data for CAB 6 XB and CAB 9 XB (Figure 3a and b) are straightforward and show only minor changes in the pattern throughout the solid range. The lowest-angle reflection is indicated, corresponding to a spacing of ca. 14 Å (CAB 6 XB) or 16 Å (CAB 9 XB) and these are compared with the lengths of the 2:1 dimers of ca. 50 Å (CAB 6 XB) or 57.5 Å (CAB 9 XB) from the structure determinations. The cooling data are shown in the Supporting Information (Figure S4a and b) and are entirely featureless until solidification. The data for CAB 10 XB (Figure 3b) are more involved, and there is much variation with temperature. Furthermore, there is a lower-angle reflection at about $2\theta = 2.5°$ (~35 Å) that appears on heating, which is very similar that that of CAB 10 in its SmA phase (Figure S5), which might imply some dissociation. Indeed, the SAXS pattern at 59

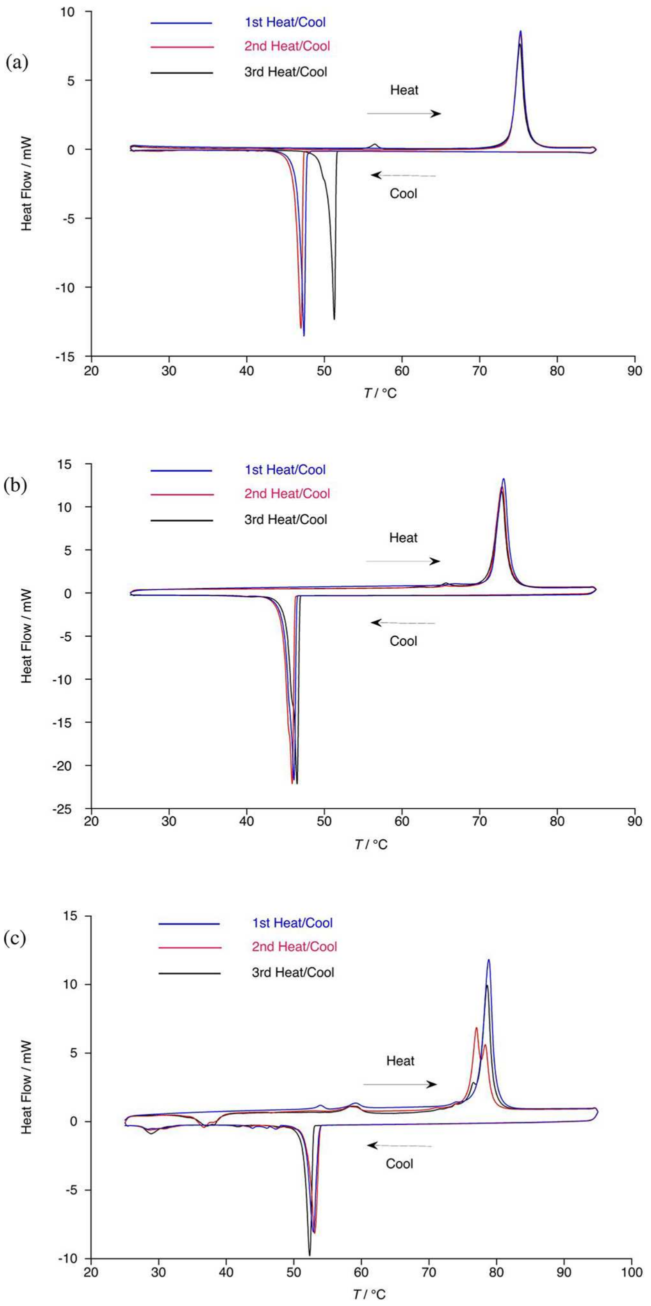


Figure 2. DSC traces for (a) CAB 6 XB, (b) CAB 9 XB, and (c) CAB 10 XB. Experimental conditions are given in the text.

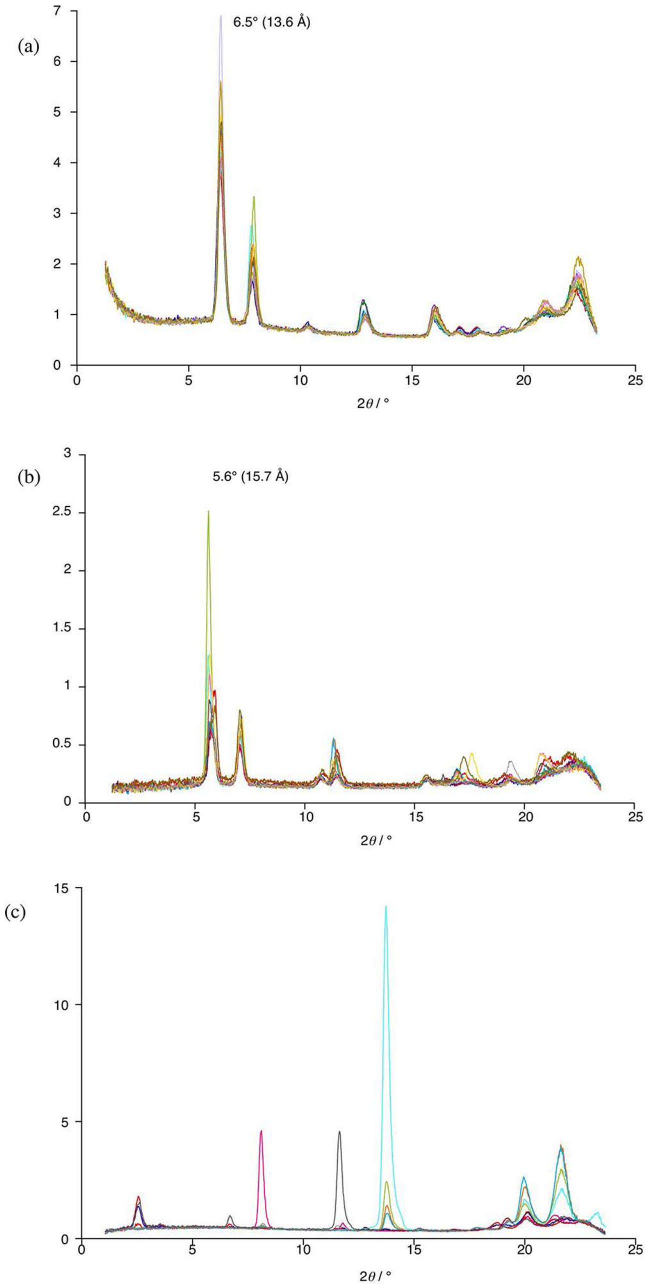


Figure 3. Small-angle X-ray scattering data: (a) CAB 6 XB (from 31–73 °C), (b) CAB 9 XB (from 27–69 °C), and (b) CAB 10 XB (from 27–79 °C). All data are collected to just below the melting point.

°C (Figure 4a) shows that reflection clearly alongside reflections from evidently solid material at $2\theta > 5°$. Similarly, it is observed on cooling, and Figure 4b shows the SAXS pattern obtained at 34 °C with again the signature of a solid material at ca. $2\theta = 8°$.

■ CONCLUSION

Reinvestigation of the thermal behavior of three examples of halogen-bonded complexes—CAB 6 XB, CAB 9 XB and CAB 10 XB—formed between alkoxycyanobiphenyls and 1,4-diiodotetrafluorobenzene—has shown unequivocally the absence of any liquid crystal properties. In discussing the differences between the two sets of observations, it became apparent that while the current work derived all experimental data from pristine crystals of the complexes obtained from the careful crystallization used to grow the single crystals, in the original study[4] the materials had been prepared using solvent-assisted grinding. Using this latter technique, it is not always straightforward to ensure precise, reproducible stoichiometry. Thus, it is the case that the LC properties reported in the earlier paper[4] are associated with free alkoxycyanobiphenyl consequent on an imprecise stoichiometry. In the study of all liquid crystals, the requirement for purity is absolute and so where the mesogenic unit is formed from components linked through specific noncovalent interactions (for example hydrogen or halogen bonding),[9] then the stoichiometry and integrity of the complete unit need to be precise. A fuller discussion of this point is found elsewhere.[3,10]

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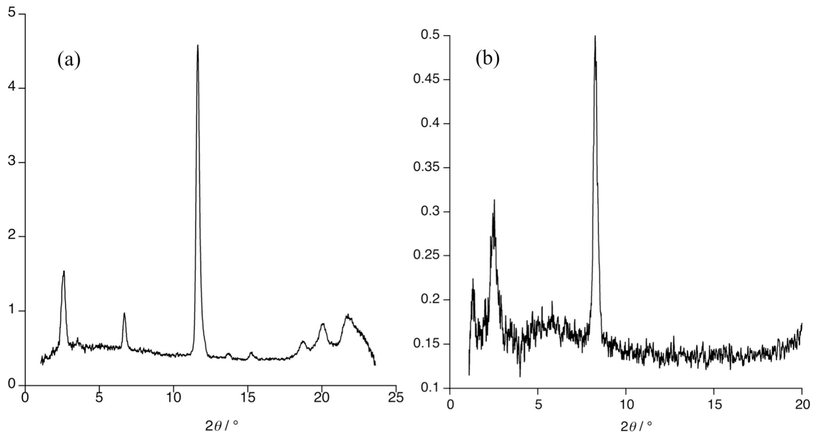

Figure 4. Small-angle X-ray scattering from CAB 10 XB (a) at 59 °C on heating and (b) at 34 °C on cooling.

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ASSOCIATED CONTENT

Data Availability Statement

There is a data archive found at 10.15124/032ba745-f0e6-44e2-9d41-39937e04da93, which contains raw data from both DSC and SAXS.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.cgd.4c01103.

> The Supporting Information contains: transition temperatures for CAB 3 to CAB 5, CAB 7, and CAB 8; DSC onset temperatures and enthalpy changes for each heat/cool run for each complex; SAXS cooling data for CAB 6 XB, CAB 9 XB, CAB 10 XB, and CAB 10 (PDF)

Accession Codes

CCDC 2376242−2376244 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

G.M.S. and C.A.T. grew the single crystals. A.C.W. and R.J.G. collected crystallographic data and solved and refined the structures. S.J.C. collected the DSC and SAXS data. D.W.B. carried out the optical microscopy. Data were interpreted by D.W.B. and S.J.C. The manuscript was written by D.W.B. and finalized through contributions of all authors, who have given their approval to the final version.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Nguyen, H. L.; Horton, P. N.; Hursthouse, M. B.; Legon, A. C.; Bruce, D. W. Halogen Bonding: A New Interaction for Liquid Crystal Formation. *J. Am. Chem. Soc.* **2004**, *126*, 16−17.

(2) Devadiga, D.; Ahipa, T. N. An up-to-date review on halogen-bonded liquid crystals. *J. Mol. Liq.* **2021**, *333*, 115961.

(3) Präsang, C.; Bruce, D. W. Halogen-bonded Liquid Crystals. *Helv. Chem. Acta* **2023**, *106*, No. e202300008.

(4) Ingle, K. S.; Bairagi, K. M.; Thakur, J. S.; Sathishkumar, R.; Chennuru, R.; Baishya, B.; Nayak, S. K. Synthesis, Structural and Theoretical Analyses of C≡N···I Halogen- Bonded Liquid Crystalline Complexes of 4-Cyano-4′-alkoxy Biphenyl Systems. *Cryst. Growth. Des.* **2023**, *23*, 1755−1767.

(5) *Flüssige Kristalle in Tabellen II*; Demus, D., Zaschke, H., Eds.; VEB: Leipzig, 1984 (ISBN 978-3342000167).

(6) Mandle, R. J.; Goodby, J. W. An interplay between molecular pairing, smectic layer spacing, dielectric anisotropy and re-entrant phenomena in ω-alkenyloxy cyanobiphenyls. *Liq. Cryst.* **2017**, *44*, 656−665.

(7) Bruce, D. W.; Metrangolo, P.; Meyer, F.; Prasang, C.; Resnati, G.; Terraneo, G.; Whitwood, A. C. Mesogenic, trimeric, halogen-bonded complexes from alkoxystilbazoles and 1,4-diiodotetrafluorobenzene. *New. J. Chem.* **2008**, *32*, 477−482.

(8) Präsang, C.; Whitwood, A. C.; Bruce, D. W. Spontaneous Symmetry Breaking in Halogen-bonded, Bent-core Liquid Crystals: Observation of a Chemically-driven Iso−N−N* Phase Sequence. *Chem. Commun.* **2008**, 2137−2139.

(9) Bruce, D. W. Liquid Crystals formed from Specific Supramolecular Interactions. In *Supramolecular Chemistry: From Molecules to Nanomaterials*; Steed, J. W., Gale, P. A., Eds.; Wiley: Chichester, 2012; pp 3493−3514.

(10) Bruce, D. W.; Metrangolo, P.; Meyer, F.; Pilati, T.; Präsang, C.; Resnati, G.; Terraneo, G.; Wainwright, S.; Whitwood, A. C. Structure-Function Relationships in Liquid-Crystalline Halogen-Bonded Complexes. *Chem.—Eur. J.* **2010**, *16*, 9511−9524.