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# Effects of Symmetry on the Stability of Columnar Liquid Crystals

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To assess the effects of molecular symmetry on the phase transitions of columnar liquid crystals, we prepared a family of 19 discotic mesogens. This series of dibenzophenazine derivatives allowed us to compare the differences in phase transitions between sixteen pairs of isomers that differed in terms of their overall symmetry. It was found that the more symmetrical isomer had a significantly higher melting temperature in all but one case, whereas symmetry appeared to have a lesser impact on clearing temperature. A similar relationship between symmetry and melting point is also observed for triphenylene-based discotic mesogens; in these systems, the clearing points show a stronger dependence on molecular symmetry.

## Introduction

In 1882, Thomas Carnelley made the observation that symmetrical molecules almost invariably have higher melting points than their less symmetrical isomers.[1] Carnelley's rule is both one of the oldest and one of the most successful generalizations relating molecular structure to self-assembly of crystalline solids; indeed, it is a rule with relatively few known exceptions,[2–4] and several studies have demonstrated that there is a correlation between a molecule's symmetry number ($\sigma$)[5] and its melting temperature.[2,3,6–8] Although symmetry appears to play an important role in determining the temperature at which a crystalline solid melts to an isotropic liquid, it is not clear whether a similar relationship holds for other order-to-disorder transitions, such as the melting of a solid to a liquid crystal or the clearing of a liquid crystal to an isotropic liquid. We were particularly interested in addressing these questions as they apply to columnar liquid crystals formed by discotic mesogens, which recently have been the subject of numerous investigations focusing on their use as semiconducting materials.[9] The ability to tune the temperature ranges over which discotic mesogens are liquid crystalline is a necessity for the practical exploitation of these mesophases.[10] In this context, breaking molecular symmetry may provide a means for shifting the melting and clearing temperatures of these materials to lower temperatures. Although there have been a limited number of reports on the effect of symmetry on the

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(5) The molecular symmetry number corresponds to the number of degenerate positions that can be adopted by a molecule by rigid rotation. This value is pertinent because it corresponds to the indistinguishable ways in which a molecule can reside in an idealized lattice, which in turn can be related to the lattice's residual entropy ($S_{\mathrm{res}}$) by $S_{\mathrm{res}} = R\ln(\sigma)$. For example, a molecule with $C_2$ symmetry has a symmetry number $\sigma = 2$, which means that there are two equivalent orientations that are related by rotation about the molecule's $C_2$ axis. It has been suggested that Carnelley's rule is a result of the fact that a crystal formed by a high symmetry molecule has a higher residual entropy and therefore its entropy of melting ($\Delta S_{\mathrm{m}}$) is smaller. Because $T_{\mathrm{m}} = \Delta H_{\mathrm{m}}/\Delta S_{\mathrm{m}}$, this leads to the prediction that higher symmetry molecules will have a higher melting points. It should be noted, however, that this interpretation has been disputed, and several researchers have suggested that the relationship between symmetry and melting point arises instead from a more efficient packing of the more symmetrical molecules. See referencs 3, 4, and 6−8.

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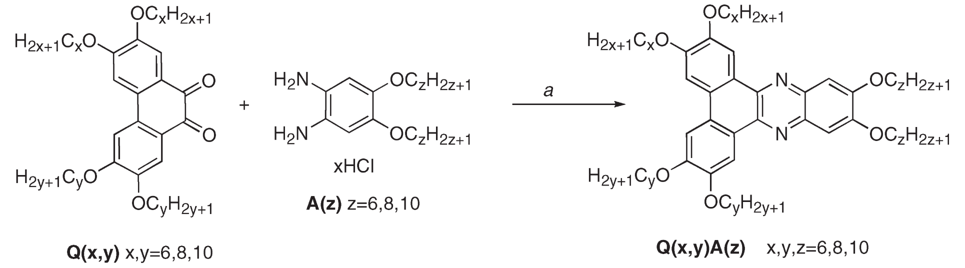
**Scheme 1. Synthesis of Q(*x*,*y*)A(*z*)** [a]

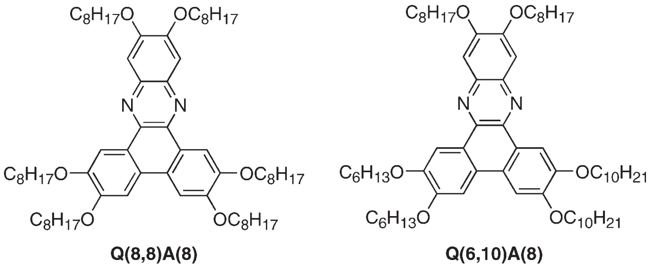


[a] Reagents and conditions: (a) NaOAc, ethanol, reflux (33−92% yield).

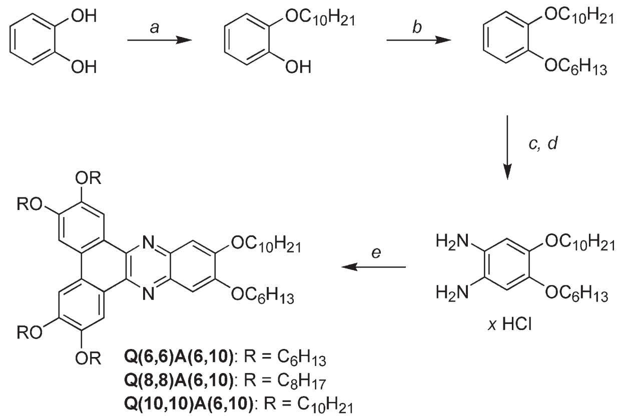
phase transitions of discotic mesogens,[11−14] to the best of our knowledge, no studies have directly addressed the relevance of Carnelley's rule to liquid crystals by examining pairs of isomers with differing symmetry.

To broach this problem, we focused our attention on hexaalkoxydibenzo[a,c]phenazines **Q(*x*,*y*)A(*z*)**, which were assembled in a modular fashion by coupling 3,4-dialkoxy-1,2-phenylene, **A(*z*)**, with 2,3,6,7-tetra(alkoxy)phenanthrene-9,10-diones, **Q(*x*,*y*)** (Scheme 1). These phenanthrene-9,10-diones are versatile precursors that have been used to prepare a wide variety of discotic mesogens[15−20] and we have previously reported an efficient synthesis of unsymmetrical diones in which $x \neq y$.[13] Moreover, Ong and coworkers have synthesized several of members of the series **Q(x,y)A(z)** in which all six side chains were of equal length (i.e., $x = y = z = 4, 6, 8, 10$, or 12).[16,21] Their results demonstrated that these mesogens tend to have very broad liquid crystalline phase ranges, which makes these promising candidates for many practical applications. For our purposes, the relatively low symmetry of this aromatic core offers the further advantage that isomers with identical sets of chains but differing symmetry can be readily prepared. For example, **Q(6,6)A(8)** and **Q(6,8)A(6)** each have four hexyloxy and two octyloxy chains, but the former compound has higher symmetry ($\sigma = 2$) than the latter ($\sigma = 1$) (see Chart 1).

**Chart 1**



**Scheme 2. Synthesis of Q(*x*,*x*)A(6,10)**[a]



[a] Reagents and conditions: (a) $C_{10}H_{21}Br$, $K_2CO_3$, $NBu_4Br$, butanone, reflux, 29%; (b) $C_6H_{13}Br$, $K_2CO_3$, $NBu_4Br$, butanone, reflux, 90%; (c) $HNO_3$, heat, 66%; (d) $SnCl_2$, $HCl_{(aq)}$, EtOH, heat, quantitative; (e) **Q(*x*, *x*)**, NaOAc, EtOH. **Q(6,6)A(6,10)**, 81%; **Q(8,8)A(6,10)**, 79%; **Q(10,10) A(6,10)**, 86%.

The sixteen isomers synthesized from series **Q(*x*,*y*)A(*z*)** facilitated the study of symmetry breaking when two pairs of chains ($x$ and $y$) differ from one another. In addition, three derivatives **Q(*x*,*x*)A(6,10)** formed from the condensation of an unsymmetrical diamine with a symmetrical dione (Scheme 2) were prepared in order to probe the effect of symmetry-breaking arising from just two chains of unequal length.

## Results

Symmetrical diones **Q(6,6)**, **Q(8,8)**, and **Q(10,10)** were synthesized according to the method of Mohr.[20] The syntheses of the unsymmetrical diones **Q(6,10)** and **Q(8,10)** have previously been reported; the same general approach, which is outlined in Scheme 3, was employed in the preparation of **Q(6,8)**.

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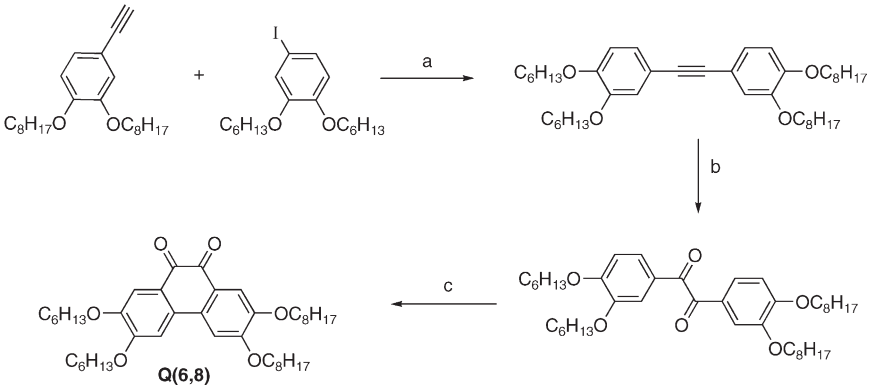
(21) Compound **Q(8,8)A(8)** was previously reported by Ong and coworkers. Although our results are in qualitative agreement with this earlier work, the $T_m$ and $T_c$ observed by Ong et al. are higher than our own by 2.6 and 6.2 °C, respectively. Because the comparison of phase transition temperatures obtained from two different instruments introduces a significant source of systematic error, we have employed the temperatures obtained in our own study for the sake of comparison. However, this choice does not change the qualitative conclusions reached herein.

**Scheme 3. Synthesis of the Q(6,8)[a]**



[a] Reagents and conditions: (a) $(i\mathrm{Pr})_2NH$, CuI, $Pd(PPh_3)_4$, THF, reflux, 66%; (b) $I_2$, DMSO, reflux, 77%; (c) $BF_3 \cdot Et_2O$, $VOF_3$, $CH_2Cl_2$, room temperature, 73%.

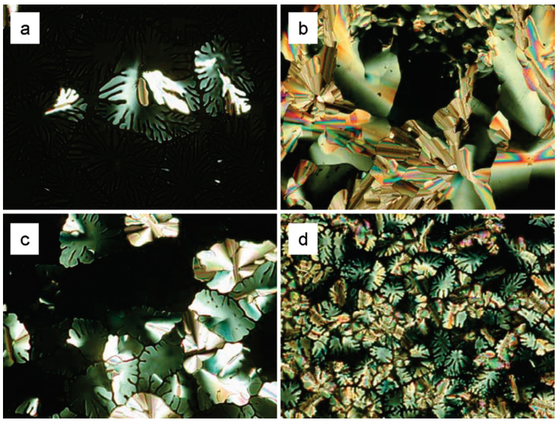


**Figure 1.** Polarized optical micrographs of columnar phases formed upon cooling from isotropic phase: (a) **Q(8,10)A(10)**, 120 °C (200×); (b) **Q(6,8)A(10)**, 110 °C (80×); (c) **Q(8,8)A(6,10)**, 130 °C (80×); (d) **Q(6,6) A(10)**, 83 °C (200×).

The diamines **A(6)**, **A(8)**, and **A(10)** were prepared according to literature procedures.[16] The unsymmetrical diamine **A(6,10)** was synthesized from the sequential alkylation of catechol to obtain 1-decyloxy-2-hexyloxybenzene, followed by dinitration and reduction with stannous chloride (Scheme 2). 3,4-Dialkoxy-1,2-phenylenediamines are unstable toward oxidation and were therefore used immediately after preparation.

All compounds in series **Q(*x*,*y*)A(*z*)** and **Q(*x*,*x*)A(*z*,*z*′)** were examined by differential scanning calorimetry (DSC) and were found to undergo two phase transitions upon heating; these were identified by polarized optical microscopy as solid to liquid crystal (melting) and liquid crystal to isotropic liquid (clearing) transitions, respectively. Samples cooled slowly into their liquid crystalline phase from the isotropic state exhibited dendritic textures when viewed by polarized optical microscopy (Figure 1), which are typical of columnar phases. The XRD of compound **Q(6,6)A(10)** exhibited two intense peaks at low angles, as well as a number of less intense peaks at higher angles; collectively, these were indexed to those of a columnar rectangular ($Col_r$) phase. The remaining 18 compounds were identified as columnar hexagonal phases ($Col_h$). Small-angle X-ray diffractograms of the liquid crystalline phases of nine of these compounds exhibit peaks that index to the (100) and (110) spacings of a hexagonal lattice. The XRD patterns of the liquid crystalline phases of the remaining compounds exhibit only a single intense peak in the low-angle region; these peaks were assigned to the (100) spacing of a hexagonal lattice. A broad peak was also observed at larger angles for each of the 19 molecules that corresponds to a distance of approximately 4.5 Å; these were attributed to the alkyl chain halo. The XRD of most compounds also exhibited a peak at angles corresponding to distances of approximately 3.5 Å, which is consistent with $\pi-\pi$ stacking between adjacent molecules within a column. The phase behaviors of all compounds are listed in Tables 1−3. XRD data for these compounds are listed in the Supporting Information.

## Discussion

To facilitate the following discussion, we introduce the term "Carnelley isomers" to denote a pair of isomers that differ in their overall symmetry. Thus, **Q(8,8)A(6)** is a Carnelley isomer of **Q(6,8)A(8)**, because the latter is less symmetrical, but not of **Q(6,6)A(10)**, an isomer that has the same symmetry. Further, the term **ΣC** is defined as the number of carbons in the side chains and is equal to $2(x + y + z)$ for series **Q(*x*,*y*)A(*z*)** and $4x + 16$ for series **Q(*x*,*x*)A (6,10)**; obviously, derivatives with the same **ΣC** value are isomers. Finally, we define $\Delta T_m$ and $\Delta T_c$ values as the difference between the melting and clearing temperatures of the lower symmetry molecule and those of its more symmetrical isomer

$$\Delta T_m = T_m(\text{unsym}) - T_m(\text{sym})$$

$$\Delta T_c = T_c(\text{unsym}) - T_c(\text{sym})$$

According to this convention, a negative $\Delta T$ value indicates that the less symmetrical isomer has a lower $T_c$ or $T_m$.

Before addressing the impact of symmetry across the entire series, it is useful to consider the effects within a family of isomers. For the series **ΣC** = 52, two high

**Table 1. Phase Behavior of Compounds in Series ΣC = 40 and ΣC = 44**

| compd | phase | $T_t$/C ($\Delta H$/J g$^{-1}$)<br>⇄ | phase | $T_t$/C ($\Delta H$/J g$^{-1}$)<br>⇄ | phase |
|---|---|---|---|---|---|
| **Q(6,6)A(8)** | Cr | 80.7 (56.2)<br>⇄<br>16.3 (−48.5) | Col$_h$ | 138.3 (4.6)<br>⇄<br>135.8 (−4.8) | I |
| **Q(6,8)A(6)** | Cr | 39.3 (22.0)<br>⇄<br>15.1 (−33.6) | Col$_h$ | 152.7 (4.3)<br>⇄<br>149.7 (−5.5) | I |
| **Q(6,6)A(6,10)** | Cr | 48.6 (38.3)<br>⇄<br>7.4 (−33.4) | Col$_h$ | 122.7 (3.2)<br>⇄<br>118.6 (−2.5) | I |
| **Q(8,8)A(6)** | Cr | 75.9 (74.0)<br>⇄<br>46.4 (−71.1) | Col$_h$ | 146.1 (3.4)<br>⇄<br>142.7 (−5.2) | I |
| **Q(6,8)A(8)** | Cr | 39.3 (22.0)<br>⇄<br>15.1 (−33.6) | Col$_h$ | 152.7 (4.3)<br>⇄<br>149.7 (−5.2) | I |
| **Q(6,6)A(10)** | Cr | 77.6 (51.0)<br>⇄<br>19.9 (−24.9) | Col$_r$ | 107.5 (2.3)<br>⇄<br>104.3 (−1.7) | I |
| **Q(6,10)A(6)** | Cr | 43.2 (42.3)<br>⇄<br>12.2 (−4.0) | Col$_h$ | 129.5 (3.5)<br>⇄<br>126.6 (−3.3) | I |

[a] Transition temperatures and enthalpies determined by DSC at a scan rate = 5 °C/min; Cr = crystal, Col$_h$ = columnar hexagonal, Col$_r$ = columnar rectangular, I = isotropic.

**Table 2. Phase Behavior of Compounds in Series ΣC = 48**

| compd | phase | $T_t$/C ($\Delta H$/J g$^{-1}$)<br>⇄ | phase | $T_t$/C ($\Delta H$/J g$^{-1}$)<br>⇄ | phase |
|---|---|---|---|---|---|
| **Q(8,8)A(8)** | Cr | 61.9 (38.7) Col$_x$ 64.0 (1.0)<br>⇄<br>30.8 (−40.9) | Col$_h$ | 141.3 (4.0)<br>⇄<br>138.6 (−4.3) | I |
| **Q(6,8)A(10)** | Cr | 39.9 (35.2)<br>⇄<br>15.2 (−3.3) | Col$_h$ | 119.7 (3.3)<br>⇄<br>117.1 (−3.3) | I |
| **Q(6,10)A(8)** | Cr | 43.4 (35.7)<br>⇄<br>15.8 (−3.7) | Col$_h$ | 128.3 (0.5)<br>⇄<br>126.0 (−1.9) | I |
| **A(8,10)A(6)** | Cr | 73.0 (60.6)<br>⇄<br>15.5 (−36.5) | Col$_h$ | 137.0 (2.2)<br>⇄<br>133.4 (−2.7) | I |
| **A(8,8)A(6,10)** | Cr | 47.5 (42.3)<br>⇄<br>6.8 (−26.2) | Col$_h$ | 137.3 (4.2)<br>⇄<br>131.1 (−3.6) | I |

[a] Transition temperatures and enthalpies determined by DSC at a scan rate = 5 °C/min. Cr = crystal, Col$_h$ = columnar hexagonal, I = isotropic.

**Table 3. Phase Behavior of Compounds in Series ΣC = 52 and ΣC = 56**

| compd | phase | $T_t$/C ($\Delta H$/J g$^{-1}$)<br>⇄ | phase | $T_t$/C ($\Delta H$/J g$^{-1}$)<br>⇄ | phase |
|---|---|---|---|---|---|
| **Q(8,8)A(10)** | Cr | 69.6 (67.8)<br>⇄<br>15.5 (−50.7) | Col$_h$ | 122.5 (0.9)<br>⇄<br>117.7 (−1.3) | I |
| **Q(8,10)A(8)** | Cr | 62.7 (52.0)<br>⇄<br>15.7 (−41.4) | Col$_h$ | 134.3 (1.7)<br>⇄<br>130.7 (−2.0) | I |
| **Q(10,10)A(6)** | Cr | 73.3 (72.1)<br>⇄<br>27.9 (−58.4) | Col$_h$ | 130.6 (3.4)<br>⇄<br>126.3 (−3.4) | I |
| **Q(6,10)A(10)** | Cr | 40.9 (37.5)<br>⇄<br>16.3 (−28.1) | Col$_h$ | 108.4 (1.61)<br>⇄<br>104.6 (−1.9) | I |
| **Q(10,10)A(8)** | Cr | 80.2 (70.0)<br>⇄<br>35.1 (−56.1) | Col$_h$ | 133.1 (4.7)<br>⇄<br>131.0 (−4.1) | I |
| **Q(8,10)A(10)** | Cr | 41.3 (36.7)<br>⇄<br>17.4 (−37.6) | Col$_h$ | 126.5 (4.24)<br>⇄<br>124.1 (−3.5) | I |
| **Q(10,10)A(6,10)** | Cr | 46.5 (26.0)<br>⇄<br>16.0 (−5.6) | Col$_h$ | 125.1 (3.2)<br>⇄<br>122.3 (−2.7) | I |

[a] Transition temperatures and enthalpies determined by DSC at a scan rate = 5 °C/min. Cr = crystal, Col$_h$ = columnar hexagonal, I = isotropic.

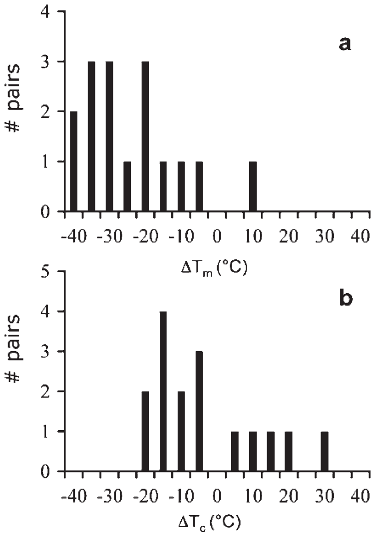


**Figure 2.** Histograms of (a) $\Delta T_m$ and (b) $\Delta T_c$ for **Q(*x*,*y*)A(*z*)** and **Q(*x*,*x*)A(*z*,*z*′)** Carnelley isomers (bin size = 5 °C).

symmetry analogs, **Q(8,8)A(10)** and **Q(10,10)A(6)**, and two lower symmetry isomers, **Q(8,10)A(8)** and **Q(6,10)A(10)**, were prepared. This afforded four pairs of Carnelley isomers: **Q(8,8)A(10)**/**Q(8,10)A(8)**, **Q(8,8)A(10)**/**Q(6,10)A(10)**, **Q(10,10)A(6)**/**Q(8,10)A(8)**, and **Q(10,10)A(6)**/**Q(6,10)A(10)**. In all four cases, the more symmetrical isomer has a melting temperature ($T_m$) that is 7−29 °C higher than its Carnelley isomer, which is in accordance with the hypothesis that Carnelley's rule applies to solid to liquid crystal transitions as well as the melting of a solid to an isotropic liquid. Quite different results were obtained for clearing temperature: in two cases of the four cases, the lower symmetry isomer has a higher clearing temperature ($T_c$), contrary to what we would expect if Carnelley's rule were also applicable to the transition from an ordered liquid to an isotropic phase.

Similar results were observed for the compounds across all series of dibenzoquinoxalines. These results are shown in the form of histograms in panels a and b in Figure 2, which plot the number of incidences of a given range of $\Delta T_m$ and $\Delta T_c$ values, respectively. A bin size of 5 °C was chosen for these histograms, so that the bin centered at $\Delta T = 0$ encompasses the range of values from −2.5 to + 2.5 °C. This bin size, while somewhat arbitrary, reflects our assumption that there is no appreciable difference between the transition temperatures of isomers for which $\Delta T = \pm 2.5$ °C. The histogram of $\Delta T_m$ shows the striking relationship between molecular symmetry and melting temperature, with a distribution strongly skewed toward negative $\Delta T_m$ values. Indeed, the less symmetrical Carnelley isomer has significantly higher melting point in only one case out of 16. The average value of $\Delta T_m$ is −23.8 °C, with an uncertainty of ±7.2 °C at a 95% confidence interval.

The single example of a positive $\Delta T_m$ value arises from the pair of isomers **Q(8,8)A(8)**/**Q(8,10)A(6)**; the lower symmetry isomer **Q(8,10)A(6)** melts at 73 °C, versus a melting temperature of 62 °C for **Q(8,8)A(8)**. These compounds are members of the series $\mathbf{\Sigma C} = 48$, which also includes three other low symmetry ($\sigma = 1$) isomers **Q(6,8)A(10)**, **Q(6,10)A(8)**, and **Q(8,8)A(6,10)**, all of which are Carnelley isomers of **Q(8,8)A(8)** and have melting points that are significantly lower than this more symmetrical isomer. All four lower symmetry isomers of **Q(8,8)A(8)** undergo liquid crystal-isotropic transitions at lower temperatures than this compound, giving rise to negative $\Delta T_c$ values.

The higher melting temperature of **Q(8,10)A(6)** relative to that of **Q(8,8)A(8)** may result from an anomalously low transition for **Q(8,8)A(8)**, an abnormally elevated one for **Q(8,10)A(6)**, or a combination of both of these effects. **Q(8,8)A(8)** melts an average of 14.6 °C ($\Delta T_m = -14.6$ °C) higher than its other three Carnelley isomers, which represents a significant elevation, albeit smaller than the average $\Delta T_m$ (−23.8 °C). On the other hand, **Q(8,10)A(6)** has a much higher melting temperature than the three isomers that it is isosymmetric with, suggesting that it possesses an unusually stable crystalline phase. It remains unclear what structural features lead to this anomalous behavior.

The histogram for $\Delta T_c$ (Figure 2b) illustrates that clearing temperatures also generally obey Carnelley's rule, although the correlation is poorer, with only 11/16 pairs having negative $\Delta T_c$ values and an average $\Delta T_c$ of $-3.2 \pm 8.3$ °C. Although there is a preponderance of cases where the more symmetrical isomer has the higher clearing point, the magnitude of $\Delta T_c$ tends to be smaller than $\Delta T_m$. Indeed, the largest depression in clearing temperature associated with symmetry breaking was 22.3 °C, which was smaller than the average lowering in the melting point (23.8 °C). Moreover, the more symmetrical isomer **Q(6,6)A(10)** was found to have a clearing temperature that was 22 and 30.5 °C lower than its two Carnelley isomers **Q(6,10)A(6)** and **Q(6,8)A(8)**, respectively. Compound **Q(6,6)A(10)** is unique in this series in that it forms a columnar rectangular ($\mathrm{Col_r}$) phase rather than a $\mathrm{Col_h}$ mesophase. The number of molecules per unit cell ($Z$) was calculated to be 2.3 based on the observed cell parameters $a = 51.9$ Å, $b = 20.2$ Å, and $c = 3.5$ Å and assuming a density of 1 g/cm$^3$. The observed reflections obey the condition $h + k = 2n$, consistent with a phase of $C2/m$ symmetry having 2 molecules per unit cell. The reflection observed at 3.5 Å suggests that the molecules are not appreciably tilted with respect to the columnar axis. Unlike truly disc-shaped molecules, which must tilt in order to pack into a rectangular array, **Q(6,6)A(10)** has an elliptical shape, and hence can pack in this manner without tilting. The clearing temperature of this compound is also almost 40 °C lower than that of its isosymmetric isomer **Q(8,8)(A6)**, which may reflect the poorer packing of elliptical molecules versus that of disc shaped mesogens.[17]

Although the clearing temperatures and melting points of discotic mesogens both appear to depend on molecular symmetry, there is no apparent correlation between the magnitude of $\Delta T_c$ and $\Delta T_m$ for a given pair of Carnelley isomers (Figure 3). The clearing temperature largely reflects the stability of the columnar phase, whereas the melting temperature is determined by the complex interplay of factors that stabilize the columnar and crystalline solid phases. Stabilization of the solid by higher molecular symmetry should raise the melting temperature, but stabilization of the columnar phase tends to counter this effect and lower the transition temperature (vide infra). Because of these competing effects, it is perhaps not surprising that there is no straightforward relationship between $\Delta T_c$ and $\Delta T_m$.

Symmetry effects also appear to be important in the case of the dibenzoquinoxaline Carnelley isomers, **Q(8,8)CN** and **Q(6,10)CN**, previously prepared in our laboratory.[13] The more symmetrical derivative **Q(8,8)CN** melts at 86 °C, versus 38 °C for **Q(6,10)CN**. A similar depression in the clearing temperature accompanies symmetry breaking, which occur at 252 and 216 °C for **Q(8,8)CN** and **Q(6,10)CN**, respectively (see Chart 2).

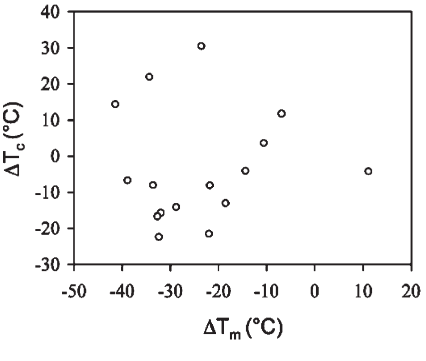
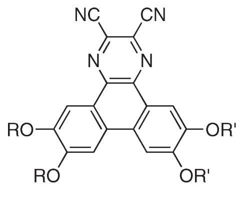


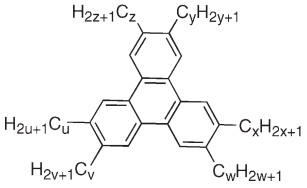
**Figure 3.** Plot of $\Delta T_m$ versus $\Delta T_c$ for the series **Q(*x*,*y*)A(*z*)** and **Q(*x*,*x*)A(*z*,*z*′)**.

**Chart 2**



**Q(8,8)CN** $R=R'=C_8H_{17}$
**Q(6,10)CN** $R=C_6H_{13}$, $R'=C_{10}H_{21}$

**Chart 3**



These observations prompted us to examine whether Carnelley's rule also applies to the phase transitions of other discotic mesogens. As already noted, we are aware of no previous attempts to examine Carnelley's rule in the context of liquid crystals. Nonetheless, a large number of triphenylene mesogens of varying symmetry have been reported in the literature over the past three decades, and this body of literature includes many pairs of Carnelley isomers. The phase behaviors of these compounds are listed in Table S3 of the Supporting Information. Separate entries are listed for derivatives that have been prepared by multiple groups with slight differences in the reported transition temperatures. These variations are generally small (< 3−4 °C), and do not affect the qualitative trends discussed below. However, in an attempt to minimize systematic errors that inevitably arise from data obtained from different research groups and different instruments, whenever possible we have compared the phase behavior of isomeric pairs using data obtained from the same publication. When this was not possible, we employed the average values of the phase transitions reported in the literature (see Chart 3).

We limit our current discussion to derivatives with linear alkyl chains; even with this restriction, our sample comprises 51 compounds and 47 pairs of Carnelley isomers. Unlike the dibenzophenazines, the triphenylene derivatives include both mesogenic and nonmesogenic compounds. This gives rise to four different types of comparisons between Carnelley isomers: (a) both isomers exhibit liquid crystalline phases, (b) both isomers are nonmesogenic, (c) the higher symmetry isomer forms an LC phase whereas the lower symmetry isomer does not, or (d) the higher symmetry isomer does not exhibit liquid crystallinity but the lower symmetry isomer is mesogenic. Although (a) is the primary focus of the present work, we will also examine the other three cases in detail, treating both the aggregate data as well as the individual scenarios listed above.

There are 22 pairs of Carnelley isomers for which both triphenylenes form liquid crystalline phases. The histograms for $\Delta T_c$ and $\Delta T_m$ for these pairs are shown in Figures 4 and 5a, respectively. As was the case for the dibenzophenazine derivatives **Q(*x*,*y*)A(*z*)** discussed above, $\Delta T_m$ and $\Delta T_c$ are heavily skewed toward negatives values. $\Delta T_m$ is significantly negative in sixteen of these cases, with an average of $-9.9 \pm 4.2$ °C. $\Delta T_c$ is negative for 18 of the pairs; the average value of $\Delta T_c$ was found to be $-14.9 \pm 6.4$ °C. These results are in qualitative agreement with those of the dibenzophenazines, with the important difference that, on average, molecular symmetry breaking in series **Q(*x*,*y*)A(*z*)** is accompanied by a larger depression of the melting point than the clearing point, whereas the reverse situation is observed for the triphenylenes, which tend to have their clearing temperatures lowered more than their melting temperatures.

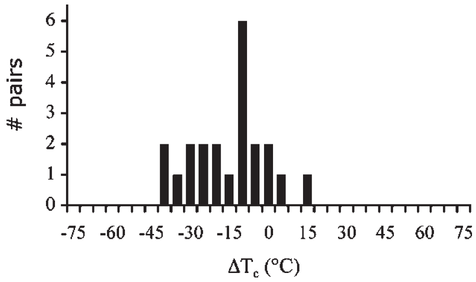


**Figure 4.** Histogram of $\Delta T_c$ for mesogenic triphenylene Carnelley isomers (bin size = 5 °C).

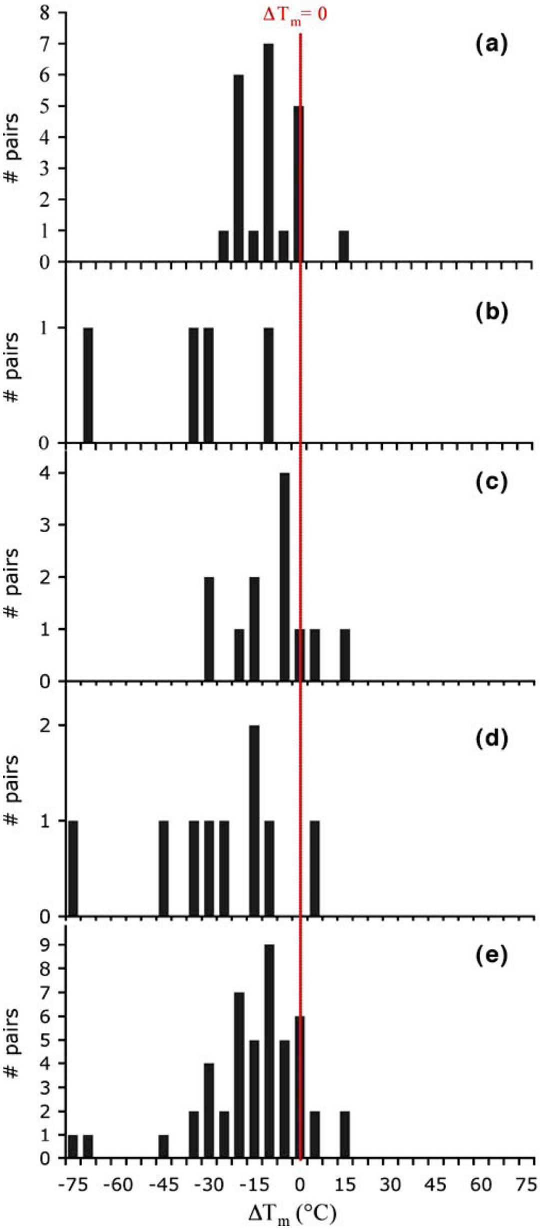


**Figure 5.** $\Delta T_m$ histograms for triphenylenes (bin size = 5 °C): (a) both isomers form a $Col_h$ phase (b) both are nonmesogenic, (c) the higher symmetry isomer has a $Col_h$ phase, the lower symmetry isomer is nonmesogenic, and (d) the higher symmetry isomer is nonmesogenic and the lower symmetry isomer forms a $Col_h$ phase. (e) Cumulative histogram for data in a−d.

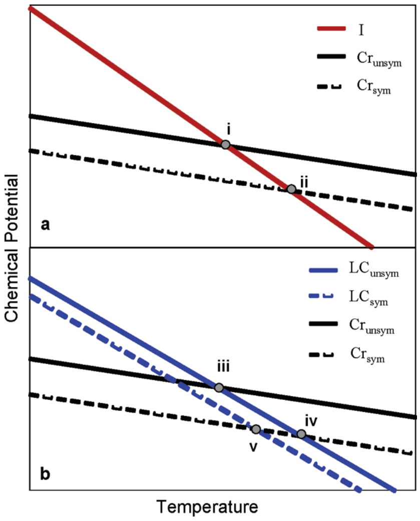


**Figure 6.** Chemical potential diagrams for the melting of (a) symmetrical ($Cr_{sym}$) and unsymmetrical ($Cr_{unsym}$) crystalline solids to an isotropic liquid, and (b) symmetrical and unsymmetrical crystalline solids to corresponding liquid crystalline phases ($LC_{unsym}$, $LC_{sym}$).

Figure 5b shows the $\Delta T_m$ histogram for the four pairs of triphenylene isomers that melt directly from crystalline solids to isotropic liquids, which corresponds to the situation for which Carnelley's rule was originally formulated. Perhaps not surprisingly, $\Delta T_m$ is negative in all cases. Although it is difficult to make generalizations from this small sample set, it is worth noting that the values of $\Delta T_m$ are generally more negative than those in Figure 5a. It therefore appears that molecular symmetry has a larger effect on the melting of a solid to an isotropic liquid than on the melting of a solid to a liquid crystal phase. This can be rationalized based on a consideration of the chemical potential of these different phases, represented schematically in Figure 6. Figure 6a shows the effect of increasing molecular symmetry on the melting of a solid directly to an isotropic liquid. Because increasing the symmetry stabilizes the crystalline solid but presumably has little effect on the isotropic liquid,$^{22}$ the intersection of the solid and isotropic curves occurs at a higher temperature (point ii) when the molecules are symmetrical than when the constituent molecules are less symmetrical (i). If the liquid crystalline phases were insensitive to symmetry effects, a disparity of similar magnitude would exist between the melting of the unsymmetrical mesogen (iii) and that of the symmetrical isomer (iv). However, the observation that clearing temperatures correlate to molecular symmetry indicates that the stability of the columnar phase is also dependent on molecular symmetry. Thus, although increasing molecular symmetry stabilizes the crystalline solid, which tends to raise the melting point, the stabilization of the liquid crystal tends to lower the melting point, resulting in a transition at point (v) instead of at (iv). Overall, the effect is a smaller difference between the melting temperatures of the symmetrical and unsymmetrical isomer ((v) versus (iii)) than for isomeric pairs that melt directly to isotropic liquids.

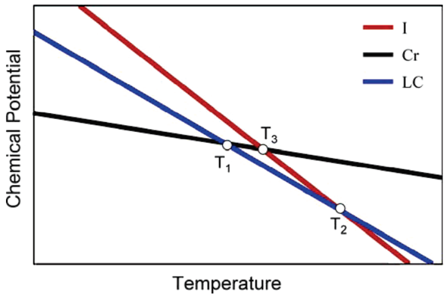


**Figure 7.** Schematic representation of the chemical potential for the transitions of a crystalline solid (black line) to a liquid crystalline phase (blue line) and isotropic liquid (red line). The melting of a solid to its liquid crystal phase occurs at $T_1$; this phase then clears at $T_2$. In the absence of a stable mesophase, melting of the solid to an isotropic phase is expected to occur at $T_3$.

The above argument suggests that the magnitude of the symmetry effect is dependent upon the nature of the melting transition under consideration. This can also be seen in the comparison of two isomers, one of which melts to a liquid crystal, the other to an isotropic phase. Figure 5d shows the histogram of $\Delta T_m$ for the Carnelley isomers in which the higher symmetry isomer melts directly to a solid, whereas the lower symmetry isomer exhibits a liquid crystalline phase. The reverse case, where the lower symmetry isomer melts to an isotropic liquid while the more symmetrical isomer is mesogenic, is shown in Figure 5c. It is apparent from comparing these two histograms with each other that the values in Figure 5d are, on average, much more negative than those in 5c. Indeed, in all but one of the nine examples where a more symmetrical molecule melts directly to an isotropic liquid while its Carnelley isomer melts to a liquid crystal phase, the melting temperature of the symmetrical isomer is significantly higher, with values of $\Delta T_m$ as large as $-77$ °C and an average value of $-27.7 \pm 17.9$ °C. In contrast, when the higher symmetry molecule melts to a liquid crystal but its isomer lacks a mesophase, $\Delta T_m$ is negative in 10 of 12 cases, with an average value of $-8.6 \pm 8.5$ °C; one of these exceptions to Carnelley's rule represents the most positive value of $\Delta T_m$ observed ($+17$ °C).

We can account for the differences between histograms c and d in Figure 5 by reference to a chemical potential diagram (Figure 7) for a hypothetical substance that melts to a liquid crystalline phase at temperature $T_1$, the point at which the curve for the solid phase (Cr) intersects that of the liquid crystalline phase (LC). This substance then undergoes a clearing transition at $T_2$, where the LC and isotropic (I) curves intersect. If for some reason this compound lacked a stable mesophase, it would instead melt at temperature, $T_3$, where the Cr and I curves cross; note that temperature $T_3$ is necessarily somewhat higher than $T_1$. This leads to the prediction that, all else being equal, a compound with a mesophase will melt at a lower temperature than an isomer that is nonmesogenic. A comparison of triphenylene isomers that have the same symmetry bears out this prediction: in most cases, the melting points of mesogenic derivatives tend to occur at lower temperatures than those of their nonmesogenic

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(22) The assumption that isotropic liquids are largely insensitive to molecular symmetry is borne out by the observation that boiling temperatures do not correlate with $\sigma$. See ref 7.

isomers. This effect should be additive with that of symmetry, so that a symmetrical molecule that lacks a mesophase will have its melting temperature elevated relative to that of its low symmetry mesogenic isomer by both of these effects, leading to more negative $\Delta T_m$ values (Figure 5d). On the other hand, when only the high symmetry isomer exhibits a columnar phase, these two effects work counter to each other, with high symmetry promoting a higher melting point while the formation of a mesophase encourages a lower transition temperature. This will result in more positive $\Delta T_m$ values (Figure 5c). Significantly, even when the nature of the transition works in opposition to symmetry, symmetry effects appear to dominate, because a majority of $\Delta T_m$ values in Figure 5c are negative. Notably, the average $\Delta T_m$ for pairs of isomers that both melt to a $Col_h$ phase was intermediate between these two cases, as one would predict.

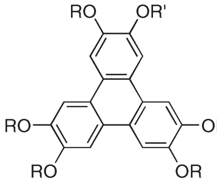
Our results, taken in conjunction with literature values for triphenylene derivatives and the pair **Q(8,8)CN**/**Q(6,10)CN**, are strongly suggestive of a strong relationship between molecular symmetry and both clearing and melting transitions. Of the 39 pairs of Carnelley isomers discussed above for which both isomers exhibit a columnar phase, the more symmetrical isomer melts at a significantly elevated temperature in 32 cases, with a smaller elevation (1−2 °C) in three further instances. The correspondence is slightly weaker for clearing temperatures, with 30/39 pairs exhibiting negative $\Delta T_c$ values.

This conclusion is to some extent at odds with those of Allen et al., who noted no correlation between molecular symmetry and transition temperatures within a small series of triphenylene derivatives **T(*n*,*m*)sym** and **T(*n*,*m*)asym**, which were prepared in order to assess the effects of alkyl chain interdigitation.[12] They found that the melting point of the **T(*n*,*m*)asym** derivative was significantly lower than that of its higher symmetry isomer in only one of four cases, whereas two pairs of isomers had similar melting points, and in one case the **T(*n*,*m*)asym** isomer melted at an appreciably higher temperature than **T(*n*,*m*)sym**. Similar behavior was observed for the clearing temperatures of these compounds. However, in all cases, the clearing and melting temperatures of both the **T(*n*,*m*)sym** and **T(*n*,*m*)asym** derivatives were uniformly lower than those of the corresponding (more symmetrical) **HAT*n*** isomer. **T(*n*,*m*)asym** derivatives were not included in the analysis shown in Figures 4 and 5, as quantitative data was not provided for these compounds in the original publication. The inclusion of these eight additional pairs of Carnelley isomers would not have appreciably altered the conclusions reached above (see Chart 4).

We have thus far considered only pairs of isomers in which differences in symmetry arise from the relative lengths of the appended linear alkoxy chains. These systems provide the opportunity to alter the molecular symmetry without inducing large perturbations in the electronic structure of the mesogenic core. Derivatives with branched chains, other types of flexible chains, or specific functional groups were excluded from our initial analysis in order to minimize competing factors that might obscure the effects of symmetry. However, a notable feature of Carnelley's rule is that it is applicable even to molecules that are electronically dissimilar.[3] It therefore is of interest, having established the validity of Carnelley's rule to LC transitions for the "simple" series described above, to determine whether more dramatic perturbations in molecular structure would counterbalance the effects of symmetry.

Recently, Hird and coworkers reported the liquid crystalline properties of a series of triphenylene derivatives of varying symmetry bearing both branched (**1**−**7**) and linear (**HAT5**, **HAT6**) chains; the transition temperatures of these compounds are listed in Table 4. A comparison of these compounds with one another and to other known triphenylene isomers (see the Supporting Infor-

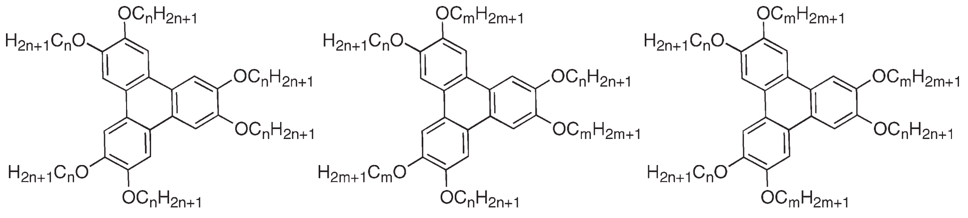
**Table 4. Phase Transitions of Triphenylene Derivatives with Branched and Linear Chains**



| | R | R′ | ΣC | $\sigma$ | $T_m$ (°C) | $T_c$ (°C) |
|---|---|---|---|---|---|---|
| **HAT5** | $-(CH_2)_4CH_3$ | $-(CH_2)_4CH_3$ | 30 | 6 | 69[a] | 122 |
| **1** | $(CH_2)_2CH(CH_3)_2$ | $(CH_2)_2CH(CH_3)_2$ | 30 | 6 | 130.3[b] | N/A |
| **2** | $-(CH_2)_5CH_3$ | $-(CH_2)_2CH_3$ | 33 | 1 | 60.6[a] | 84.8 |
| **3** | $-(CH_2)_5CH_3$ | $-CH(CH_3)_2$ | 33 | 1 | 54.6[b] | NA |
| **HAT6** | $-(CH_2)_5CH_3$ | $-(CH_2)_5CH_3$ | 36 | 6 | 67.6[a] | 100.1 |
| **4** | $-(CH_2)_3CH(CH_3)_2$ | $-(CH_2)_3CH(CH_3)_2$ | 36 | 6 | 91.8[a] | 122.1 |
| **5** | $-CH_2CH(CH_2CH_3)_2$ | $-CH_2CH(CH_2CH_3)_2$ | 36 | 6 | 29.5[a] | 120.0 |
| **6** | $-(CH_2)_5CH_3$ | $-(CH_2)_3CH(CH_3)_2$ | 36 | 1 | 61.5[a] | 105.0 |
| **7** | $-(CH_2)_5CH_3$ | $-CH_2CH(CH_2CH_3)_2$ | 36 | 1 | 44.4[a] | 78.1 |

[a] Cr−$Col_h$ transition. [b] Cr−I transition. All values taken from ref 14.

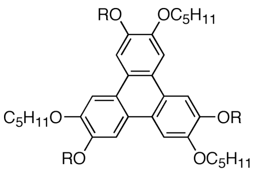
**Chart 4**



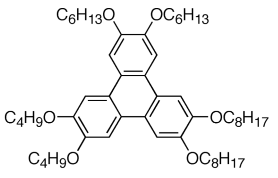
**HATn**
**n=4,5,6,8**

**T(n,m)sym**
**n=3, m=5**
**n=4, m=6**
**n=5, m=7**
**n=5, m=9**

**T(n,m)asym**
**n=3, m=5**
**n=4, m=6**
**n=5, m=7**
**n=5, m=9**



**8** R=$C_6H_{13}$ Cr 48°C $Col_h$ 106°C I
**9** R=$C_7H_{15}$ Cr 58°C $Col_h$ 91°C I



**10** R=$C_6H_{13}$ Cr 48°C $Col_h$ 72°C I

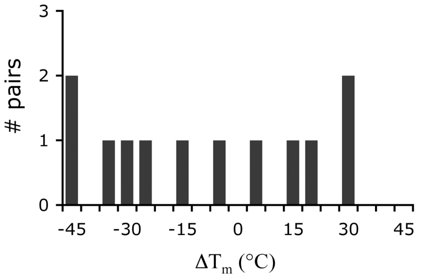


**Figure 8.** Histogram of $\Delta T_m$ for mesogenic triphenylene Carnelley isomers, $\Sigma C = 36$, in which one or both of the isomers possesses branched alkyl chains (bin size = 5 °C).

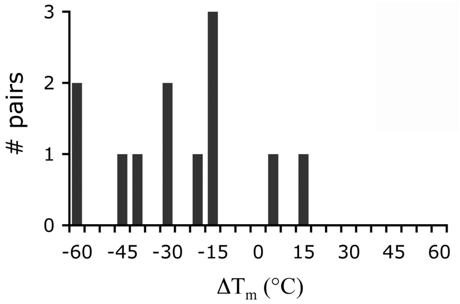
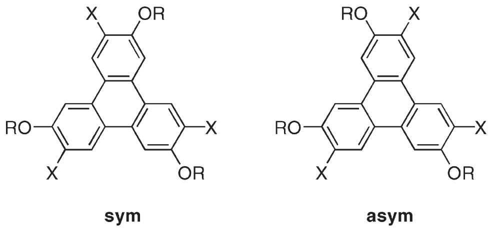


**Figure 9.** Histogram of $\Delta T_c$ for mesogenic triphenylene Carnelley isomers, $\Sigma C = 36$, in which one or both of the isomers possesses branched alkyl chains (bin size = 5 °C).

mation, Table S3), indicates that there is a weak correspondence between $\sigma$ and melting temperature. The largest number of comparisons arise from the series $\Sigma C = 36$, which includes 12 pairs of Carnelley isomers in which one or both of the molecules possesses at least one branched side chain. The results of $\Delta T_m$ and $\Delta T_c$ for these compounds are shown in Figures 8 and 9, respectively. Only seven of twelve pairs have a negative $\Delta T_m$ values. Remarkably, the relationship is much stronger for $\Delta T_c$; here, all but two pairs of isomers have negative values. These trends suggest that branching contributes more than symmetry in determining the stability of a crystalline solid, whereas the reverse is true for liquid crystal phases. Likewise, **3** ($\sigma = 1$) melts at 54.6 °C, as compared to $T_m = 48$ °C for its isomer **8** ($\sigma = 6$). The lower melting point of **8** may be partly explained by the fact that it undergoes a Cr-$Col_h$ transition, whereas **3** melts directly an isotropic liquid. Even in cases where Carnelley's rule is obeyed, branching appears to play a large role. Although the branched chain derivative **1** has a much higher melting temperature than its less symmetrical isomers, this transition is also more than 60 °C higher than that of **HAT5**, which is isosymmetric; indeed, the disparity between these two isomers' melting points is much larger than the differences between the melting point of **HAT5** and any of its lower symmetry isomers.

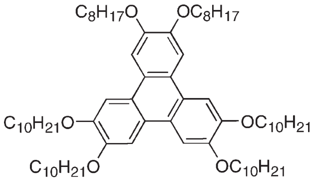
**Table 5. Phase Behavior of Functionalized Triphenylene Derivatives**



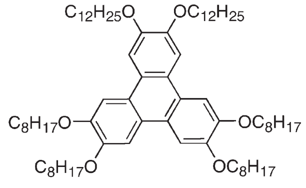
| entry | R | X | $T_m$ (°C) sym | $T_m$ (°C) asym | $T_c$ (°C) sym | $T_c$ (°C) asym | ref |
|---|---|---|---|---|---|---|---|
| **11** | $C_5H_{11}$ | Br | 187 | 104 | 216 | 195 | 23 |
| **12** | $C_5H_{11}$ | $CCSi(CH_3)_3$ | 213 | 117 | 236 | 217 | 23 |
| **13** | $C_5H_{11}$ | $OCOC_3H_7$ | 132.7 | 61.7 | 253.9 | 230.2 | 24 |
| **14** | $C_5H_{11}$ | $OCOC_4H_9$ | 130.6 | 82.5 | 244.6 | 227.6 | 24 |
| **15** | $C_5H_{11}$ | $OCOC_5H_{11}$ | 109.9 | 69.2 | 218.4 | 203.3 | 24 |
| **16** | $C_5H_{11}$ | $OCOC_7H_{15}$ | 61.8 | 61.9 | 168.3 | 155.3 | 24 |
| **17** | $C_5H_{11}$ | $OCOC_8H_{17}$ | 31.5[a] | 56.5 | N/A | 126.7 | 24 |
| **18** | $C_5H_{11}$ | $OCOCH_3$ | 185[a] | 146.5[a] | N/A | N/A | 24 |
| **F4H4** | $C_4H_{11}$ | $O(CH_2)_3CF_3$ | 118 | 139 | 181 | 180 | 25 |
| **F6H6** | $C_6H_{13}$ | $O(CH_2)_3(CF_2)_2CF_3$ | 74 | 88 | 180 | 178 | 25 |
| **F7H7** | $C_7H_{15}$ | $O(CH_2)_3(CF_2)_3CF_3$ | 57 | 67 | 184 | 181 | 25 |
| **F9H9** | $C_9H_{19}$ | $O(CH_2)_3(CF_2)_5CF_3$ | 51 | 51 | 184 | 182 | 25 |

[a] Cr−I transition.

Symmetry breaking may also result from the placement of functional groups at different positions around the periphery of the aromatic core; several examples of Carnelley isomers that arise in this manner are listed in Table 5. The isomeric triphenylene pairs in entries **11−16** largely follow Carnelley's rule, with the solid to liquid crystalline transition of the more symmetrical compound being significantly elevated in the first five cases. Indeed, the pairs **11−15** exhibit some of the most negative $\Delta T_m$ values reported, ranging from −40 °C to −96 °C. In contrast, the isomers listed in entry **16** melt at almost identical temperatures. The clearing temperatures of **11−16** also correlate strongly with molecular symmetry; in every case, the more symmetrical isomer exhibits a higher clearing temperature. The acetate derivatives **18sym** and **18asym** both melt directly to isotropic liquids, adhering to Carnelley's rule with $\Delta T_m = -38.5$ °C. An exception to the rule is observed with **17sym**, which melts to an isotropic liquid at 36 °C, whereas its lower symmetry isomer melts to a columnar phase at 56 °C, which then clears at 126.7 °C.



**22**



**23**

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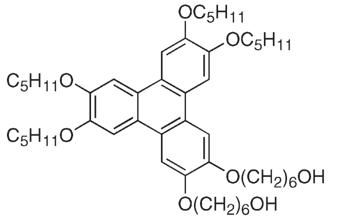
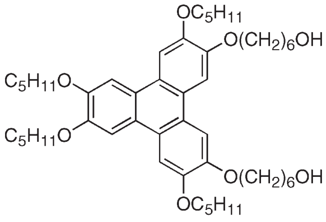
(23) Rego, J. A.; Kumar, S.; Dmochowski, I. J.; Ringsdorf, H. *Chem. Commun.* **1996**, 1031–32.
(24) Manickam, M.; Kumar, S. *Mol. Cryst. Liq. Cryst.* **1999**, *326*, 165–76.
(25) Terasawa, N.; Monobe, H. *Liq. Cryst.* **2007**, *34*, 447–55.

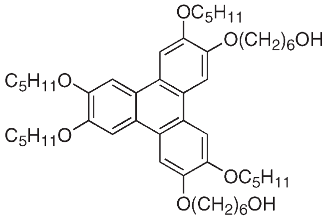
**Chart 5**



**19** ($\sigma$=2)



**20** ($\sigma$=2)



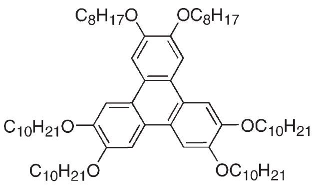
**21** ($\sigma$=1)

Henderson and coworkers reported a series of three triphenylene derivatives **19**−**21** (see Chart 5).[26] The two higher symmetry isomers, **19** and **20**, melt directly to isotropic liquids at 66 and 65 °C, respectively. The lower symmetry isomer, **21**, exhibits a columnar phase between 49 and 67 °C; this conforms to the trend represented in Figure 5d, in which the melting of an unsymmetrical mesogen to a liquid crystalline phase occurs at a lower temperature than a symmetrical isomer that melts to an isotropic liquid.

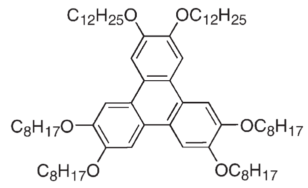
A striking example of the limitations of Carnelley's rule as it applies to discotic mesogens comes from a recent study on triphenylene derivatives bearing a mixture of fluorinated and nonfluorinated alkyl chains.[25] Tarasawa and Monobe reported the phase behavior of a series of symmetrical and unsymmetrical mesogens, **F(*n*)H(*n*)sym** and **F(*n*)H(*n*)asym** (Table 5). Remarkably, of the four pairs of Carnelley isomers included in that study, three had positive $\Delta T_m$ values, whereas the remaining pair melted at the same temperature. Breaking molecular symmetry had a negligible effect on the clearing transitions. It is not clear why Carnelley's rule breaks down so dramatically for this series of compounds, although this exceptional behavior may originate from more advantageous fluorophilic/fluorophobic interactions for the less symmetrical molecules in the solid state; it has been noted that exceptions to Carnelley's rule commonly arise because of specific functional group interactions.[3]

Finally, it must be emphasized that symmetry is clearly not the only factor that governs the phase transitions of the molecules discussed in this study. Although differences in the electronic structure of within a series of isomers in the family **Q(*x*,*y*)A(*z*)** and **Q(*x*,*x*)A(*z*,*z*′)** are likely negligible, appreciable changes in molecular shape do exist between pairs of isomers, which likely has a significant impact on their ability to pack in the solid and columnar phases. In practice, it is difficult to separate the effects of shape and symmetry, but it is possible to get a sense of the importance of shape changes by examining isomers that have the same symmetry. For example, we have already noted that the isomers **Q(8,8)A(6)** and **Q(6,6)A(10)** are isosymmetric ($\sigma$ = 2), yet display markedly different phase behavior; the former exhibits a Col$_h$ phase that clears at 146 °C, whereas the latter forms a Col$_r$ phase that clears at 107.5 °C. Although the melting points of these two compounds are approximately the same (76 and 78 °C, respectively), this similarity may obscure underlying differences between the solid phases of these two compounds. The melting temperature of a solid to a columnar phase will be determined by the relative stabilities of both phases, not just that of the solid. The lower stability of the columnar phase of **Q(6,6)A(10)** compared to that of **Q(8,8)A(6)**, which is evident from their markedly different clearing temperatures, is expected to raise the melting point of the former compound (vide supra). That these compounds have approximately the same melting temperature therefore may reflect a coincidental destabilization of **Q(6,6)A(10)**'s solid phase. This argument underscores the key point that melting point trends, which are far from straightforward even for solid to isotropic transitions, are even harder to predict for materials that possess a mesophase.

**Chart 6**



**22**



**23**

The impact of molecular shape can also be seen between other sets of same-symmetry isomers. Consider the four isomers **Q(8,8)A(6,10)**, **Q(6,10)A(8)**, **Q(6,8)A(10)**, and **Q (8,10)A(6)**, all of which have the same symmetry ($\sigma$ = 1). The clearing temperatures of these compounds exhibit considerable variation, ranging from 119 to 137 °C. Likewise, although the melting points of **Q(8,8)A(6,10)**, **Q(6,10)A(8)**, and **Q(6,8)A(10)** span a relatively narrow range (40−48 °C), **Q(8,10)A(6)** melts at 73 °C. Because these differences cannot be ascribed to changes in molecular symmetry, nor are they likely to arise from electronic differences between the mesogens, they must to due to the molecules' differing shapes. Such effects are also expected to be operative between Carnelley isomers.

Shape effects may also be partially responsible for the greater apparent sensitivity of the clearing temperatures of triphenylene derivatives to molecular symmetry. Because the triphenylene core is highly symmetrical, symmetry breaking tends to give rise to more anisotropic and less "disclike" structures, which may cause a further decrease in the clearing temperature. Such shape effects are evident, for example, in the case of the two isosymmetrical derivatives **22** and **23** (see Chart 6), which have clearing temperatures of 86 and 61 °C, respectively.[11d] As

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(26) Henderson, P.; Beyer, D.; Jonas, U.; Karthaus, O.; Ringsdorf, H.; Heiney, P. A.; Maliszewskyj, N. C.; Ghosh, S. S.; Mindyuk, O. Y.; Josefowicz, J. Y. *J. Am. Chem. Soc.* **1997**, *119*, 4740–8.

anticipated, the more anisotropic derivative **23** has the lower clearing temperature. In contrast, the dibenzophenazine core is inherently less symmetrical and more anisotropic, so lowering the overall symmetry can, in some cases, lead to a structure that is actually less elliptical. This may explain why the clearing temperature of **Q(6,6)A(8)** is considerably lower than that of its less symmetrical but more disc shaped Carnelley isomer **Q(6,8)A(6)**. Further investigations into the role of shape anisotropy are clearly warranted.

In conclusion, we have demonstrated that Carnelley's rule, which was originally formulated in the nineteenth century for the melting of solids to isotropic liquids, is also a useful generalization of the effects of molecular symmetry on the transitions of crystalline solids to columnar liquid crystalline phases and columnar-isotropic transition temperatures. The comparison of isomers, which is at the heart of Carnelley's rule, is a particularly useful way to broach the problem of molecular symmetry because it facilitates comparisons between molecules with similar electronic properties, thus minimizing effects arising from differences in electrostatic interactions and dispersion forces, which are known to stabilize columnar phases.[18] Although it is not possible at present to make a quantitative prediction of the effects of molecular symmetry in any particular instance, the observation that less symmetrical molecules undergo Cr–Col and Col–I transitions at lower temperatures does have important implications for the design of materials and may provide a means for controlling the phase ranges of discotic mesogens.

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**Supporting Information Available:** Experimental section including synthesis and characterization of all new compounds, XRD data for all mesogenic compounds, and tabulated data for literature triphenylene derivatives (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.