

Structural Factors Controlling the Self-Assembly of Columnar Liquid Crystals

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Abstract: A series of disc-shaped molecules were prepared by the condensation of 1,2-diamines with 2,3,6,7-tetrakis(hexyloxy)phenanthrene-9,10-dione to investigate the relationship between changes in molecular structure and the self-assembly of columnar liquid crystalline phases. A comparison of compounds with different core sizes indicated that molecules with larger aromatic cores had a greater propensity to form columnar phases, as did compounds substituted with electron-withdrawing groups. In contrast, molecules with electron-donating substituents were nonmesogenic. The clearing temperature of columnar phases increased linearly with the electron-withdrawing ability of the substituents, as quantified by Hammett σ -values. The observed trends can be rationalized in terms of the strength of π - π interactions between aromatic cores in the liquid crystalline phases and suggest that both electrostatic interactions and dispersion forces play important roles in the self-assembly of these materials.

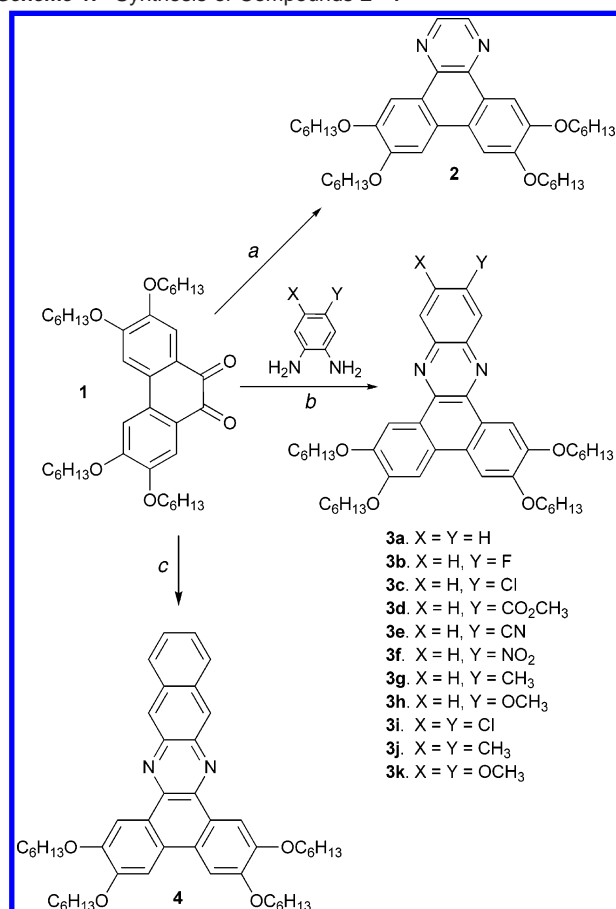
Introduction

Columnar liquid crystals have emerged as a promising class of materials for light-emitting diodes,¹ photovoltaic devices,² and field effect transistors.³ These liquid crystals exhibit a host of attractive properties, including high charge carrier mobilities,⁴ a lack of grain boundaries, and the potential to be uniformly aligned.^{3,5–10} In addition to their practical importance, the ability of disc-shaped molecules to spontaneously form columnar

nanostructures represents a striking example of self-assembly driven largely by π - π interactions. Any factor that alters the strength of π -stacking between neighboring molecules should therefore have a dramatic impact on the propensity of these molecules to form columnar mesophases. Studying the relationship between a molecule's structure and its tendency to self-assemble into columns can therefore provide valuable insight into the nature and strength of noncovalent interactions between discotic mesogens, in addition to facilitating the design of new liquid crystalline materials.

Despite the large number of discotic mesogens that have been prepared in the thirty years since their discovery, only a few studies have attempted to relate phase behavior to factors such as core size^{11–14} or substituents effects.^{15–20} Most series of substituted discotic mesogens examined to date have been

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Scheme 1. Synthesis of Compounds 2–4^a

^a Reagents and conditions: (a) 1,2-ethylenediamine, AcOH; (b) AcOH; (c) 3,4-diaminonaphthalene, AcOH.

obtained by post-functionalization of an existing triphenylene core, an approach that tends to place a practical constraint on the number of compounds that can be easily prepared and that limits the scope of structure–property studies. In an attempt to address this problem, we have undertaken the study of disc-shaped molecules derived from the coupling of a series of 1,2-diamines with a versatile precursor molecule, 2,3,6,7-tetra(hexyloxy)phenanthrene-9,10-dione **1** (Scheme 1). The intrinsic modularity of our synthetic approach, taken together with the large number of ortho-diamines available as starting materials, greatly facilitates the preparation of a broad family of potential mesogens that should allow us to systematically

Table 1. Phase Behavior of **2**, **3a–k**, and **4**

	Phase	T_i^a (°C) ($\Delta H/J\text{ g}^{-1}$) ^a	Phase ^b
2	Cr	86.1 (1.3)	I
		65.0 (-0.9)	
3a	Cr	170.0 (101.8)	I
		140.1 (-108.2)	
3b	Cr	161.3 (90.7)	I
		118.3 (-83.9)	Col _h
3c	Cr	137.2 (64.7)	I
		79.8 (-56.16)	Col _h
3d ^c	Cr	111.3 (39.1)	I
		200.6 (4.7)	Col _h
3e	Cr	101.1 (14.5)	I
		59.8 (-13.7)	Col _h
3f	Cr	131.4 (66.5)	I
		101.59 (-53.3)	Col _h
3g	Cr	124.5 (43.2)	I
		92.1 (-40.1)	
3h	Cr	148.5 (38.8)	I
		110.1 (-40.9)	
3i	Cr	141.9 (67.4)	I
		92.9 (-68.3)	Col _h
3j	Cr	154.9 (91.6)	I
		126.5 (-95.0)	
3k	Cr ₁	135.8 (7.8)	Cr ₂
		170.5 (96.2)	I
4	Cr	122.5 (77.7)	I
		75.6 (-65.1)	Col _h
		171.5 (7.4)	I
		167.6 (-6.9)	

^a Transition temperatures and enthalpies were determined by DSC (scan rate = 10 °C/min.). ^b Cr = crystal, Col_h = columnar hexagonal, I = isotropic. ^c Ref 22b.

probe the effects of functional groups and core size on columnar self-assembly.

Results

2, **3a–k**, and **4** were prepared by the condensation of the appropriate 1,2-diamines with **1** in refluxing acetic acid. The diamines employed in this study were all either obtained commercially or prepared in one or two steps according to literature procedures. The phase behaviors of these condensation products were examined by polarized optical microscopy (POM), differential scanning calorimetry (DSC), and variable temperature X-ray diffraction (XRD) experiments, the results of which are summarized in Tables 1 and 2. **2**, **3a**, **3g**, **3h**, **3j**, and **3k** failed to exhibit any liquid crystalline phases but instead melted directly from crystalline solids to isotropic liquids. The fluorinated derivative **3b** is not liquid crystalline on heating but forms a monotropic liquid crystal phase upon cooling from the isotropic state. On the basis of the dendritic texture observed

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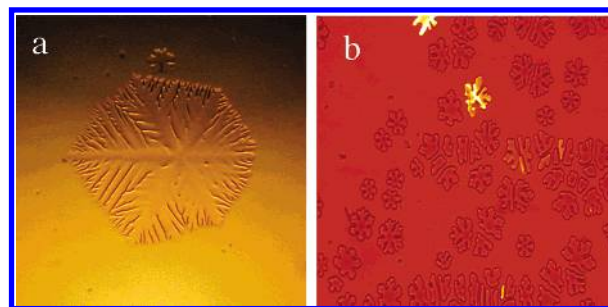
Table 2. X-ray Diffraction Data of Liquid Crystalline Compounds

	temperature (°C)	d-spacing (Å)	Miller index (hkl)	phase (lattice constant)
3c	170	16.3	(100)	Col _h (a = 18.8 Å)
		4.9	alkyl halo	
3d^a	150	3.5	π - π	Col _h (a = 20.0 Å)
		17.3	(100)	
		4.3	alkyl halo	
3e	150	3.5	π - π	Col _h (a = 19.0 Å)
		16.4	(100)	
		9.6	(110)	
		4.4	alkyl halo	
3f	150	3.5	π - π	Col _h (a = 19.2 Å)
		16.7	(100)	
		9.3	(110)	
		4.7	alkyl halo	
3i	170	3.5	π - π	Col _h (a = 19.6 Å)
		16.9	(100)	
		10.2	(110)	
4	130	4.5	alkyl halo	Col _h (a = 19.3 Å)
		3.5	π - π	
		16.7	(100)	

^a Ref 22b.**Figure 1.** Polarized optical photomicrograph of monotropic phase of **3b** at 158 °C (100× magnification).

by POM (Figure 1), this monotropic phase was identified as a hexagonal columnar phase (Col_h). Unfortunately, due to the thermal instability of this phase, we were unable to confirm its identity by XRD experiments.

Examination of the remaining compounds by DSC revealed that each undergoes two phase transitions upon heating, which were identified by polarized optical microscopy as solid-to-liquid crystal and liquid crystal-to-isotropic liquid transitions, respectively. Samples cooled slowly into their liquid crystalline phase from the isotropic state exhibited dendritic textures when viewed by polarized optical microscopy. Representative optical micrographs are shown in Figure 2. These textures are typical of columnar phases, and the observation of domains with approximately 6-fold symmetry suggests that these are Col_h phases. XRD experiments corroborate this assignment. Small-angle X-ray diffractograms of the liquid crystalline phases of **3e**, **3f**, and **3i** each exhibit one intense peak and a second, smaller peak that index to the (100) and (110) peaks of a hexagonal lattice. Each of the XRD patterns of the liquid crystalline phases of **3c**, **3d**, and **4** have only a single intense peak in the low-angle region, which was assigned to the (100) spacings of hexagonal

**Figure 2.** Polarized optical photomicrographs of (a) **3i** at 235 °C and (b) **4** at 167 °C (100× magnification).

lattices. Broad peaks were also observed for all molecules at larger angles that correspond to distances of approximately 4.5 and 3.5 Å, which were attributed to the alkyl chain halo and π - π stacking distances, respectively. The presence of a π - π peak in the XRD indicates that there is a degree of ordering within the columns.

Discussion

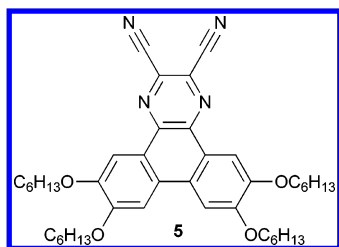
The trends in phase behavior, summarized in Table 1, demonstrate that even relatively small changes in the core structure can have a dramatic impact on the ability of the molecules to form liquid crystalline phases. Because the addition of one or more substituents is necessarily accompanied by an increase in the size of the molecule, we first wanted to address the effect of core size on mesophase behavior. **2**, **3a**, and **4**, which were prepared by the condensation of **1** with 1,2-ethylenediamine, 1,2-phenylenediamine, and 3,4-diaminonaphthalene, respectively, comprise a series in which the core size increases progressively from four to six rings. Although the two smaller members of this series, **2** and **3a**, are non-mesogenic, the naphthalene derivative **4** is liquid crystalline over a relatively large temperature range (122.5–171.5 °C). This implies that increased core size leads to a greater propensity to form columnar phases, which is consistent with earlier observations that discotic mesogens with large cores tend to be liquid crystalline over broad temperature ranges.^{11–14,16b,23}

The effect of core size on the mesogenic behavior can be understood in terms of the interactions between neighboring molecules within a columnar phase. Current models of π - π interactions indicate that electrostatic and dispersion forces are the most important contributors to the overall energy of most π -stacked structures.^{24–29} Because dispersion forces are favored

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by both increased surface areas and higher polarizabilities,³⁰ it is reasonable that larger molecules, such as **4**, show a greater tendency to π -stack and, hence, to assemble into columnar liquid crystalline phases.

Although **2** is nonmesogenic, its dicyano derivative, **5**, possesses a Col_h phase over an extremely broad temperature range (72–256 °C).²¹ The greater tendency of nitrile-substituted derivatives to form columnar phases has also been observed for a longer-chain analogue of **5**²⁰ and demonstrates the importance of functional groups to the self-assembly process. To carry out a more comprehensive investigation of substituent effects, we turned our attention to **3a–k**, which were prepared by the condensation of **1** with appropriately substituted 1,2-phenylenediamines.



Approximately half of the compounds in series **3** were found to assemble into ordered columnar hexagonal phases, whereas the remainder melted directly from crystalline solids into isotropic liquids. There is a striking correlation between the tendency of these molecules to form columnar phases and the electron-withdrawing or -donating ability of the functional groups attached to the core. Compounds with electron-withdrawing groups (–F, –Cl, –CO₂CH₃, –CN, and –NO₂) all formed Col_h phases, whereas those with relatively electron-donating groups (–H, –CH₃, and –OCH₃) were all found to be nonmesogenic. It is worth noting that compound **3b**, which bears only a weakly electron-withdrawing fluoro substituent, is unique in this series in that it forms only a metastable monotropic phase. Derivatives with more strongly electron-withdrawing groups than fluorine all exhibit thermodynamically stable enantiotropic columnar phases, whereas more electron-rich analogues failed to form mesophases.

It is perhaps also notable that the nitro-derivative **3f**, which is the most electron-deficient mesogen in this series, also has the highest clearing temperature. A quantitative treatment of the relationship between the substituent effects and phase stability can be obtained by comparing Hammett parameters,³¹ which provide a convenient measure of the withdrawing or donating ability of a functional group, with the clearing temperatures, T_c . A linear correlation was obtained when the T_c of the monosubstituted mesogens **3c–f** were plotted versus

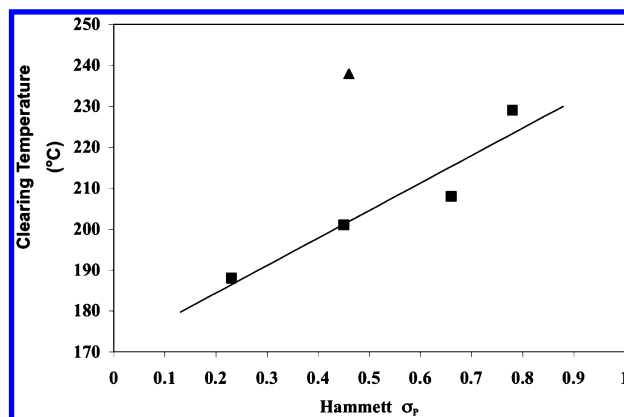


Figure 3. Plot of Hammett σ_p versus clearing temperature (T_c). Best-fit line derived from linear regression on monosubstituted derivatives **3c–f** (■) only; disubstituted compound **3i** (▲) was excluded from this analysis (see text).

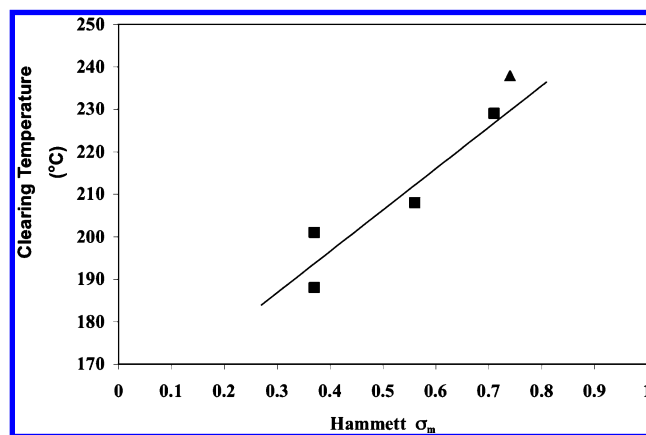


Figure 4. Plot of Hammett σ_m versus clearing temperature (T_c). Best-fit line derived from linear regression on monosubstituted derivatives **3c–f** (■) only; disubstituted compound **3i** (▲) was excluded from this analysis (see text).

either Hammett σ_p (Figure 3) or σ_m values (Figure 4), with R^2 values of 0.90 and 0.88, respectively. This observation provides quantitative evidence that the liquid crystalline ordering is related to the electron-withdrawing character of the substituents, because a higher clearing temperature corresponds to a more thermodynamically stable phase. A similar relationship has previously been reported for the columnar phases formed by tetrahedral metallomesogens,³² but to the best of our knowledge, no correlation of this type has previously been investigated for discotic mesogens.

As with the core-size effects described above, the correlation between clearing temperatures and Hammett parameters can be rationalized in terms of π – π interactions within the columnar phases. Cozzi and Siegel have shown that π -stacking is favored by the addition of electron-withdrawing groups, which help to minimize the repulsive interactions between adjacent aromatic π -systems.^{24,28} Several groups have shown that σ_p parameters correlate well with the strength of arene–arene interactions in the gas phase,²⁵ solution,²⁸ and calamitic liquid crystalline phases.²⁹ The observation of a similar linear relationship suggests that the same mechanism is responsible for stabilizing columnar phases. The relationship between σ_m values and π -stacking is less well-established,³³ although these parameters

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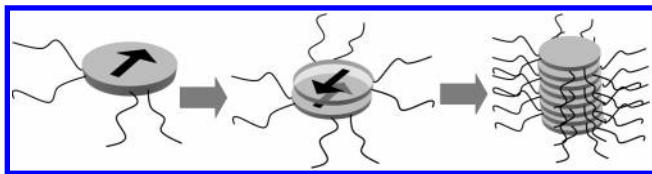


Figure 5. Schematic representation of antiferroelectric ordering in columnar phases. Adjacent molecules within a column adopt an antiparallel orientation. Arrows represent direction of molecular dipole.

do perform better than σ_p values in at least one theoretical study of π – π interactions²⁵ and have been found to correlate well with the strength of cation– π interactions.³⁴

Dipole–dipole interactions may also contribute to the preferential formation of columnar phases by molecules bearing electron-withdrawing groups. The intercolumnar distances obtained by XRD studies are consistent with molecules within the columns having antiferroelectric ordering; in other words, the adjacent mesogens will be approximately antiparallel with respect to one another (Figure 5). Such an arrangement would explain how these low-symmetry molecules are able to form fairly symmetrical columns, which can then pack into hexagonal arrays. The addition of electron-withdrawing groups should lead to an increase in the molecular dipole moment, which will favor the antiparallel orientation of adjacent molecules within the columns. Dipole–dipole interactions are also believed to play a significant role in the stabilization of mesophases formed by bent-rod³⁵ and calamitic mesogens³⁶ and have been suggested as an important stabilizing feature in other dipolar discotic mesogens.^{19,37}

No significant correlation was found between the group polarizabilities³⁹ and the clearing temperatures of the mesogenic compounds **3c–f**, suggesting that dispersion forces play only a secondary role in the observed trends. This conclusion is also supported by the failure of **3g–h** and **3j–k** to form columnar phases, despite the methyl and methoxy substituents having comparable polarizabilities to chloro or cyano groups, respectively. The absence of an observed relationship between group polarizabilities and the tendency to organize into columnar phases may be due to the large size of the aromatic cores under

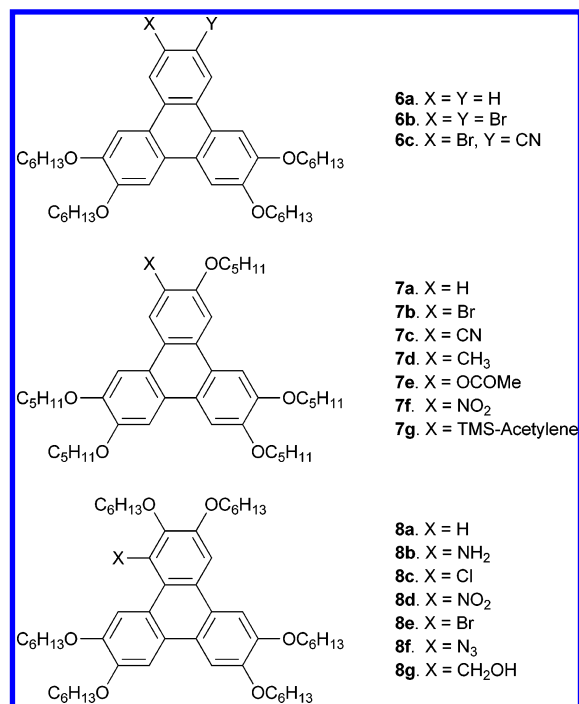
investigation. Because group polarizabilities are additive,³⁰ the relative contribution of the functional groups to the overall molecular polarizability will be much smaller in the present case than for simple benzene derivatives, for which there is a discernible correlation between arene–arene interactions and group polarizabilities.^{25,27} Any effects arising from the variation in dispersion forces across the series **3a–k** therefore may be masked by the competing electrostatic perturbations induced by the functional groups.

The dichlorinated derivative, **3i**, which was the only disubstituted mesogenic compound studied, was excluded from our initial analysis of clearing temperatures. Hammett parameters for this compound can be obtained by assuming that substituent effects are strictly additive and employing σ_p and σ_m values that are twice those used for the monochlorinated derivative **3c**. On the basis of these assigned values of $\sigma_p = 0.46$ and $\sigma_m = 0.74$ and extrapolating from the trends obtained for the monosubstituted series, the clearing temperature of **3i** is predicted to be either 202 (σ_p) or 230 °C (σ_m), as compared to the observed value of 237.5 °C. Likewise, when the data for **3i** is included with the monosubstituted derivatives **3c–f**, the correlation of clearing temperature with σ_p becomes dramatically worse ($R^2 = 0.34$) whereas the correlation with σ_m is slightly improved ($R^2 = 0.91$). This suggests that σ_m is a better descriptor of substituent effects in these systems than σ_p .

Although the least-squares fit is better for σ_m than σ_p , it is not clear a priori whether a better correlation should be obtained when a more symmetrical molecule such as **3i** is included alongside its lower symmetry analogues. Reducing the symmetry of a discotic mesogen has been shown to depress the clearing temperature,²¹ presumably because unsymmetrical molecules do not pack as well as symmetrical ones. We would therefore expect that the more symmetrical mesogen **3i** would have a higher clearing temperature than predicted based on the behavior of its lower-symmetry analogues. Such an effect could explain the discrepancy between the observed clearing temperature of **3i** and its σ_p value. This argument needs to be treated with some caution, because studies of symmetry effects on discotic mesogens have invariably focused on the effects of desymmetrizing the flexible side chains. Whether a similarly large symmetry effect would occur in the case of rigid groups attached to the core remains an unanswered question.

If the above discussion of symmetry effects correctly explains the apparent failure of σ_p values when **3i** is included in the series, then the accurate prediction of this compound's transition temperature by σ_m values may be merely coincidental. There are some reasons to distrust the reliability of σ_m values in the present context. The value of σ_m is 0.37 for fluorine, which is virtually identical to that of chlorine. On the basis of these values, compounds **3b** and **3c** are expected to have similar phase behavior, which they clearly do not. In contrast, a fluorine substituent is only mildly electron withdrawing according to the σ_p scale, which is consistent with **3b** forming only a monotropic phase with a relatively low clearing temperature. A similar argument can be made with respect to the methoxy-substituted derivatives **3h** and **3k**, because alkoxy groups are electron withdrawing according to σ_m scale but electron donating according to σ_p . The failure of these compounds to form columnar phases is, therefore, more consistent with σ_p than σ_m .

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- (38) Although it is in principle possible to calculate dipole moments using molecular modeling, it is difficult in practice to obtain meaningful values for these systems. Gas phase AM1 calculations indicate that these compounds possess several nearly isoenergetic conformational isomers associated with different orientations of the alkoxy chains. The magnitude and, in some cases, the sign of the molecular dipole moment depend strongly on the conformation of these chains and, in particular, on the orientation of the oxygen lone pair electrons. Because we lack a detailed knowledge of which of these conformers is favored in the liquid crystal phase, these calculations cannot be reliably applied to the quantitative determination of the dipole moment of the mesogens within the columns. We do note, however, that the observed trends in T_c do qualitatively parallel the experimentally determined dipole moments of the corresponding substituted benzene derivatives.
- (39) Group polarizabilities were estimated from the molecular polarizabilities of the corresponding monosubstituted benzene derivatives. See: David R. Lide, Ed. *CRC Handbook of Chemistry and Physics*; CRC: Boca Raton, FL, 2005; Chapter 10.



The observed relationship between the nature of the functional group and the mesophase stability in series **3** prompted us to reexamine the trends obtained by other researchers working with substituted discotic mesogens. Indeed, it has often been noted that electron-withdrawing groups often tend to promote the formation of columnar phases. For example, although the unsubstituted tetrakis(hexyloxy)triphenylene **6a** is nonmesogenic, its bromo and cyano derivatives **6b–c** both form columnar phases.¹⁶ Moreover, replacing a bromine atom with the more electron-withdrawing cyano group was found to cause an increase in the clearing temperature. Only limited conclusions can be made from such a small number of mesogenic compounds spanning a narrow range of Hammett parameters. A more comprehensive treatment is possible with the series **7a–g**.¹⁷ Again, the parent compound (**7a**) melts directly from the solid state to an isotropic liquid, whereas its substituted

derivatives tend to form columnar phases. In this case, we found a weaker correlation to Hammett σ_p and σ_m parameters ($R^2 = 0.82$ and 0.73 , respectively), although, perhaps significantly, the linear fit improves to $R^2 = 0.90$ (σ_p) and 0.89 (σ_m) when the highly polarizable TMS–acetylene derivative is excluded from this analysis. Several triphenylene derivatives substituted at the 1-position (**8a–g**)¹⁸ have also been reported. Although the clearing points in this series show a marked dependence on the nature of the functional group, a less than straightforward relationship exists between the electronic properties of these substituents and the liquid crystal-to-isotropic transition temperatures; nitro groups, however, were found to increase the clearing temperature. The lack of a clear correlation in this series is likely due to the additional complication introduced by steric effects, because the presence of functional groups at this hindered position causes large distortions of the core away from planarity.

In conclusion, we have examined a large number of disc-shaped molecules to elucidate how changes in the core structure alter the propensity of these compounds to self-assemble into columnar liquid crystalline phases. There is both a qualitative relationship between the functional groups and whether a columnar phase is observed as well as a quantitative correlation of clearing temperatures of the mesogenic compounds with the electron-withdrawing ability of the substituents. This trend can most likely be explained by the changes in electrostatic interactions between molecules within the columns, which favor stacking between electron-deficient aromatic rings.

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Supporting Information Available: Full synthetic and analytical details for all new compounds; XRD I(Q) curves for liquid crystalline phases. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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