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Molecular structure and the twist-bend nematic phase: the role of spacer length in liquid crystal dimers

Daniel A. Paterson, Rebecca Walker, John M. D. Storey and Corrie T. Imrie

Department of Chemistry, School of Natural and Computing Sciences, University of Aberdeen, Aberdeen, UK

ABSTRACT
The liquid crystal dimers, the 1-(4-substitutedazobenzene-4'-yloxy)-4-(4-cyanobiphenyl-4'-y)lbutanes (CB4AOB), are reported in which the terminal substituent is either a methyl, methoxy, butyl, butyloxy, cyano or nitro group. The butyloxy spacer endows these dimers with the required molecular curvature to exhibit the twist-bend nematic phase in addition to showing the conventional nematic phase. Their transitional properties are compared to those of the corresponding dimers with either a pentyloxy or hexyloxy spacer. As expected, the even-membered pentyloxy-based dimers show the highest nematic–isotropic transition temperature, \( T_{\text{NI}} \), and exhibit smectic behaviour. These observations are attributed to their linear molecular shapes. The values of both the twist-bend nematic–nematic transition temperature, \( T_{\text{N}_{\text{II}}N_{\text{I}}} \), and \( T_{\text{NI}} \) increase on passing from the butyloxy to hexyloxy spacer, but the change in \( T_{\text{NI}} \) is greater than that in \( T_{\text{N}_{\text{II}}N_{\text{I}}} \). Thus, the ratio \( T_{\text{N}_{\text{II}}N_{\text{I}}} / T_{\text{NI}} \) is greater for the shorter spacer reinforcing the view that molecular curvature drives the formation of the \( N_{\text{TB}} \) phase relative to the \( N \) phase. By comparison, the melting point decreases on passing from the butyloxy to hexyloxy spacer. Thus, increasing molecular curvature simultaneously increases both the melting point and \( N_{\text{TB}} \) phase stability and this highlights the design challenge in obtaining dimers that exhibit enantiotropic \( N_{\text{TB}}^{-1} \) transitions.

Introduction
The twist-bend nematic phase, \( N_{\text{TB}} \), is a fascinating liquid crystal phase in which achiral molecules spontaneously assemble into chiral arrangements and was the first example of spontaneous chiral symmetry breaking in a fluid with no spatial ordering [1–4]. The \( N_{\text{TB}} \) phase was predicted using symmetry arguments by Dozov [5] and at the root of this prediction is the assertion that bent molecules have a strong tendency to pack into bent structures. Pure uniform bend, however, cannot fill space and must be accompanied by other local deformations of the director and specifically, either twist or splay. In the case of twist, this gives rise to the \( N_{\text{TB}} \) phase in which the director forms a heliconical structure and is tilted with respect to the helical axis. The symmetry breaking is spontaneous such that left- and right-handed helices are degenerate and, hence, form in equal amounts. A key feature of the \( N_{\text{TB}} \) phase is a surprisingly short pitch length, typically corresponding to just a few molecular lengths. This degeneracy is removed by molecular chirality, and the chiral twist-bend nematic phase is observed [6,7]. The \( N_{\text{TB}} \) phase is normally formed on
cooling a conventional nematic phase and only rarely is a direct \(N_{TB}\)-isotropic phase transition observed \([8–13]\). The \(N_{TB}\) phase is not only of very significant fundamental interest but also has considerable application potential \([14–19]\). Dozov also predicted the existence of twist-bend smectic phases and these have recently been found experimentally \([20–24]\).

A great many molecules have now been reported to show the \(N_{TB}\) phase, and these include liquid crystal dimers (for recent examples, see references \([10,21,25–38]\)), higher oligomers \([27,39–47]\), rigid bent core mesogens \([48,49]\), hydrogen-bonded systems \([50–55]\) and polymers \([56]\). The common structural feature to each of these structures, and in complete accord with Dozov’s prediction \([5]\), is molecular curvature. The importance of this was further underlined by predictions made using a Maier-Saupe theory for V-shaped molecules that the \(N_{TB}\)-N transition temperature is particularly sensitive to the bend angle \([57]\). Thus, for bend angles between 130° and 150° an \(N_{TB}\)-N transition is observed, and for angles smaller than 130° the N phase disappears and a direct \(N_{TB}\)-I transition observed. For angles larger than 150°, the \(N_{TB}\)-N transition is predicted only to occur at very low temperatures.

In the vast majority of twist-bend nematogens, the required molecular curvature for the observation of the \(N_{TB}\) phase is realised using odd-membered liquid crystal dimers \([58–74]\). In a liquid crystal dimer, two mesogenic groups are linked through a flexible spacer, and if an odd number of atoms connects the two groups, then the molecule is, on average, bent \([75,76]\). The bend angle in such molecules depends on a number of factors including the nature of the links between the spacer and mesogenic units. The length of the spacer also governs the molecular curvature and as the spacer is increased in length, there is an increased number of conformations available to it and the liquid crystal field preferentially selects the more linear of these \([75]\). This is apparent in the dependence of the \(N-I\) transition temperature, \(T_{NI}\), on spacer length for a homologous series of liquid crystal dimers. For short chain lengths, a pronounced alternation in \(T_{NI}\) is observed in which even members exhibit the higher values, but this attenuates on increasing spacer length \([75]\). Whereas an odd member is bent, in an even-membered dimer the two mesogenic units are essentially parallel and the molecule is linear. The linear even-members are more compatible with the nematic environment, and hence higher values of \(T_{NI}\) are observed. As the spacer length is increased, the difference in average shape between odd and even members decreases and the values of \(T_{NI}\) become similar.

In designing twist-bend nematogens based on odd-membered liquid crystal dimers, it would appear, therefore, that a short spacer would be the preferred choice in order to obtain a more pronounced molecular curvature. In practice, however, this has not been the case, and the overwhelming majority of twist-bend nematogens have spacer lengths of seven, nine or eleven atoms, and it is much less common to find examples containing three or five atoms (see recent review \([73]\)). The reasons for this are straightforward. In any given homologous series of dimers in which the length of the spacer is varied, the short odd-members tend to have high melting points and low liquid crystal transition temperatures, typically showing monotropic phase behaviour \([77,78]\). On increasing the spacer length, the melting points of the odd members tend to fall and the liquid crystal transition temperatures increase sharply before passing through a maximum and tending towards a limiting value \([75,76]\).

In order to obtain a better understanding of the role of short odd-membered spacers in the formation of the \(N_{TB}\) phase, here we report a set of dimers based on an odd-membered spacer containing five atoms, namely a butyloxy spacer, the 1-(4-substitutedazobenzene-4’-yloxy)-4-(4-cyanobiphenyl-4’-yl)butanes, see Figure 1. We refer to these dimers using the acronym CB4OABX in which CB denotes cyanobiphenyl, 4O the butyloxy spacer, AB azobenzene and X the terminal group. In order to establish the role played by molecular curvature, we also report the properties of the corresponding linear even-membered CB5OABX dimers based on a pentyloxy spacer and compare their properties with those of the longer odd-membered CB6OABX dimers reported previously \([79,80]\).

The CB\(n\)OABX dimers \((n = 4,5,6)\) are prepared by the cyanation of the corresponding 1-(4-substitutedazobenzene-4’-yloxy)-\(\omega\)-(4-bromobiphenyl-4’-yl)alkanes, see Figure 2, and we also compare the transitional properties of these materials. By analogy, the acronym used to refer to these sets of dimers is Br\(\text{Br}n\)OABX in which BrB denotes bromobiphenyl.

![Figure 1. Molecular structure of the CB4OABX dimers.](image1)

![Figure 2. Molecular structure of the BrBrnOABX dimers.](image2)
**Experimental**

**Synthesis**

The synthetic route used to obtain the CBnOABX dimers is shown in Scheme 1 and is based upon that described for the preparation of the CB6OABX dimers [79]. We note, however, that we have recently reported a convenient, one-pot synthetic method to obtain the ω-bromo-1-((4-cyanobiphenyl-4′-yl)alkanes [81] that would significantly simplify the preparation of the CBnOABX dimers. The preparation of the 4-hydroxy-4′-substitutedazobenzenes has been described in detail elsewhere [82–85]. The synthesis and characterisation of the CB4OABX and CB5OABX dimers and their intermediates are fully described in the ESI.

**Thermal characterisation**

The thermal behaviour of the materials was studied using differential scanning calorimetry (DSC) using a Mettler Toledo DSC1 equipped with a TSO 801RO sample robot and calibrated using indium and zinc standards. Heating and cooling rates were 10°C min⁻¹, with a 3-minute isotherm between heating and cooling segments. Thermal data were extracted from the second heating trace unless otherwise stated. Samples were run in duplicate, and an average of the two measurements of temperature and change in entropy is reported. Phase characterisation was performed using polarised optical microscopy (POM), using either a Zeiss Axio Imager. A2m microscope equipped with a Linkam THMS600 heating stage or an Olympus BH2 polarising light microscope equipped with a Linkam TMS92 hot stage. Planar aligned cells with an ITO conducting layer and cell thickness of 2.9–3.5 μm were purchased from INSTEC.

**Molecular modelling**

The geometric parameters of the dimers studied were obtained using quantum mechanical DFT calculations with Gaussian 09 software [86]. Optimisation of the molecular structures was carried out at the B3LYP/6-31 G(d) level of theory. Visualisations of the space-filling models were produced post-optimisation using the QuteMol package [87].

**Results and discussion**

**CB4OABX dimers**

Table 1 lists the transitional properties of the CB4OABX dimers. All six CB4OABX dimers exhibit nematic behaviour and all, but X = CN and NO₂, also show the N₂₁₇

![Scheme 1. Synthesis of the CBnOABX dimers.](image)

<table>
<thead>
<tr>
<th>Dimer</th>
<th>T(°C)</th>
<th>T(X,°C)</th>
<th>T(N,°C)</th>
<th>T(N)/T(X)</th>
<th>ΔS_C1</th>
<th>ΔS_N/H,O</th>
<th>ΔS_H,O</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB4OABMe</td>
<td>151</td>
<td>77</td>
<td>123</td>
<td>0.88</td>
<td>10.87</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>CB4OABOMe</td>
<td>130</td>
<td>96</td>
<td>147</td>
<td>0.88</td>
<td>13.08</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>CB4OABBu</td>
<td>109</td>
<td>68</td>
<td>101</td>
<td>0.91</td>
<td>8.05</td>
<td>0.08</td>
<td>0.10</td>
</tr>
<tr>
<td>CB4OABOBu</td>
<td>142</td>
<td>98</td>
<td>136</td>
<td>0.91</td>
<td>17.25</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>CB4OABCN</td>
<td>169</td>
<td>–</td>
<td>171</td>
<td>–</td>
<td>13.95</td>
<td>–</td>
<td>0.36</td>
</tr>
<tr>
<td>CB4OABNO₂</td>
<td>145</td>
<td>–</td>
<td>132</td>
<td>–</td>
<td>10.66</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

*Denotes values taken on cooling DSC traces.

†Denotes values measured using POM.
phase. All nematic, N, phases were assigned on the basis of the observation of a schlieren texture containing both two and four brush point singularities and which flashed when subjected to mechanical stress, see Figure 3(a). The values of the scaled nematic–isotropic entropy change, $\Delta S_{NI}/R$, listed in Table 1 are consistent with this assignment [88]. The transition from the nematic to the twist-bend nematic, $N_{TB}$, phase was accompanied by the cessation of the flickering associated with director fluctuations and the formation of a somewhat ill-defined blocky schlieren texture, Figure 3(b,c). The monotropic nature of the $N_{TB}$ phases precluded their study using X-ray diffraction, and to confirm this assignment, a phase diagram was constructed using binary mixtures of CB4OABOMe and the standard twist-bend nematogen, CB7CB [1], see Figure 4. Complete miscibility was observed for the range of compositions studied, and all the mixtures exhibited two nematic phases, at higher temperatures the conventional N phase and at lower temperatures the $N_{TB}$ phase. These were identified on the basis of the observation of either a characteristic nematic schlieren texture or the blocky $N_{TB}$ schlieren texture, see Figure 5. The value of $T_{N_{TB}N}$ measured for CB4OABOMe fits perfectly the $N_{TB}$–N line in the phase diagram and confirms the $N_{TB}$ phase assignment.

Figure 3. (Colour online) (a) The schlieren texture of the N phase for a sample sandwiched between untreated glass slides, (b) the uniform nematic texture and (c) the blocky schlieren texture of the $N_{TB}$ phase seen for CB4OABOMe in a cell treated for planar alignment.

Figure 4. Phase diagram constructed for binary mixtures of CB4OABOMe and CB7CB. Triangles denote N–I transition temperatures and squares $N_{TB}$–N transition temperatures. Melting points have been omitted for the sake of clarity.
The transitional properties of the CB5OABX dimers are listed in Table 2. All six dimers are enantiotropic nematicogens, and the nematic phase was identified using polarised light microscopy as described earlier; a representative texture is shown as Figure 6(a). On cooling the nematic phase of CB5OABMe and CB5OABOBu, a focal conic fan texture developed, see Figure 6(b), indicating the formation of a smectic phase. The monotropic nature of these smectic phases and their tendency to crystallise precluded their study using X-ray diffraction.

Table 2. The transitional properties of the CB5OABX dimers.

<table>
<thead>
<tr>
<th>Dimer</th>
<th>T_Cr/°C</th>
<th>T_SmB/°C</th>
<th>T_NI/°C</th>
<th>ΔS_Cr/R</th>
<th>ΔS_SmB/R</th>
<th>ΔS_NI/R</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB5OABMe</td>
<td>149</td>
<td>133*</td>
<td>227</td>
<td>7.52</td>
<td>0.06*</td>
<td>1.81</td>
</tr>
<tr>
<td>CB5OABOMe</td>
<td>180</td>
<td>243</td>
<td>6.98</td>
<td>–</td>
<td>1.77</td>
<td></td>
</tr>
<tr>
<td>CB5OABBu</td>
<td>125</td>
<td>–</td>
<td>209</td>
<td>4.59</td>
<td>–</td>
<td>1.67</td>
</tr>
<tr>
<td>CB5OABOBu</td>
<td>156</td>
<td>120*</td>
<td>232</td>
<td>6.68</td>
<td>0.29*</td>
<td>2.02</td>
</tr>
<tr>
<td>CB5OABCN</td>
<td>150</td>
<td>–</td>
<td>245</td>
<td>6.58</td>
<td>–</td>
<td>1.87</td>
</tr>
<tr>
<td>CB5OABNO₂</td>
<td>146</td>
<td>–</td>
<td>232</td>
<td>9.07</td>
<td>–</td>
<td>1.31</td>
</tr>
</tbody>
</table>

*Denotes values taken on cooling traces of DSC.

Comparison of the CBnOABX dimers

The melting points of the CBnOABX dimers are compared in Figure 7. For any given X, the melting point is the lowest for the CB6OABX dimer with the exception of X = OMe for which CB6OABOMe melts 5°C higher than CB4OABOMe. This exception to the general trend may be attributed to the favourable mixed mesogenic unit that is facilitated by the longer spacer. It is clear that the even-membered dimers tend to have the highest melting points reflecting the greater ability of the more linear even-membered dimers to pack into a crystalline
structure, see Figure 8. The notable exception to this trend is the much higher melting point seen for CB4OABCN compared to CB5OABCN, but the physical significance of this observation is not clear. The different trends in the melting points for a given value of n on varying X may reflect, in part, the role played by the spacer in the packing of the molecules in order to maximise the interaction between the unlike mesogenic units and the ability to form intercalated arrangements [90,91]. It is noteworthy, however, that the dimer containing the butyl terminal group has the lowest melting point for each value of n, and this reflects both the flexibility of the butyl chain, and that it protrudes out of the plane of the phenyl ring to which it is attached [92].

The values of T_{NI} for the CBnOABX dimers show a more regular dependence on X (Figure 9) than do their melting points (Figure 7). Specifically, the values of T_{NI} shown by the CB5OABX dimers are higher than those of the corresponding odd-membered dimers, and this may be understood in terms of the linear shape adopted by even-membered dimers as described earlier and is shown in Figure 8. The values of T_{NI} shown by the dimers with n = 6 are greater than those of the corresponding dimers with n = 4. This reflects the rather general observation that within a homologous

Figure 7. (Colour online) A comparison of the melting points of the CBnOABX dimers. The value of n is indicated on each bar, and the terminal substituents, X, are arranged in order of increasing van der Waals volume [89].

(a) (b) (c)

Figure 8. (Colour online) Space filling models for (a) CB4OABOMe, (b) CB6OABOMe and (c) CB5OABOMe.
series of dimers in which the length of the spacer is varied, the clearing temperature of the odd members tends to pass through the maximum value on increasing spacer length, whereas those of the even members simply fall [75]. This behaviour may be accounted for in terms of the average shapes of the dimers that may be visualised, to a first approximation, in terms of the all-trans conformation, and it is apparent that the shorter odd-membered spacer gives rise to a more pronounced molecular curvature, see Figure 8. On increasing the length of the odd-membered spacer from \( n = 4 \) to \( n = 6 \), the enhanced flexibility allows the dimer to adopt more linear conformers, and this increases \( T_{NI} \). For long odd-membered spacers, the dilution of the mesogenic units offsets this effect and \( T_{NI} \) falls. For a given value of \( n \), the values of \( T_{NI} \) on varying \( X \) may be understood in terms of how the terminal substituent changes the shape and polarisability of the mesogenic unit to which it is attached. As with the melting points, the lowest values of \( T_{NI} \) are observed for the butyl substituent and again, this reflects that the butyl chain protrudes at an angle from the plane of the phenyl ring to which it is attached [93–95].

The values of the scaled entropy change associated with the N–I transition, \( \Delta S_{NI}/R \), are several times larger for the CB5OABX dimers than for the corresponding odd-membered dimers. This may be understood in terms of the conformational and orientational contributions to the total entropy change. Although in the previous discussion we noted that, to a first approximation, the alternation in the values of \( T_{NI} \) on increasing \( n \) may be understood in terms of the change in shape as represented by the all-trans conformation, such an explanation does not account for the very much larger values of \( \Delta S_{NI}/R \) seen for even-membered dimers. Instead, we must remember that the spacer is flexible and that even-membered dimers have a greater number of conformations in which the two mesogenic units are more or less parallel, and these conformers are preferentially selected by the nematic environment. This gives rise to a greater conformational change at \( T_{NI} \) for even-membered than odd-membered dimers. It has been estimated that this accounts for around 20% of the total entropy change seen for an even-membered dimer, whereas this conformational contribution is vanishingly small for an odd-membered dimer [77]. The major contribution to the large difference in \( \Delta S_{NI}/R \) between odd- and even-membered dimers, however, arises from the alternation in the long-range orientational order [77,96]. The value of \( \Delta S_{NI}/R \) increases on passing from \( n = 4 \) to \( n = 6 \) for any given terminal substituent \( X \), and this reflects the decrease in molecular biaxiality on increasing spacer length [97,98]. This reinforces the view that the shorter odd-membered dimers exhibit a more pronounced molecular curvature.

All six members of the CB6OABX dimers exhibit the \( N_{TB} \) phase, whereas, as we have seen, just four members of the CB4OABX dimers do, with no \( N_{TB} \) phase seen for

\[\text{Figure 9. (Colour online) A comparison of the nematic–isotropic transition temperatures of the CBnOABX dimers. The value of } n \text{ is indicated on each bar, and the terminal substituents, } X, \text{ are arranged in order of increasing van der Waals volume [89].}\]
X = CN and NO₂, see Table 1. The CB4OABX dimers show lower values of T_N1 than their CB6OABX counterparts by around 12°C, a smaller reduction than seen for T_N1 of around 17°C. It should be noted that, if this average reduction in T_N1 is applied to the X = CN and NO₂ dimers with n = 4, then the expected values of T_N1 are considerably lower than the lowest temperature to which their nematic phases could be cooled prior to crystallisation, 122°C and 111°C, respectively. It may appear counter-intuitive that the values of T_N1 are lower for the CB4OABX dimers than their more linear CB6OABX counterparts, Figure 8. This indicates that the stability of the N_TB phase is not simply associated with molecular curvature. Instead, the increase in molecular flexibility on increasing n facilitates a better interaction between mesogenic groups and this compensates for the loss of entropy due to the additional polar order in the N_TB phase [57], counteracting the reduction in molecular curvature, and the stability of the N_TB phase increases. This also accounts for the observed increase in the value of T_N1. It is noteworthy, however, that although the absolute values of T_N1 increase on moving from n = 4–6, the scaled temperature T_N1/T_N1 decreases (Table 1), indicating that the stability of the N_TB phase increases relative to that of the N phase as molecular curvature increases. As expected, the linear even-membered CB5OABX dimers do not exhibit the N_TB phase but instead show smectic behaviour for X = Me and OBu, see Table 7. This reflects the greater ease of packing linear molecules into a lamellar phase.

**BrBnOABX dimers**

The BrB4OABX dimers did not show liquid crystallinity, and their melting points are listed in Table 3. These are higher than those of the corresponding BrB6OABX dimers [79], and the differences range from 13°C for X = OMe to 35°C for X = CN. The BrB6OABX dimers with X = Me and NO₂ also did not exhibit liquid crystalline behaviour. The remaining four members showed conventional nematic phases and their values of T_N1 were lower than those of the corresponding CB6OABX dimers by, on average, 32°C. This was attributed to the decrease in structural

<table>
<thead>
<tr>
<th>Table 3. The melting points and associated scaled entropy changes of the BrB4OABX dimers.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimer</td>
</tr>
<tr>
<td>---------------------------</td>
</tr>
<tr>
<td>BrB4OABMe</td>
</tr>
<tr>
<td>BrB4OABOMe</td>
</tr>
<tr>
<td>BrB4OABBu</td>
</tr>
<tr>
<td>BrB4OABOBu</td>
</tr>
<tr>
<td>BrB4OABCN</td>
</tr>
<tr>
<td>BrB4OABNO₂</td>
</tr>
</tbody>
</table>

The transitional properties of the BrB5OABX series are listed in Table 4. All six dimers exhibited an enantiotropic nematic phase identified on the basis of the observation of a characteristic schlieren texture when viewed through the polarised light microscope and a representative texture is shown as Figure 10(a). In addition, on cooling the nematic phase of BrB5OABCN, a fan-like texture developed, indicating the formation of a smectic phase, see Figure 10(b). The rapid crystallisation of this phase precluded its study using X-ray diffraction, although the value of the entropy change associated with the transition strongly suggests a liquid-like smectic phase. The values of T_N1 are on average 22°C lower for the BrB5OABX dimers compared to those of the corresponding CB5OABX dimers, and this may again be attributed to the change in structural anisotropy and reduced tendency to self-organise in an anti-parallel fashion. A smectic phase is observed for BrB5OABCN, whereas only an N phase is seen for CB5OABCN and this may be cooled to much lower temperatures than the value of T_SmN seen for BrB5OABCN. The physical significance of this observation is unclear. The values of T_N1 shown by the
BrB5OABCN dimers are, on average, 85°C higher than those of the corresponding Br6OABCN dimers, and this may be attributed to the difference in shape between even and odd-membered dimers as discussed earlier.

Conclusions

The higher melting points seen for the CB4OABX dimers compared to those of the corresponding CB6OABX materials support the emerging observation that short odd-membered spacers, although promoting molecular bend, paradoxically appear to enhance packing efficiency in the crystal phase. This suggests that the reduction in the melting point on increasing spacer length is associated with the increase in molecular flexibility and, therefore, entropically driven. The values of both $T_{NI}$ and $T_{NI,N}$ are lower for the CB4OABX dimers than for the corresponding CB6OABX materials but the reduction is greater for T_{NI}. Thus, where applicable, the scaled transition temperature, $T_{NI,N}/T_{NI}$, is in fact higher for the dimer with the shorter spacer, indicating that direct $N_{TB}$-isotropic transitions are more likely to be observed for short odd-membered spacers, as appears to be the case in the very limited number of examples observed to date [8–11]. The challenge is now to design short, odd-membered dimers having low melting points in order to realise an enantiotropic $N_{TB}$–I transition.

Disclosure statement

No potential conflict of interest was reported by the author(s).

References


Figure 10. (Colour online) (a) The schlieren nematic and (b) fan-like optical textures observed for a sample of BrB5OABCN sandwiched between untreated glass slides.


[47] Simpson FP, Mandle RJ, Moore JN, et al. Investigating the Cusp between the nano-and macro-sciences in


