Helical Twist and Spontaneous Polarization Direction in Ferroelectric Smectic Liquid Crystals. 2

J. W. Goodby* and E. Chin

Contribution from AT&T Bell Laboratories, Murray Hill, New Jersey 07974.
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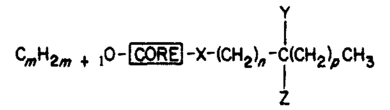
Abstract: Previous studies have shown that there are simple relationships between the helical twist sense, spontaneous polarization direction, and orientational ordering in ferroelectric liquid crystals. These macroscopic properties are related to the microscopic properties of molecular structure, steric shape, and spatial configuration. This present study develops the original concepts further to include changes to the tilt orientation and conformational structure of the molecules. This allows the prediction of the spontaneous polarization direction for a given molecular species. The twist sense, however, is found to be rather insensitive to these changes and still adheres to the guidelines given previously.

(I) Introduction

Previous investigations[1,2] concerning the helical twist sense and the spontaneous polarization direction in lamellar, helical, and ferroelectric smectic phases,[3] C*, I*, and F*, have yielded a simple relationship between these macroscopic properties and certain microscopic features of molecular architecture. Simply, for materials already studied, there appears to be a one-to-one relationship between the spiral ordering (normal to the lamellae) of the tilt orientation of the molecules of the ferroelectric, or as it has alternatively been called the helielectric phase,[4] and the spontaneous polarization direction[5] relative to the tilt axis for systems containing a single asymmetric center. For example, for homologous series with the general structure I



$$C_mH_{2m+1}O\text{-}\boxed{\text{CORE}}\text{-}X\text{-}(CH_2)_n\text{-}\overset{\displaystyle Y}{\underset{\displaystyle Z}{C}}(CH_2)_pCH_3 \qquad \text{(I)}$$

where X is a spacer unit, e.g., COO or O, Y and Z are lateral substituents at the asymmetric center, one usually being hydrogen, and *m*, *n*, and *p* are integers with *m* usually greater than eight and *n* varying from 0 to 5, and which exhibit smectic C*, I*, or F* phases, then the following general relationships are usually observed for the helical twist sense of the phase and the spontaneous polarization direction:[1,2]

$$d(+) \equiv \text{LH helix} \equiv \text{Ps}(-)$$

$$l(-) \equiv \text{RH helix} \equiv \text{Ps}(+)$$

These are related to the microscopic features of molecular structure as shown below:

$$-IRe,\ -ISo,\ +IRo,\ +ISe \equiv d(+),\ \text{Ps}(-)$$

and

$$-IRo,\ -ISe,\ +IRe,\ +ISo \equiv l(-),\ \text{Ps}(+)$$

where *R* or *S* is the absolute spatial configuration of the chiral center,[6] e or o is the odd or even parity (position) of the chiral center relative to the core (i.e., $n + 1$),[1,2] +I or −I is the inductive effect of the lateral substituents at the chiral center, $d(+)$ or $l(-)$ is the rotation of plane polarized light through the helical structure of the phase,[1,2,7,19] LH or RH is the helical twist direction,[8] and Ps(+) or Ps(−) is the spontaneous polarization direction relative to the tilt axis.[5] These rules appear to support a previously proposed model for phases where the aromatic cores of the constituent molecules are more tilted with respect to the layer normal than the overall molecular structures.[9] Thus, the optic tilt angle is greater than the steric tilt angle obtained by X-ray diffraction.[10] Moreover, the zigzag packing of the molecules has already been used as a basis for a theoretical steric model of the C phase.[9]

This present study involves a number of materials that do not fall into the above classification and therefore become exceptions to the rules defined in our previous investigation. However, the results obtained reveal a more detailed model of the ferroelectric smectic state. For example, the results show that the spontaneous polarization direction is dependent on the spatial orientation of the dipole resulting from the relative electronegativities of the substituents at the chiral center with respect to the molecular long axis and not totally on the artificial designations of the sequence rule (*R* and *S*) or parity (odd or even). Furthermore, smectic C* materials have been found where the tilt angle of the core (optic) is less than the steric tilt angle, the reverse of previous indications. This results in the inversion of the previously expounded rules.

(II) Experimental Section

The materials characterized in this study, except for derivatives of (*S*)-2,6-dimethylheptanoic acid (2M6M7),[11] were prepared by trivial methods which have already been reported elsewhere.[2,12-14] Derivatives of (*S*)-2,6-dimethylheptanoic acid were prepared by first hydrogenating (*S*)-β-citronellol (Aldrich) in the presence of Adams' catalyst and then oxidizing the resulting alcohol to the acid with Jones' reagent. The structures of the materials prepared were confirmed by IR spectroscopy and NMR spectrometry, and their purities were determined by thin-layer chromatography, reverse-phase HPLC utilizing an octadecylsiloxane (25 × 0.46 cm), 5 μm pore, column as the stationary phase and acetonitrile as the mobile phase, and elemental analysis.

Transition temperatures and phase classifications for the compounds were determined by thermal, optical, polarized-light microscopy employing a Zeiss Universal polarizing microscope in conjunction with a Mettler FP52 microfurnace and FP5 control unit. Enthalpies of transition and consequently transition temperatures were also determined by

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[1] Goodby, J. W. *Science* **1986**, *231*, 350.

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[4] Brand, H. R.; Cladis, P. E. *J. Phys.* (*Paris*) **1984**, *45*, 1053. Brand, H. R.; Cladis, P. E. *Mol. Cryst. Liq. Cryst.* **1984**, *114*, 207.

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[12] Goodby, J. W.; Leslie, T. M. In *Liquid Crystals and Ordered Fluids*; Griffin, A. C., Johnson, J. F., Eds.; New York, 1984; Vol. 4, p 1.

[13] Goodby, J. W.; Leslie, T. M. *Mol. Cryst. Liq. Cryst.* **1984**, *110*, 175.

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[15] Brand, H. R.; Cladis, P. E. *Mol. Cryst. Liq. Cryst.* **1984**, *114*, 207. Budai, J.; Pindak, R.; Davey, S. C.; Goodby, J. W. *J. Phys.* (*Paris*) *Lett.* **1984**, *45*, L1053.

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Table I

group	compound[a]	abs config	parity	helix	rotation	Ps
A	$C_8H_{17}PhPhCOOPh2M4$[15]	*S*	e	LH	*d*	Ps(+)
	$C_{12}H_{25}OPhCOOPhCH{:}C(CN)COO2M4$	*S*	e	LH	*d*	Ps(+)
	$C_7H_{15}OPhCOOPhCH{:}C(CN)COO2M4$	*S*	e	LH	*d*	PS(+)
	$C_8H_{17}OPhCOOPhCH{:}C(CN)COO2M4$	*S*	e	LH	*d*	Ps(+)
	$C_{10}H_{21}OPhCOOPhO2M4$	*S*	o	RH	*l*	Ps(−)
	$C_{12}H_{25}PhSOCPhPhO2M4$	*S*	o	RH	*l*	Ps(−)
B	$C_{14}H_{29}OPhCOOPhCO2M6M7$	*S*	o	RH	*l*	Ps(+)
	$C_8H_{17}OPhPhCOOPhCO2M6M7$	*S*	o	RH	*l*	Ps(+)
C	$C_9H_{19}OPhCOOPhCOO4M6$	*S*	e	LH	*d*	Ps(+)
	$C_7H_{15}OPhOCOPhO4M6$	*S*	o	RH	*l*	Ps(−)
	$C_9H_{19}OPhOCOPhO4M6$	*S*	o	RH	*l*	Ps(−)

[a] Where 2M4 = 2-methylbutyl, 2M6M7 = 2,6-dimethylheptyl, 4M6 = 4-methylhexyl, Ph = 1,4-substituted phenyl ring.

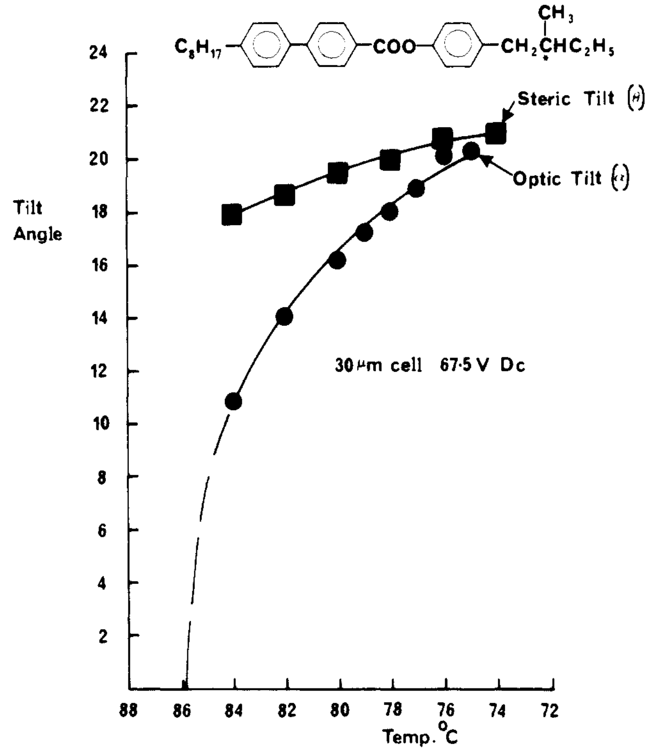

Figure 1. The change in steric tilt angle (θ) and optic tilt angle (α) in degrees vs. temperature for the smectic C* phase of (*S*)-4-(2-methylbutyl)phenyl 4′-*n*-octylbiphenyl-4-carboxylate.

differential scanning calorimetry with a Perkin-Elmer DSC-4 TADS system. Determination of the spontaneous polarization direction, pitch of the helical phase, twist sense of the helix, and optic tilt angle were made as described previously.[2]

(III) Results

A number of materials were investigated in order to ascertain their phase classification, their spontaneous polarization directions, and their twist senses. The substances are grouped together into three sections in Table I with respect to their properties. Table II gives their phase sequences and transition temperatures.

The measurement of the optical tilt angle (α) as a function of falling temperature has been described previously.[2,10] The results obtained for (*S*)-4-(2-methylbutyl)phenyl 4′-*n*-octylbiphenyl-4-carboxylate (8SI)[16] are shown in Figure 1 for a holding voltage of 67.5 V across a cell with a 30-μm-plate separation. The steric tilt angle (θ) determined by X-ray diffraction for the same compound is also shown as a function of falling temperature in Figure 1. The steric tilt angle was determined from the calculated (theoretical) molecular length and the observed lamellar spacing as a function of temperature.[15]

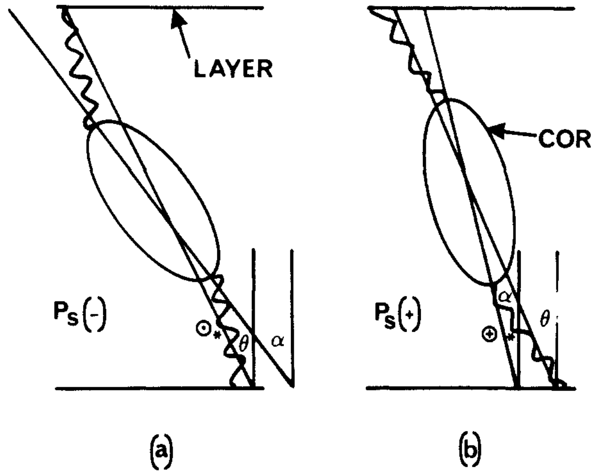

Figure 2. The two tilt orientations that are possible for smectic C* phases which incorporate zigzag shaped molecules.

(IV) Discussion

(1) Molecular Tilt Orientation and Spontaneous Polarization Direction. In previous studies,[1,2] a one-to-one relationship between the helical twist sense (*d* or *l*) and the spontaneous polarization direction (Ps(±)) was found, e.g.

$$Ps(-) \equiv d(+) \equiv \text{LH helix}$$

$$Ps(+) \equiv l(-) \equiv \text{RH helix}$$

For the materials shown in Table I, group A, however, there is an inversion of the above rules to give the following relationships:

$$Ps(-) \equiv l(-) \equiv \text{RH helix}$$

$$Ps(+) \equiv d(+) \equiv \text{LH helix}$$

Closer examination of these materials reveals that the relationships between the optical properties (*d* or *l*) and the molecular properties (*R* or *S*, parity (o or e), and electronegativity) are maintained. Therefore, the spontaneous polarization direction relative to the tilt axis of the phase has altered or vice versa.

In an earlier study[2] one possible explanation for the above first set of relationships involved the tilt orientation of the molecules within their layers. It was suggested that the rigid aromatic cores of the molecules were tilted more than the overall tilt of the molecules. Hence the optic tilt angle (α) is greater than the steric tilt angle (θ) determined by X-ray diffraction. In this orientation, for a zigzag shaped molecule in its all-trans conformation, the spontaneous polarization direction is fixed by the spatial configuration of the chiral center and the lateral component of the dipole moment associated with it, as shown in Figure 2a. Thus the steric model fits the rules obtained. One hypothesis for the inversion of the initial guidelines for materials in group A lies in a change in the tilt orientation of the molecules. The rigid aromatic cores in this case may be packed in a more upright orientation relative to the layer planes than the molecules as a whole (see Figure 2b),

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[16] (*S*)-4-(2-Methylbutyl)phenyl 4′-*n*-octylbiphenyl-4-carboxylate (8SI) is now commercially available as CE8 marketed by BDH Chemicals.

Table II

compound[a]	transition temperatures
	Section A
$C_8H_{17}PhPhCOOPh2M4$[15]	$\mathrm{Iso} \underset{141}{\longleftrightarrow} \mathrm{Ch} \underset{138}{\longleftrightarrow} S_A \underset{81}{\longleftrightarrow} S_C^* \underset{71}{\longleftrightarrow} S_I^* \underset{66}{\longleftrightarrow} S_J^* \underset{62}{\longleftrightarrow} S_G^* \quad \underset{48}{\mathrm{mp}}$
$C_{13}H_{25}OPhCOOPhCH{:}C(CN)COO2M4$[12]	$\mathrm{Iso} \underset{89}{\longleftrightarrow} S_A \underset{72}{\longleftrightarrow} S_C^* \quad \underset{81.5}{\mathrm{mp}}$
$C_7H_{15}OPhCOOPhCH{:}C(CN)COO2M4$[12]	$\mathrm{Iso} \underset{82.5}{\text{——}} \mathrm{Ch} \underset{74}{\longleftrightarrow} S_A \underset{58}{\longleftrightarrow} S_C^* \quad \underset{75}{\mathrm{mp}}$
$C_8H_{17}OPhCOOPhCH{:}C(CN)COO2M4$[12]	$\mathrm{Iso} \underset{85.5}{\text{——}} \mathrm{Ch} \underset{82.5}{\text{——}} S_A \underset{60.5}{\text{——}} S_C^* \quad \underset{86}{\mathrm{mp}}$
$C_{10}H_{21}OPhCOOPhO2M4$	$\mathrm{Iso} \underset{66}{\text{——}} \mathrm{Ch} \underset{64.5}{\text{——}} S_A \underset{45.5}{\text{——}} S_C^* \quad \underset{42.5}{\mathrm{mp}}$
$C_{12}H_{25}OPhSOCPhPhO2M4$	$\mathrm{Iso} \underset{172}{\longleftrightarrow} \mathrm{Ch} \underset{168}{\longleftrightarrow} S_A \underset{136}{\longleftrightarrow} S_C^* \underset{113}{\longleftrightarrow} S_I^* \underset{105}{\longleftrightarrow} S_F^* \underset{81}{\longleftrightarrow} S_G^* \underset{68}{\longleftrightarrow} S_H^* \quad \underset{82}{\mathrm{mp}}$
	Section B
$C_{14}H_{29}OPhCOOPhCO2M6M7$	$\mathrm{Iso} \underset{63.4}{\text{——}} S_A \underset{57.4}{\text{——}} S_C^* \quad \underset{69}{\mathrm{mp}}$
$C_8H_{17}OPhPhCOOPhCO2M6M7$	$\mathrm{Iso} \underset{173}{\longleftrightarrow} S_A \underset{138}{\longleftrightarrow} S_C^* \underset{74}{\longleftrightarrow} S_I^* \quad \underset{98}{\mathrm{mp}}$
	Section C
$C_9H_{19}OPhCOOPhCOO4M6$	$\mathrm{Iso} \underset{58}{\longleftrightarrow} S_A \underset{40}{\longleftrightarrow} S_C^* \quad \underset{34}{\mathrm{mp}}$
$C_7H_{15}OPhOCOPhO4M6$[12]	$\mathrm{Iso} \underset{64}{\text{——}} \mathrm{Ch} \underset{46.5}{\longleftrightarrow} S_C^* \quad \underset{30}{\mathrm{mp}}$
$C_9H_{19}OPhOCOPhO4M6$[12]	$\mathrm{Iso} \underset{57}{\longleftrightarrow} \mathrm{Ch} \underset{45}{\longleftrightarrow} S_C^* \quad \underset{32}{\mathrm{mp}}$

[a] Where 2M4 = 2-methylbutyl, 4M6 = 4-methylhexyl, 2M6M7 = 2,6-dimethylheptyl, Ph = 1,4-substituted phenyl ring.

i.e., the reverse of that postulated previously.

From Figure 2 it can be seen that when a zigzag shaped molecule which has its dipole pointing out of the page and its tilt axis in the plane of the page (Figure 2a), is flipped 180° about its tilt axis, then for the same spatial configuration about the chiral center, the same parity, and the same conformation, there is a change in the sign of the spontaneous polarization because the dipole now lies below the plane containing the tilt axis (i.e., into the page), and therefore the molecule has the reverse relationship between tilt and lateral dipolar component. In the first case the optic tilt angle (α) associated with the delocalized electrons and dipolar nature of the core is greater than the steric tilt angle (θ) of the overall molecule, while in the second variation α is now less than θ.

This hypothesis was tested for one of the materials in group A, 4-(2-methylbutyl)phenyl 4′-*n*-octylbiphenyl-4-carboxylate (8SI). The optic tilt angle, as a function of falling temperature from the A to C* transition, obtained by electric field studies described previously, is shown in Figure 1. Also shown in this figure for comparison is the steric tilt angle (θ) obtained by measurement of the lamellar spacing as a function of falling temperature.[15] The tilt angle (θ) is determined by assuming the molecular length of 8SI is 29.25 Å—the theoretically calculated length of the molecule in its all-trans conformation. It can be seen from this figure that the optic tilt is less than the steric tilt as hypothesized. This gives rise to the possibility that two types of C* phase exist, as proposed in Figure 2a,b.

Moreover, it is also known that the average tilt angle for smectic C phases commonly saturates about 25° after a transition from an A phase or the isotropic liquid, or it can saturate at a higher value of approximately 45° after a direct transition from the cholesteric or isotropic liquid phase. Therefore, four extreme variants of the smectic C phase become possible, as shown in Figure 3. These variations can be structurally immisible when two materials with differing phase structures are mixed together. Injections of orthogonal phases, A, B hexatic, B crystal, and E into phase diagrams involving tilted phases[15,17,18] have long been a mystery, but for the above hypothesis of the C phase it is possible to invisage high and low tilt materials with differing tilt orientations being incompatible, and thus the tilts compensating for each other consequently producing orthogonal phases.[18]

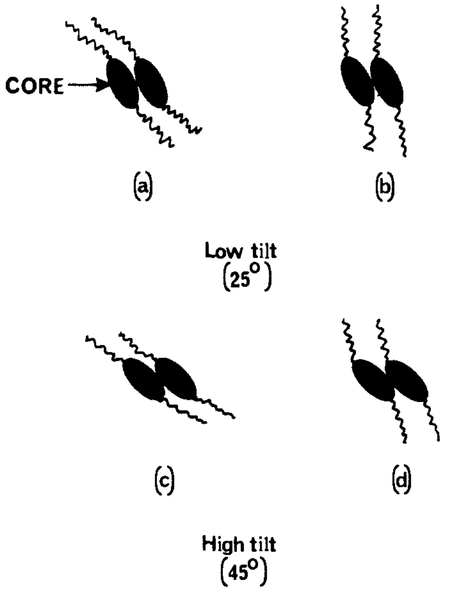

Figure 3. The four possible tilt variations of the smectic C phase: (a and b) low-tilt variations ($\alpha \sim 25°$), (c and d) high-tilt variations ($\alpha \sim 45°$). The low-tilt format is usually obtained from a smectic A phase on cooling while the high-tilt format is obtained normally from a cholesteric phase.

The majority of materials studied so far, however, are expected to fall into the classes depicted in Figure 3b,d where the core of the molecule is more tilted than the overall structure. Figure 3b is for the low-tilt variation usually obtained for an AC* phase sequence, and Figure 3d is for the high-tilt situation obtained for a ChC* sequence.

There are a number of possible reasons for the above hypothesis ranging from steric to dipolar factors. Consider first the steric properties; the two compounds II and III have the same spontaneous polarization direction but opposite helical twist senses. The twist senses of both materials, however, agree with the original guidelines given by Gray and McDonnell.[19] Compound III

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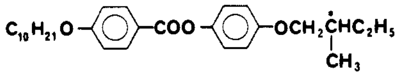
[17] Goodby, J. W.; Gray, G. W. *J. Phys. (Paris) Colloq. C3* **1979**, *40*, 363.

[18] Goodby, J. W.; Gray, G. W. *Mol. Cryst. Liq. Cryst., Lett.* **1979**, *56*, 43. Goodby, J. W., unpublished results.

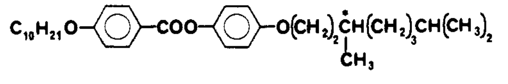
[19] Gray, G. W.; McDonnell, D. G. *Mol. Cryst. Liq. Cryst. Lett.* **1977**, *34*, 211.

(II)



$ISO \leftrightarrow Ch \leftrightarrow S_A \leftrightarrow S_C^*$ Sol $P_s(-)$

(III)



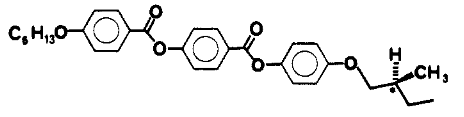
$ISO \leftrightarrow S_A \leftrightarrow S_C^*$ Sed $P_s(-)$

conforms to the usual Ps(−) equivalent to *d*(+) group while substance II is of the Ps(−) equivalent to *l*(−) class. The longer terminal chiral alkoxy moiety ((*S*)-3,7-dimethyloctyl) always seems to possess the classification defined previously for a 3(b) system (3(b) = variations b in Figure 3), i.e., Ps(+) ≡ *l*(−), Ps(−) ≡ d(+). However, closer inspection of the other materials in group A (Table I) shows that they all contain the (*S*)-2-methylbutyl moiety, which is much shorter in length than the (*S*)-3,7-dimethyloctyl group. Thus the prime difference between these two materials is one of terminal alkyl chain length. The resulting implication is that III has a type 3(b) structure while II has a type 3(a) ordering. When the terminal alkyl chains are sufficiently long type 3(b) gives better $\sigma\sigma$ and $\pi\pi$ overlap at the expence of $\pi\sigma$ interactions than would type 3(a) for the same molecular structure. Alternatively, it could be argued that the 2-methylbutyl group adjacent to the core does not exhibit much of an off-axis effect and the overall molecular structure is not really of a zigzag shape. The 2-methylbutyl group possibly acts as an extension to the core, thus a 3(a) type packing becomes more favorable. This suggests that the steric shape as a function of the size of the three regions of the zigzag shaped molecular structure (aliphatic–aromatic–aliphatic) plays an important role in molecular packing orientations, even though the molecules are undergoing rapid reorientational motion about their long axes.[20]

An added feature of the terminal alkyl chain extension is the effect caused by the inclusion of a spacer unit which is conjugated to the core, but similar in structure to the chain, e.g., COO. The off-axis zigzag effect about the core of the trans alkyl–aromatic–alkyl organization is not perceived until the terminal chains are sufficiently long enough because of the large cross-sectional area of the core (see Figure 4). When a spacer group is inserted between the core and the terminal chain it increases the off-axis effect, yet because of its rigidity and conjugation it also acts as part of the core. Hence this latter effect is pronounced in measurements of the pitch and the spontaneous polarization where the magnitudes of the results obtained indicate the spacer group acts as though it were part of the core, i.e., similar pitch lengths and values for the spontaneous polarizations are obtained for molecular structures which differ only by the inclusion or exclusion of a spacer unit. However, in the determination of the sign of the spontaneous polarization the spacer acts like the terminal chain in that its size determines the extent of the off-axis zigzag effect, which in turn effects the conformational structure. For example, in Figure 4a, the terminal chiral chain is short and acts almost as part of the core thus giving a *Sol*(−) Ps(−) classification, but when a larger (longer) spacer unit is introduced the classification changes to *Sed*(+) Ps(−), a reversal from Ps(−) ≡ *l*(−) to Ps(−) ≡ *d*(+).

These effects become more pronounced as the size and shape of the core is changed; for example, its effective width could be increased by the insertion of another benzoyloxy moiety to give a three-ring system IV. This system has a *Sol*(−) Ps(−) classification,[21] i.e., the short 2-methylbutyl chain does not exhibit a strong off-axis tendency and therefore acts as part of the core. However, the longer 4-methylhexyl analogue reverts back to a *Sol*(−) Ps(+) classification because of its longer terminal chain and greater off-axis effect. Yet, in two ring systems (see later) for the 4-methylhexyl derivative, the off-axis effect is larger relative to the core length, thus conformational changes can occur producing a *Sol*(−) Ps(−) result.

(IV)



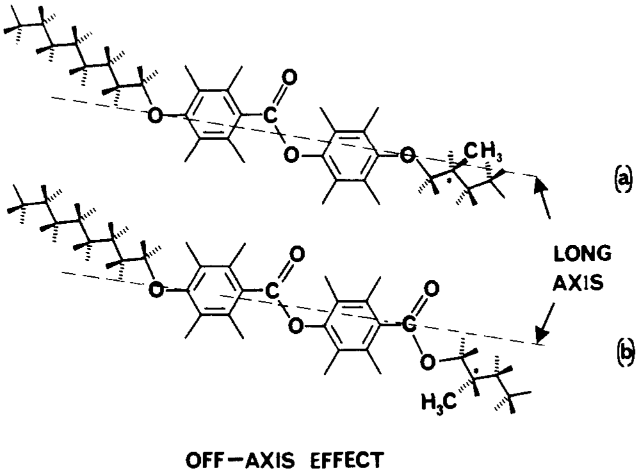


Figure 4. The off-axis steric effect producing the zigzag shape of the molecule.

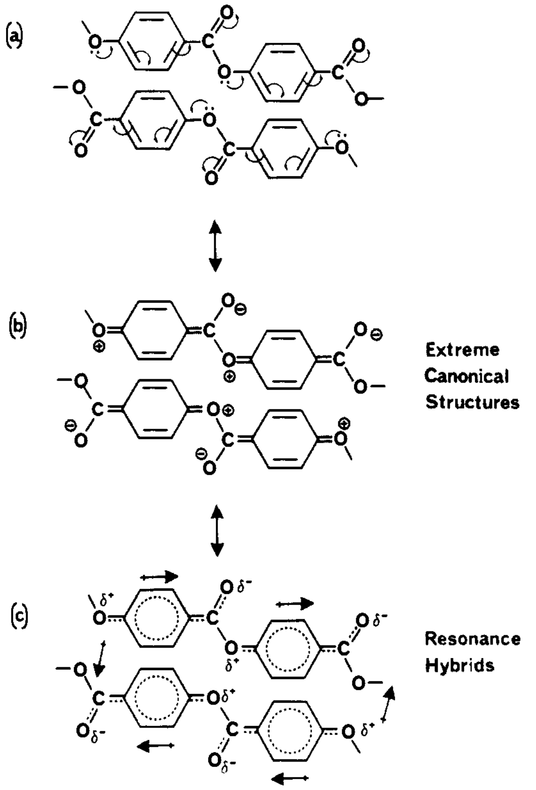


Figure 5. Perturbation of the molecular orbitals of one molecule by its nearest neighbors, producing a stabilized structure.

Secondly the dipolar properties of the material also have a marked influence on the type of tilted smectic phase formed. Particularly, the lateral dipolar interactions associated with terminal outboard dipoles[22-25] dominate phase structure and incidence

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[20] Leadbetter, A. J.; Richardson, R. M. In *The Molecular Physics of Liquid Crystals*; Luckhurst, G. R., Gray, G. W., Eds.; Academic Press: London, 1979; Chapter 20.

[21] Patel, J. S.; Goodby, J. W., to be submitted.

[22] McMillan, W. L. *Phys. Rev. A* **1973**, *8*, 1921.

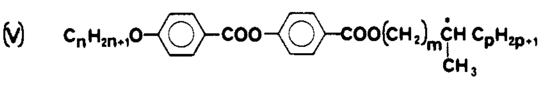
[23] Goodby, J. W.; Gray, G. W.; McDonnell, D. G. *Mol. Cryst. Liq. Cryst. Lett.* **1972**, *34*, 1983.

[24] de Jeu, W. H. *J. Phys.* (*Paris*) **1977**, *38*, 1265.

[25] Van der Meer, B. W.; Vertogen, G. *J. Phys.* (*Paris*) *Colloq. C3* **1979**, *40*, 222.

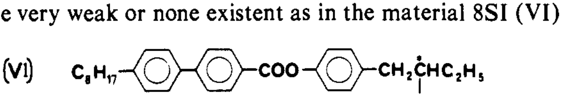
in smectic liquid crystals. For example, in the homologous series V for small values of *m* (so that the material has a large spontaneous polarization in order that it can be studied in electric field experiments) and a given reduced temperature $(T - T_{\text{A-C}} = -5°)$, approximately the same value for the optic tilt angle (α) was found irrespective of the values of *n* or *p* (provided the material was in its C* phase).[11] This would indicate that the core–core intermolecular interaction dominates in this case. If, as generally assumed, the molecules have a mixed head-to-tail arrangement within the layers, this could produce interactions of the type shown in Figure 5a, leading to perturbations of the molecular orbitals as shown in Figure 5b. This gives a stabilized structure (Figure 5c) which has a staggered core–core overlap conducive to a type 3(b) structure. This occurs when the dipolar interactions between neighbors are complementary and are not too weak or too strong.

(V)

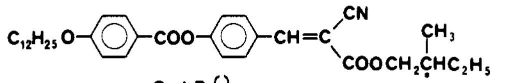


However, where such polarizations, perturbations, or interactions are very weak or none existent as in the material 8SI (VI), no staggering of the cores occurs. This could possibly lead to a less core tilted interaction as in type 3(a), and consequently a Ps(+) ≡ *d*(+) or Ps(−) ≡ *l*(−) classification, which is the result obtained for compound VI. When the strength of the lateral dipoles is very large, then these interactions dominate. Thus the core–core packing structure is dependent on these dipolar interactions to a greater extent. For example, consider the two compounds VII and VIII; the interactions of the cyano group with neighboring core structures may be so strong that the cores are not too staggered for compound VII because the interactions hold them together in a more upright position, thus producing a 3(a) situation, and *d*(+) ≡ Ps(+). In the second material VIII this interaction is not present and therefore it reverts back to a type 3(b) situation, i.e., *d*(+) ≡ Ps(−).

(VI)

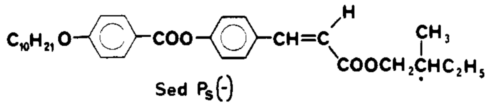


(VII)



Sed P_s(+)

(VIII)

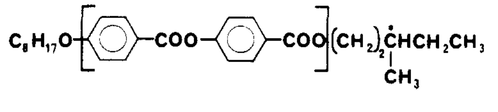


Sed P_s(−)

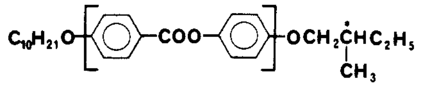
The tilt orientation of the cores, and therefore the tilt orientation of the molecules, appears to be effected by the gross zigzag shape of the molecule and the local dipolar interactions between the cores. These dipolar interactions are obviously dependent on intermolecular distances which in turn are controlled by steric interactions.

(2) Spatial Dipolar Orientation, Parity, and Sequence Rule. Gray and McDonnell's initial rules for cholesterics[19] gave the parity from the core as the atom count from the last phenyl ring to the asymmetric center. This in effect evades the issue as to the extent of the core structure particularly when conjugated spacer groups are involved. Normally the core is defined as the most extended rigid structure within the molecular framework, or the portion with the most delocalized electrons (i.e., the conjugated region). If either of these definitions is used for compounds IX and X shown below, then the parity count should start at the end of the core where the core is the region in parentheses. In both of these systems the count starts from a bond which is almost coaxial with the long axis of the core. However, consider a structure where the direction of this bond is no longer coaxial, as in the materials in Table I, section B, XI and XII. In both of these materials the atom count is even whichever definition of the core is used, therefore both systems should be classified as *Sed* + *l*Ps(−). However, the results obtained for the twist sense and spontaneous polarization direction are *l*(−) and Ps(+), respectively, i.e., that for an *So* + *l* classification. Closer inspection of these materials shows that they have similar spatial orientations of their asymmetric centers relative to their long axes as a *Sol* + *l*Ps(+) system shown by structure IX.

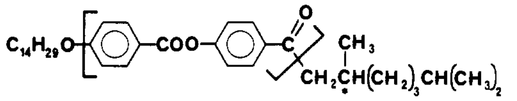
(IX)



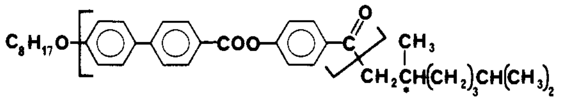
(X)



(XI)



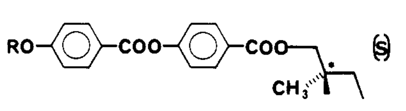
(XII)



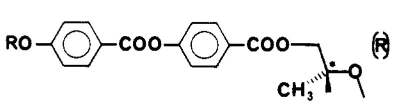
Clearly the spacer unit acts as part of the terminal chain that bears the chiral center for the purposes of parity, and therefore the use of an atom count is an arbitrary one dependent on where the count begins. To avoid confusion the atom count should begin from the last bond of the core which is approximately coaxial with the long axis of the core.

Similary, the use of the spatial configuration designations of *R* and *S* is also arbitrary because they are used to define the system in terms of atomic number and not in relative electronegativities of the substituents about the asymmetric center. For example, the two materials XIII and XIV have similar spatial configurations relative to their molecular long axes, and therefore the spatial orientation of the dipole at the chiral center for each compound will be similar. Thus the two should have the same classification of twist sense and spontaneous polarization direction even though they have opposite spatial configuration designations.

(XIII)



(XIV)



The spatial orientation of the electron density at the chiral center relative to the overall molecular structure appears to be the primary factor in determining the signs of the twist sense or spontaneous polarization. The artificial designations *R* or *S*, e or o have to be applied bearing these factors in mind.

(3) Molecular Conformations. So far only materials in their all-trans conformations about their aromatic cores have been considered. In particular the sign of the spontaneous polarization has always been determined from a molecular structure in which the flexible bonds between the core and the chiral center are assumed to be in their trans format. However, even if the molecular structure of the smectogen has a local trans conformation about the core, it is unlikely that the terminal aliphatic chain will remain in this conformation further down the skeleton away from the core.[26] In fact, because of the molecular rotational aspects, it is more likely to bend back into line with the long axis of the core than to become more zigzag shaped. In this situation where the chiral center is removed a number atoms from the core, gauche conformers have an increasing chance of occurring between the core and asymmetric center. When an odd number of these conformational changes occurs there is an inversion of the lateral

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(26) Samulski, E. T.; Dong, R. Y. *J. Chem. Phys.* **1982**, *77*, 5090.

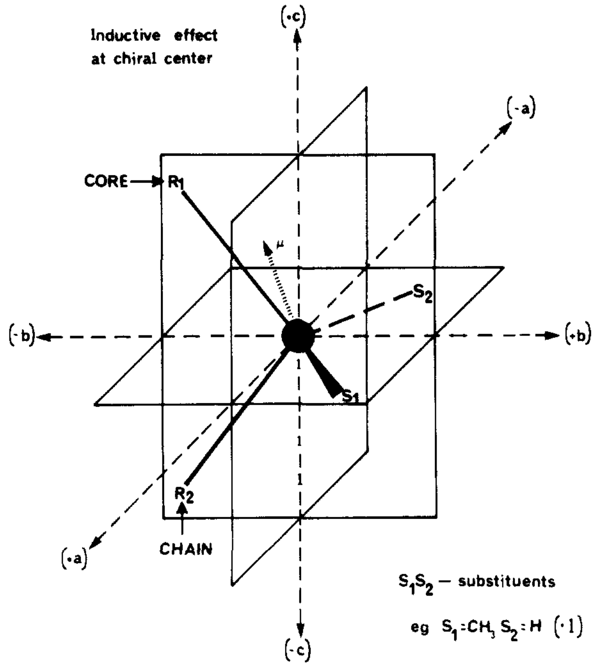


Figure 6. The spatial orientation about the chiral center, where S_1 and S_2 are the substituents, R_1 is the core, and R_2 is the terminal alkyl chain. If S_2 is hydrogen and S_1 is an electron-donating group, the dipole lies on the negative *b* side of the *ac* plane, i.e., +*I* effect.

component of the dipole at the chiral center relative to the long axis, and consequently there should be a change in the sign of the spontaneous polarization.

Materials in Table I, section C, fall into this category; typically these are all derivatives of (*S*)-4-methylhexanol, thus the chiral center is removed at least five atoms from the core in each case because of the inclusion of a spacer group. There is ample flexible chain and off-axis effect between the core and the chiral center in these examples for gauche conformations to occur. All three materials have the same twist sense as predicted by Gray and McDonnell rules,[19] but all have the opposite sign for the spontaneous polarization for a 3(b) group where the core is more tilted than the overall structure. One possible explanation for this inversion of the sign of the spontaneous polarization is that they are in fact members of the 3(a) group where the core is more upright than the overall structure. In this case gauche conformers would decrease the off-axis zigzag effect with the terminal chain becoming aligned with the core, but conversly a conformational change accompanying a tilt change would lead to the normally expected sign of the spontaneous polarization. This switch to a 3(a) group is also doubtful for the following reasons, firstly, extension of the terminal chain favors a 3(b) structure, and secondly, the spontaneous polarization is low and the pitch is large for these materials (in comparison to their 2-methylbutyl analogues). The second two factors and the sign of the spontaneous polarization are better explained by an increasing gauche population competing with the trans conformers consequently resulting in long pitch and low spontaneous polarization.

A conformational change for these materials in a 3(b) ordering would therefore invert the sign of the spontaneous polarization. The results show that if this conformational change occurs then the twist sense does not necessarily alter accordingly. Hence the twist direction is not dependent on the component of the dipole at the chiral center which is lateral to the tilt axis.

(4) Spatial Dipolar Orientation at the Chiral Center. From the hypotheses so far it is apparent that while the twist sense and spontaneous polarization direction are possibly linked to similar dipolar properties at the chiral center, they are also sensitive to differing electronic interactions. The twist sense, for example, is dependent on the inductive (±*I*) effect of the substituents bound to the chiral carbon atom,[2] whereas the spontaneous polarization is sensitive to the direction of the lateral component of this dipole relative to the long axis of the material. This can be visualized in Figure 6 where S_1 and S_2 are lateral substituents at the chiral center, R_1 is the core, and R_2 is the longest terminal carbon chain. The twist sense appears to be sensitive to the dipole direction at the chiral center relative to the *ac* plane, while the spontaneous polarization is determined by its lateral component relative to the tilt axis, i.e., along the *c* direction. The spontaneous polarization is sensitive to changes in the zigzag tilt orientation of the molecules in their layers and to conformational changes in the flexible backbone between the core and the chiral center. However, these changes do not affect the twist sense which seems to be only dependent on the inductive effect relative to the *ac* plane shown in Figure 6, the parity from the core, and the spatial orientation of the dipole at the chiral center.

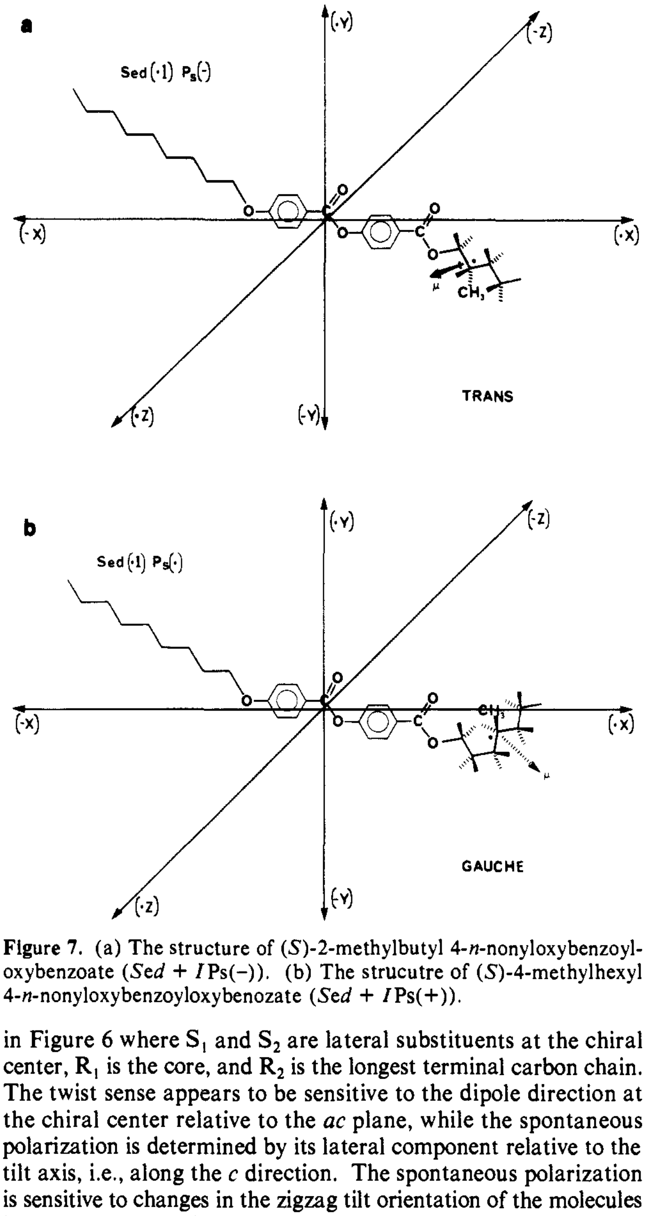


Figure 7. (a) The structure of (*S*)-2-methylbutyl 4-*n*-nonyloxybenzoyloxybenzoate (*Sed* + *I*Ps(−)). (b) The strucutre of (*S*)-4-methylhexyl 4-*n*-nonyloxybenzoyloxybenozate (*Sed* + *I*Ps(+)).

The spontaneous polarization direction can therefore be determined by a simple dipolar model in which the lateral component is determined relative to the tilt axis to give the sign of the spontaneous polarization.

The spontaneous polarization direction can be determined by a simple construction of the molecular structure of the compound within a three coordinate axis system as shown in Figure 7a. The core lies approximately along the *x* axis, and the longest terminal chain not carrying the chiral center is placed in the $-x + y$ quadrant of the *xy* plane. The terminal chain carrying the asymmetric center is then placed in the $+x - y$ quadrant, and the positions of the lateral substituents are fixed by the absolute spatial configuration. The direction of the lateral component of the dipole at the chiral center, i.e., in the $+z$ or $-z$ direction, is determined by the relative inductive effects of the lateral substituents. The *z* direction is now the polar twofold axis of the phase; rotation about this axis by 180° brings the molecule into a similar orientation. Other rotations do not produce this particular type of arrangement, thus this zigzag structuring gives a better description of Meyer's symmetry arguments[3] for ferroelectricity in these phases than cylindrical structures. Rotation about the *z* axis also effectively changes the layer ordering; when the chains are in the $-x + y$, $+x - y$ quadrants a type 3(b) system is obtained, and when the chains are in the $+x + y$, $-x - y$ quadrants a type 3(a) class is obtained. This rotation (based on previous results) fixes the sign of the spontaneous polarization.

Gauche conformers can also be accounted for in this construction by simply changing the all-trans conformation to ones including gauche bonds, as shown in Figure 7b. Comparing the structures 7(a) to 7(b) predicts a change in the sign of the spontaneous polarization for these two (*Sed*) homologues even when they have the same tilt orientation.

Unlike the case for the spontaneous polarization direction, a fuller understanding of the factors that influence the twist sense has still not been achieved, and therefore the root cause and mechanism of the twist in dissymmetric smectic phases remains unresolved. Finally, it is interesting to note that the same relationships which apply to smectics also operate for cholesterics. The spiral ordering in these two modifications occurs in different directions, lateral to the long axis in cholesterics and normal to the layers in tilted smectic phases. Seemingly this would support the evidence already obtained that the twist sense is not sensitive to dipolar orientational ordering.

(V) Conclusion

A hypothesis has been developed to explain the anomalous materials discovered which do not fit the spontaneous polarization direction–twist sense rules for ferroelectric liquid crystals proposed previously. This hypothesis proposes that changes in the steric tilt orientation of the molecules or conformational changes within the molecular structure are responsible for changes to the direction of the spontaneous polarization. The twist sense on the other hand was found in all these cases to be in agreement with the previous results and therefore it appears to be insensitive to orientational or conformational changes. The spontaneous polarization direction can be determined by examining the spatial orientation of the lateral component of the dipole at the chiral center relative to the tilt axis of the phase. The twist sense, however, is not sensitive to this lateral component, and therefore it is not effected by changes in its direction relative to the molecular long axis. However, it is still difficult to isolate single microscopic factors that determine the twist sense, and hence the root cause of the twist still remains an enigma. Thus, further studies of materials with different chiral groups bound to the liquid crystal core need to be made in order to substantiate these relationships and to elucidate the twist mechanism.

Acknowledgment. The authors are grateful to Dr. J. S. Patel for many useful discussions.

Registry No. II, 74109-50-5; V ($m = 3$, $n = 9$, $p = 2$), 102808-42-4; VI, 70116-35-7; VII, 90937-74-9; XI, 102808-40-2; XII, 102808-41-3; $C_7H_{15}OPhCOOPhCH{=}C(CN)COO2M4$, 90937-70-5; $C_8H_{17}OPhCOOPhCH{=}C(CN)COO2M4$, 90937-71-6; $C_{12}H_{25}PhSOCPhPhO2M4$, 102829-71-0; $C_7H_{15}OPhOCOPhO4M6$, 90937-55-6; $C_9H_{19}OPhOCOPhO4M6$, 90937-57-8.

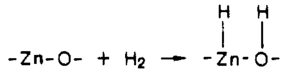
Hydrogen on Zinc Oxide. Theory of Its Heterolytic Adsorption

Alfred B. Anderson* and Jeffrey A. Nichols†

Contribution from the Chemistry Department, Case Western Reserve University, Cleveland, Ohio 44106. Received December 9, 1985

Abstract: An atom superposition and electron delocalization molecular orbital study is made of the adsorption of hydrogen species on the $(10\bar{1}0)$ prism surface of zinc oxide. 4s + 4p surface states on Zn^{2+} play a role in $H^\bullet$ adsorption on Zn^{2+} and O^{2-} surface sites. In the former case they provide the covalent stabilization of the Zn^{2+}–$H^\bullet$ bond and in the latter case they are reduced, allowing a strong O^{2-}–H^+ bond to form. Because of this, H_2 adsorbs heterolytically, yielding Zn^{2+}–H^- and O^{2-}–H^+ as the products of dissociative chemisorption. Our findings, which are based on calculations on a $Zn_{14}O_{14}$ cluster model, including surface relaxation, of the $(10\bar{1}0)$ surface are used to discuss the conductivities of the polar (0001) and $(000\bar{1})$ cleavage surfaces, the former consisting of Zn^{2+} and the latter of O^{2-}. It is suggested that the conductivities which are established when $H^\bullet$ adsorbs on either surface are the consequences of surface and edge sites associated with step defects and the reduction of step Zn^{2+} surface face and edge states when $H^\bullet$ adsorbs to step face and edge O^{2-} ions, respectively. Heterolytic adsorption of H_2 does not change the insulating property of ZnO.

Zinc oxide powder catalysts have been known for 25 years from infrared spectra to adsorb molecular hydrogen heterolytically[1]



$$-Zn-O- + H_2 \rightarrow -\overset{\overset{\displaystyle H}{|}}{Zn}-\overset{\overset{\displaystyle H}{|}}{O}- \qquad (1)$$

covering 5–10% of the surface sites.[2] This rapidly reversible reaction at room temperture provides active hydrogen atoms which hydrogenate ethylene and CO to form ethane and methanol. These processes are catalytic.

Heterolytic H_2 chemisorption does not change the conductivity of ZnO, which is an insulator.[2] This also indicates the adsorption is heterolytic, with H^- bonded to Zn^{2+} and H^+ bonded to O^{2-}. A second type of IR inactive and nonconductivity inducing hydrogen adsorption, called type II, takes place slowly and irreversibly.[1-3] Type II hydrogen does not exchange easily with the reversibly adsorbed type I form. Nothing is known about the form and location of type II hydrogen though it has been speculated that it may partially penetrate into bulk octahedral sites of the wurtzite structure crystal.[3] We shall not consider it further.

Hydrogen atom adsorption at 90 K on the polar (0001) and $(000\bar{1})$ cleavage surfaces causes the surface conductivity to increase.[4,5] The (0001) surface has Zn^{2+} in its top layer and the

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* Address inquiries to this author.

† Permanent address: Chemistry Department, Malone College, Canton, Ohio 44709.

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(2) Kokes, R. J. *Acc. Chem. Res.* **1973**, *6*, 222 and references therein.
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(4) Moormann, H.; Kohl, D.; Heiland, G. *Surf. Sci.* **1979**, *80*, 261.
(5) Heiland, G.; Kunstmann, P. *Surf. Sci.* **1969**, *13*, 72.

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