deuterium.) The highest occupied molecular orbital in donors like Me_2S is predominantly a nonbonding orbital on the heteroatom; however, this orbital has a contribution which is bonding in the β C-H stretching mode which is the most important in determining β-deuterium secondary isotope effects. For example, measurements of the detailed spectra of dimethyl sulfide and $(CD_3)_2S$ show the deuterated compound to have a higher ionization potential by about 230 cal/mol.[22] If this difference were fully realized at the transition state, the isotope effect on ET reaction of Me_2S would be predicted to be 1.39 at 80°. Thus the ET reactions listed in Table II probably have early transition states.[7]

We conclude that the dichotomy we have proposed is supported by isotope effect theory. Although more examples need to be studied, it appears that an isotope effect test does divide these reactions into SN2 and ET types and that this test can be used to probe whether radicals produced in donor-acceptor reactions arise from an ET mechanism.

Acknowledgment. This research was supported in part by the National Science Foundation, Grant GP38051X1. W.H.H., Jr., was an N.D.E.A. Fellow from 1970 to 1973 and an LSU dissertation Year Fellow Sept 1973-July 1974. We acknowledge helpful discussions with Professor Kendall N. Houk and Dr. Phillip Mollere.

References and Notes

(1) (a) Part I: W. A. Pryor, J. H. Coco, W. H. Daly, and K. N. Houk, *J. Amer. Chem. Soc.*, **96**, 5591 (1974); (b) part II: W. A. Pryor and W. H. Hendrickson, Jr., preceding paper.

(2) (a) G. A. Russell, R. D. Norris, and E. J. Panek, *J. Amer. Chem. Soc.*, **93**, 5839 (1971); G. A. Russell and W. C. Danen, *ibid.*, **88**, 5663 (1966); (b) N. Kornblum, T. M. Davies, G. W. Earl, G. S. Greene, N. L. Holy, R. C. Kerber, J. W. Manthey, M. T. Musser, and D. H. Snow, *ibid.*, **89**, 5714 (1967); (c) K. Tokumaru and O. Simamura, *Bull. Chem. Soc. Jpn.*, **36**, 333 (1963); (d) K. A. Bilevitch, N. N. Pubnov, and O. Yu. Okhlobystein, *Tetrahedron Lett.* 3465 (1968); (e) B. I. Shapiro, S. D. Stavrova, and I. P. Chikhackeva, *Dokl. Akad. Nauk SSSR*, **195**, 104 (1970); (f) J. F. Bunnett and B. F. Gloor, *J. Org. Chem.*, **39**, 382 (1974); (g) L. A. Hull, G. T. Davis, D. H. Rosenblatt, H. K. R. Williams, and R. C. Weglein, *J. Amer. Chem. Soc.*, **89**, 1163 (1967); (h) G. R. Chalfont and M. J. Perkins, *J. Chem. Soc. B*, 245 (1971); (I) S. Bank and D. A. Noyd, *J. Amer. Chem. Soc.*, **95**, 8203 (1973).

(3) (a) N. N. Semenov, "Some Problems of Chemical Kinetics and Reactivity," Vol. 1, translated by J. E. S. Bradley, Pergamon Press, New York, N.Y., 1958, pp 260–271; (b) W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N.Y., 1966, pp 117, 119–124, 180–186, 290; (c) K. A. Bilevitch and O. Yu. Okhlobystin, *Russ. Chem. Rev.*, **37**, 954 (1968); (d) J. F. Garst in "Free Radicals," Vol. 1, J. D. Kochl, Ed., Wiley, New York, N.Y., 1973, p 503ff.

(4) (a) W. A. Pryor, Abstracts of Papers, Presented to the International Symposium on Organic Free Radicals, Sirmione, Italy, June 1974; (b) W. A. Pryor and W. H. Hendrickson, Jr., Abstracts of Papers, American Chemical Society Meeting, Houston, Texas, Dec 1974.

(5) T. Sato, K. Takemoto, and M. Imoto, *J. Macromol. Sci., Chem.*, **2**, 69 (1968); *Makromol. Chem.*, **104**, 297 (1967); *ibid.*, **98**, 66 (1966); *ibid.*, **95**, 117 (1966).

(6) (a) D. M. Graham and R. B. Mesrobian, *Can. J. Chem.*, **41**, 2938 (1963); (b) K. F. O'Driscoll, P. F. Lyons, and R. Patsiga, *J. Polymer Sci., Part A*, **3**, 1567 (1965); (c) K. F. O'Driscoll and E. N. Ricchezza, *Makromol. Chem.*, **47**, 15 (1961); (d) C. Walling and N. Indictor, *J. Amer. Chem. Soc.*, **80**, 58i4 (1958); (e) W. A. Pryor and H. T. Bickley, *J. Org. Chem.*, **37**, 2885 (1972); (f) F. D. Greene, W. Adam, and J. E. Cantrill, *J. Amer. Chem. Soc.*, **83**, 3461 (1961); (g) F. D. Greene and W. Adam, *J. Org. Chem.*, **29**, 136 (1964); (h) this work. (i) D. B. Denny, W. F. Goodyear, and B. Goldstein, *J. Amer. Chem. Soc.*, **83**, 1726 (1961); (j) W. G. Bentrude and J. C. Martin, *ibid.*, **84**, 1561 (1962); (k) D. L. Tulene, W. G. Bentrude, and J. C. Martin, *ibid.*, **85**, 1938 (1963); (l) J. C. Martin and M. M. Chau, *ibid.*, **96**, 3319 (1974); (m) T. W. Koenig and J. C. Martin, *J. Org. Chem.*, **29**, 1520 (1964).

(7) The ρ for a complete ET would be expected to be large. For example, ρ for ionization of $ArCH_2\cdot$ in the gas phase is about -20.[8a] Thus $\rho \simeq 2$ for ET indicates an early transition state (TS). The scale of ρ values for SN2 reactions may be different,[8b] and $\rho \simeq 2$ may not indicate as early as a TS for a SN2 as for an ET reaction.

(8) (a) A. G. Harrison, P. Kebarle, and F. P. Lossing, *J. Amer. Chem. Soc.*, **83**, 777 (1961); (b) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N.Y., 1963, pp 178–182.

(9) Oxygen transfer products appear to be associated with ionic reactions, *i.e.*, $(CH_3)_2S{=}O$, epoxide, and $Ph_3P{=}O$ (reactions 3, 5, and 7 of Table I).

(10) Reactions cannot be divided into SN2 and ET types on the basis of their responsiveness to measures of solvent polarity such as dielectric constant or *Z*; see note 12 in ref 6e. The rates of SN2 reactions of the type studied here usually do not depend on solvent polarity.[8e,i] These ET reactions also usually show little dependence on solvent polarity, perhaps because they have very early TS's with little charge development.[7] Furthermore, radical production would be expected to depend on many solvent parameters. In particular, these solvent characteristics must be considered: viscosity,[11] complex formation between radicals (or ground states) and solvents,[12] the H bonding ability of solvents,[13] internal pressure,[14] and polarity.[15] Thus, effects of solvent polarity alone will only be discernible in a closely controlled series of solvents.

(11) (a) T. Koening and H. Fischer, ref 3d, p 157; (b) W. A. Pryor and K. Smith, *J. Amer. Chem. Soc.*, **92**, 5403 (1970).

(12) (a) Ref 3b, p 158ff; (b) J. C. Martin, ref 3d, Vol. II, p 493ff.

(13) (a) E. Niki and Y. Kamiya, *J. Amer. Chem. Soc.*, **96**, 2129 (1974); (b) G. Modena and P. E. Todesco, *J. Chem. Soc.*, 4920 (1962); (c) R. Curci, R. A. DiPrete, J. O. Edwards, and G. Modena, *J. Org. Chem.*, **35**, 740 (1970); (d) P. H. Emslie and R. Foster, *Recl. Trav. Chim. Pays-Bas*, **84**, 255 (1965); (e) O. B. Nagy, J. B. Nagy, and A. Bruylants, *J. Chem. Soc., Perkin Trans. 2*, 968 (1972); (f) J. A. Howard and E. Furlnsky, *Can. J. Chem.* **51**, 3738 (1973).

(14) M. R. J. Dack, *J. Chem. Educ.*, **51**, 231 (1974).

(15) E. M. Kosower, "Introduction to Physical Organic Chemistry," Wiley, New York, N.Y., 1968.

(16) (a) J. M. Harris, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 2551 (1971); (b) V. J. Shiner, Jr., and R. D. Fisher, *ibid.*, **93**, 2553 (1971); (c) L. R. C. Barclay, J. R. Mercer, and J. C. Hudson, *Can. J. Chem.*, **50**, 3965 (1972); (d) V. J. Shiner, Jr., W. E. Buddenbaum, B. L. Murr, and G. Lamaty, *J. Amer. Chem. Soc.*, **90**, 418 (1968).

(17) M. Wolfsberg, *Annu. Rev. Phys. Chem.*, **20**, 449 (1969).

(18) (a) M. Wolfsberg and M. J. Stern, *Pure Appl. Chem.*, **8**, 225 (1964); (b) J. Bron, *Can. J. Chem.*, **52**, 903 (1974).

(19) (a) E. D. Kaplan and E. R. Thorton, *J. Amer. Chem. Soc.*, **89**, 6644 (1967); (b) K. T. Leffek and A. F. Matheson, *Can. J. Chem.*, **49**, 439 (1971).

(20) The observed isotope effect (IE) of an SN2 reaction in which the product-forming step involves the abstraction of a β-hydrogen atom of the nucleophile (eq 1) may contain a contribution from a primary IE. For eq

$$(CH_3)_2S + XOOY \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (CH_3)_2\overset{+}{S}OY + XO^- \xrightarrow{k_d} CH_3S(OY){=}CH_2 + XOH \quad (1)$$

1, $k_{obsd} = k_1k_d/(k_{-1} + k_d)$. If k_{-1} is smaller than k_d, then k_{obsd} equals k_1, and the observed IE will be that on k_1. However, if k_{-1} is larger than k_d, then $k_{obsd} = k_1k_d/k_{-1}$, and the observed IE will contain a contribution from a primary IE on k_d. Therefore, the contribution from a primary IE to that observed will depend on k_d/k_{-1}. For example, in the reaction of phenylmethyl-d_3 sulfoxide with acetic anhydride, k_d is smaller than k_{-1} and the observed IE for this SN2 reaction is 2.9.[21] In the reaction of Me_2S with BPO, an inverse IE is observed, indicative that $k_d \gg k_{-1}$. The SN2 displacement of Me_2S on TBP should also have an inverse IE, and, since we observe a normal IE for this reaction, it must have an ET mechanism.

(21) S. Oae and M. Kise, *Tetrahedron Lett.*, 2261 (1968).

(22) R. McDiarmid, *J. Chem. Phys.*, **61**, 274 (1974). The Frank–Condon envelope technique was used; the difference between the proteum and deuterium compounds does not depend on the method used.

William A. Pryor,* William H. Hendrickson, Jr.
Department of Chemistry, Louisiana State University
Baton Rouge, Louisiana 70803

Received August 7, 1974

Surface Modified Mass Spectrometry

Sir:

The addition of a collision gas to the analyzer of a mass spectrometer causes ion-molecule reactions.[1] These processes, which occur at relative kinetic energies in the kilovolt range, are a valuable source of data on thermochemistry and ion structure and a useful adjunct to analytical mass spectrometry.[2,3]

We now report that it is possible to substitute a surface for the collision gas and so to effect processes which are analogous to high energy ion-molecule reactions. Thus, a surface-induced reaction has been observed corresponding to the process of collision-induced dissociation (CID), in which the ion converts translational to internal energy in the ion-molecule reaction and subsequently fragments. For an ion AB^+ and a surface S, this surface-induced dissociation (SID) is given as

$$AB^+ + S \longrightarrow AB^{+*}$$
$$AB^{+*} \longrightarrow A^+ + B$$

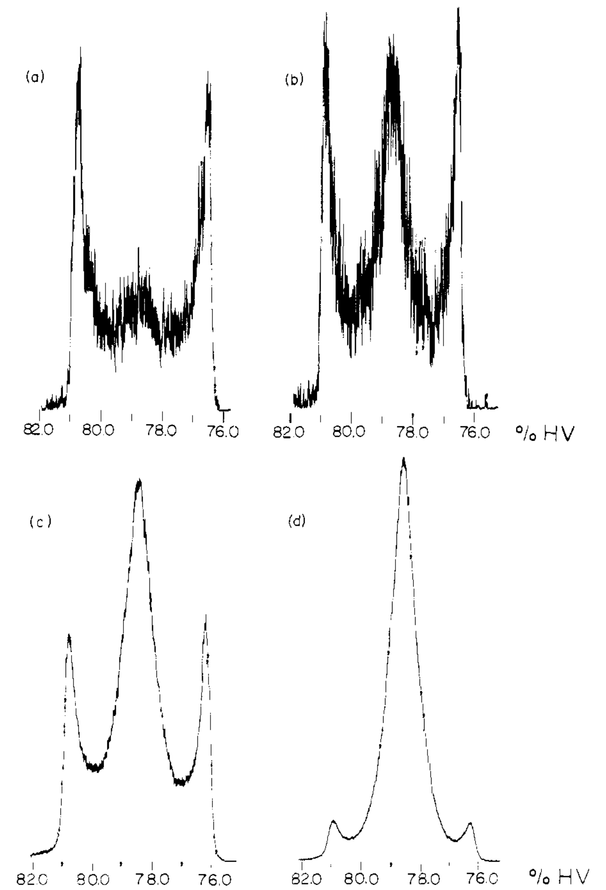


Figure 1. The reaction $CO_2^{2+} \rightarrow CO^{+\cdot} + O^{+\cdot}$ studied by kinetic energy analysis of the product $CO^{+\cdot}$ (*m/e* 28). The peaks were plotted by scanning the ion accelerating voltage (HV), and the abscissa is given as a fraction of the accelerating voltage required to transmit nonreacting ions. Peaks a and b were recorded prior to instrument modification and peaks c and d in the presence of the surface.

In addition, various charge transfer processes corresponding to those already known as high energy ion-molecule reactions have also been seen in the ion-surface experiments.

To effect these ion-surface reactions, the ion beam in the RMH-2 mass spectrometer[4] was shrouded by a 5 cm long stainless steel tube of rectangular cross section (9 × 3 mm) entered ~6 cm after the source slit. Experiments done before and after installation of the shroud were compared in assessing the nature of the ion-surface reactions.

Figure 1 provides an example of the efficient surface-induced reactions which have been encountered. The broad dished peak (a) is due to the unimolecular charge separation reaction in which the $CO^{+\cdot}$ product is analyzed:

$$CO_2^{2+} \longrightarrow CO^{+\cdot} + O^{+\cdot}$$

The effect of adding air as collision gas in the original instrument configuration is to produce the center component seen in part b. It is believed[5] that collision effects charge exchange and that some of the $CO_2^{+\cdot}$ ions formed retain sufficient internal energy to fragment spontaneously. When this experiment was repeated in the presence of the shroud, but in the absence of collision gas (pressure in analyzer 4×10^{-7} Torr), the peak shape seen in Figure 1c was recorded. Clearly the surface-induced process parallels the CID reaction. When collision gas (air) is now added so that both surface-induced and collision-induced processes occur (Figure 1d) the center component, as expected, is further enhanced but is qualitatively of the same shape and width.

As another example, consider the surface-induced dissociation of the methane molecular ion by the reaction

$$CH_4^{+\cdot} \longrightarrow CH_3^{+} + H\cdot$$

The corresponding unimolecular process occurs with a small kinetic energy release as well as being unusually sensitive to collision-induced dissociation, the latter process giving a somewhat shifted and much broader peak.[6] Before introduction of the shroud the relative heights of the two peaks were 4:1 at an indicated source pressure of 1.1×10^{-6} Torr and an analyzer pressure of 1.2×10^{-7} Torr. After the modification the situation was reversed with the broad peak now dominant even at analyzer pressures of less than 10^{-7} Torr. Thus the SID reaction gives rise to a peak which is analogous to the CID peak. The SID peak intensity in this and other cases was comparable to that produced by introducing $\sim 10^{-5}$ Torr of pressure into the entire first field-free region of the instrument. Evidence that an SID process is indeed being studied comes from the above pressure data and also from the fact that in analogous surface-induced charge transfer reactions the kinetic energy loss was quite different to that observed in collision-induced processes. For example, the charge exchange of doubly charged argon ions ($Ar^{2+} \rightarrow Ar^{+\cdot}$) has been studied both before[7] and after the instrumental modification. Using argon as collision gas, two peaks are observed in the kinetic energy spectrum of the product $Ar^{+\cdot}$ ions; one at 7.0 eV energy loss, due to excitation of the argon target, and another one at 2.2 eV energy gain, which was shown to be due to interaction with background air. After the shroud had been introduced, a third peak was observed at exactly zero kinetic energy change. This peak was independent of the collision gas pressure in the analyzer, and, in fact, it was the only peak observed when this pressure was reduced to 1×10^{-7} Torr. The conclusion is that it clearly represents the charge exchange reaction occurring with the surface.

For inelastic collisions of $Ar^{+\cdot}$ on argon the kinetic energy losses of the $Ar^{+\cdot}$ products were measured as 13, 32, and 48 eV. After introduction of the surface, a fourth intense peak appeared at 8.5 eV energy loss, which again persisted with no collision gas present, and thus must arise from the interaction with the surface. A similar observation was made in studying the charge inversion reaction[8] $Br^{+} \rightarrow Br^{-}$, a new pressure insensitive peak appearing at a smaller kinetic energy loss after the instrument modification. This reaction is particularly interesting since it involves transfer of two electrons from the surface. The kinetic energy lost by the ion contains a contribution due to the work function of the surface.

The close similarities between SID and CID reactions are expected since the function of the collision partner is to allow the conversion of translational energy of the ion into internal energy. The nature of the collision gas has only minor effects on the process. Replacement of the gaseous target by a solid therefore had advantages in terms of experimental convenience. The surface-induced dissociations (SID) studied here gave rise to peaks of intensity comparable to CID peaks and also showed the effects of kinetic energy loss and kinetic energy release on the position and width of the peak, respectively. The slit dimensions of the instrument restrict ion-surface interactions to very small scattering angles[9] (0.05° for specular scattering in the x-z plane which is believed to be the dominant process) so that the elastic energy loss is negligible (<1 eV).

While charge stripping has previously been observed on slit surfaces,[10] the reactions reported here are apparently novel. The grazing incidence arrangement of ion beam and surface is noteworthy. The interaction time of an 8 kV ion with a gas molecule is of the order of 10^{-14} sec (assuming a mass of 100 and an interaction range of 10^{-7} cm) while the interaction time in these experiments is of the order of 4 ×

10^{-11} sec.[11] Hence, even very low probability long range events become much more likely, and good signal intensity is obtained. This work suggests the possibility that a surface might be substituted for a collision gas as a convenient, simple and efficient method of exciting gaseous ions.

Acknowledgment We thank the National Science Foundation for its support of this work.

References and Notes

(1) J. J. Thomson, "Rays of Positive Electricity and Their Applications to Chemical Analysis", Green and Co. London, 1913, pp. 27–39.
(2) R. G. Cooks, J. H. Beynon, R. M. Caprioli, and G. R. Lester, "Metastable Ions", Elsevier, Amsterdam, 1973.
(3) R. G. Cooks and J. H. Beynon, *MTP* (*Med. Tech. Publ. Co.*) *Rev. Sci., Phys. Chem.*, in press.
(4) J. H. Beynon, W. E. Baitinger, J. W. Amy, and T. Komatsu, *Int. J. Mass Spectrom. Ion Phys.*, **3**, 47 (1969).
(5) Reference 2, p 80.
(6) B. H. Solka, J. H. Beynon, and R. G. Cooks, submitted for publication.
(7) T. Ast, D. T. Terwilliger, J. H. Beynon, and R. G. Cooks, *J. Chem. Phys.*, in press.
(8) T. Keough, J. H. Beynon, and R. G. Cooks, *Int. J. Mass Spectrom. Ion Phys.*, in press.
(9) The maximum angle is defined by the final slit height (5 mm) and the surface to detector distance (289 cm).
(10) (a) A. S. Newton, A. F. Sciamanna, and R. Clampitt, *J. Chem. Phys.*, **47**, 4843 (1967); (b) K. Okuno, Y. Kaneko, and I. Kanomata in "Recent Developments in Mass Spectrometry", K. Ogata and T. Hayakawa, Ed., University of Tokyo Press, 1970, p 830.
(11) Calculated assuming an average scattering angle of 0.025° and an interaction range of 10 Å. We thank a referee for comments on this point.

R. G. Cooks,* D. T. Terwilliger, T. Ast
J. H. Beynon, T. Keough
Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

Received August 26, 1974

Novel Stable Chiral Nematic (Cholesteric) Liquid Crystals

Sir:

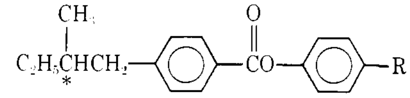
We wish to report the preparation of useful novel cholesteric liquid crystal materials possessing a combination of highly desirable properties: right-handed cholesteric type, very small optical pitch, and high chemical stability.

Liquid crystals with cholesteric properties have traditionally and most generally been based on the cholesteryl moiety.[1,2] In general, other optically active or chiral molecules with potential liquid crystal properties may also have a cholesteric mesophase. This type of cholesteric liquid crystal has also been called a chiral nematic liquid crystal.[3]

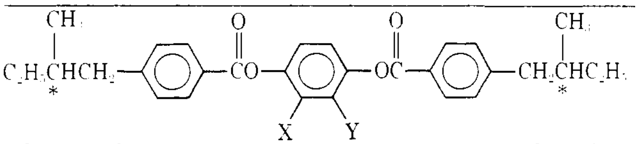
Examples of chiral nematic liquid crystals have been based on optically active 4-(2-methylalkoxy)biphenyl derivatives[4,5] and Schiff bases incorporating the optically active 2-methylbutyl group[6-10] or 1-deuteriobutoxy group.[11] These materials have large optical-pitch characteristics and/or are relatively unstable with respect to hydrolytic stability; in fact, the only materials known with small optical-pitch values are the hydrolytically unstable optically active 4′-alkoxybenzal-4-(2-methylbutyl)anilines (optical-pitch values ~0.35 μm), which have the optically active 2-methylbutyl group bonded directly to an aromatic ring without the intermediacy of an oxygen atom or other functionality.[3]

Our interest in and work with relatively stable ester-type liquid crystals,[12-14] led us to the investigation of optically active esters. We developed a synthesis for optically active 4-(2-methylbutyl)benzoyl chloride, which is obtained from the corresponding (+)-2-methylbutylbenzene[3] by means of a direct reaction with oxalyl chloride and aluminum chloride or via conversion of the alkylbenzene to the acetophenone, which is oxidized with hypochlorite to give the free acid. Simple phenyl benzoates as well as symmetrical and unsymmetrical phenylene diesters are prepared in the usual way[13,14] from reactions with phenols, hydroquinones, or 4′-substituted phenyl 4-hydroxybenzoates. We chose the optically active alkyl (rather than alkoxy) group because previous work[3] implied but did not show that this end group in general should favor chiral nematics with small optical-pitch values.

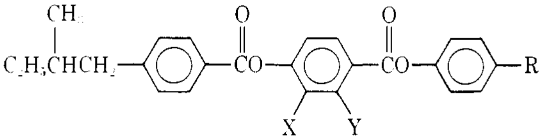
Table I. Chiral Nematic Esters



Compound no.	R	Mp, °C	Optical pitch, μm
1	C_3H_7	0	0.24
2	C_8H_{17}	−2	0.28
3	OCH_3	46	0.24
4	OC_6H_{13}	20 (13)[a]	0.29
5	OC_9H_{19}	27 (26)[a]	0.27
6	$OC_{12}H_{25}$	31	0.33
7	$O{=}COC_4H_9$	23	0.25
8	CN	37 (0)[a]	0.21



Compound no.	X	Y	Range, °C	Optical pitch, μm
9	H	H	$_{123}\underline{Ch}_{132}$	0.15
10	Cl	Cl	$_{98}\underline{S}_{103}\underline{Ch}_{111}$	0.18
11	CH_3	H	$_{71}\underline{S}_{93}$	0.17



Compound no.	R	X	Y	Range, °C	Optical pitch, μm
12	C_3H_7	H	Cl	$_{35}\underline{Ch}_{92}$	0.32
13	C_4H_9	H	Cl	$_{40}\underline{Ch}_{86}$	0.32
14	C_5H_{11}	H	Cl	$_{47}\underline{Ch}_{95}$	0.32
15	C_5H_{11}	Cl	H	$_{68}\underline{Ch}_{102}$	0.37
16	C_6H_{13}	H	Cl	$_{36}\underline{Ch}_{80}$	0.32
17	C_8H_{17}	H	Cl	$_{36}\underline{Ch}_{83}$	0.34

[a] Monotropic

Typical examples of three types of chiral nematic esters are shown in Table I. The simple esters often exhibit a monotropic mesophase (**4**, **5**, **8**) and the phenylene diesters **9–17** are enantiotropic, wherein the phenylene diesters **12–17** with unsymmetrical ester linkages have the lower and broader ranges. As expected, the simple-ester alkyl derivatives **1** and **2** are lower melting than the alkoxy derivatives **3–6**. The simple-ester cyano derivative **8** is monotropic, but compatible with other mesomorphic esters as a mixture component of high positive dielectric anisotropy. Chiral nematic phenylene diesters with unsymmetrical ester linkages have broad cholesteric ranges extending from just above room temperature. As with the nematic esters of this type[12,14] the position of the lateral chlorine atom has a pronounced effect upon the lower end of the mesomorphic range (compare **14** with **15**). These diesters are obviously well-suited for components in broad range mixtures.

Measurements of the "handedness" of these new cholesteric materials indicate that they possess right-handed cho-