peratures reported by Gallagher and Fenn[15] as well as by Hüber-Walchli and Nibeler.[17]

Figure 1 shows the dependence of k_{expt} for reaction 1 on the translational temperature present in the jet. The measured rates are approximately one order of magnitude greater than those at 300 K and show a significant negative temperature dependence. Since the neutral H_2 does not have a permanent dipole moment, the temperature dependence suggests that the reaction mechanism proceeds through a long-lived collision complex. Competition between reactive branching and complex dissociation can then lead to negative temperature dependence in the net reaction rate coefficient. The deuterated analogue to reaction (1) exhibits an

$$C_2D_2^+ + D_2 \rightarrow C_2D_3^+ + D \qquad (3)$$

observed rate that is about 3 times slower than reaction 1. From the vibrational frequencies of all reactants and products,[18] we calculate that reaction 3 should be 1.4 kcal mol^{-1} less exothermic than reaction 1. Although the observed kinetic isotope effect may originate from the zero point energy effects, it could also be a manifestation of reactive branching involving H/D tunneling through a barrier. A simple reinterpretation of the data of Adams and Smith on the endothermicity of the reaction would then lead to a barrier height of at least 1.6 kcal mol^{-1}.[7] Reactant collisions would initially form a $(C_2H_4)^{+*}$ complex, which would then branch between dissociative and reactive tunneling channels.

$$C_2H_2^+ + H_2 \underset{k_d}{\overset{k_c}{\rightleftharpoons}} (C_2H_4)^{+*} \xrightarrow{k_t} C_2H_3^+ + H \qquad (4)$$

The total energy of the $(C_2H_4)^{+*}$ complex is determined by the relative collision energy and the rotational energy of the H_2. Assuming rapid energy randomization, k_t and k_d are only functions of the total energy of the collision complex. The rotationally excited H_2 molecules cannot drive the reaction over the barrier. As the translational temperature is decreased in our experiments, the rotational temperature drops in proportion, yet the observed rate coefficient is found to rapidly increase. This strongly implies that the observed reaction in the jet is not being driven by excited rotational states. Reactive tunneling of a hydrogen atom from a low energy collision complex could be the dominant mechanism at low temperatures.

From phase space calculations,[19] we estimate that the lifetime for a 2 K collision with H_2 in $j = 1$ is about 5000 times shorter than that for $j = 0$. If our above mechanism is correct, the observed low reaction efficiency and the calculated lifetimes suggest that only collisions with $H_2(j=0)$ lead to complexes where tunneling can effectively compete with complex dissociation to reactants. This point is supported by the observed low-temperature behavior of the rate. A collision involving $H_2(j=1)$ brings 122 cm^{-1} of rotational energy into the complex. A small change in the collision energy (±0.5 cm^{-1}) would have an insignificant effect on the lifetime of the collision complex. Therefore, the rate coefficient will remain relatively constant, and no temperature dependence from $k(\epsilon,j=1)$ would be observed. Since the relative population of $j = 1$ is approximately 3 times that of $j = 0$ due to spin statistics, the observed temperature dependence in itself suggests that only $j = 0$ collisions result in reaction. Using the experimental rotational distributions of Gallagher and Fenn,[15] we can then determine $k(T,j=0)$ from k_{obsd}. This calculation suggests a rate coefficient of $(6.2 \pm 3) \times 10^{-10}$ cm^3 s^{-1} for reaction 1 involving pure para-H_2 at 2 K and a true kinetic isotope effect of 6. The fact that the reaction occurs at 2 K allows us to establish a new upper limit to the heat of formation of $C_2H_3^+$ of $\Delta H°_{f_0} \leq$ 265.9 kcal mol^{-1}. This result is also supported by dissociative photoionization studies of C_2H_6 and C_2H_3Cl.[20,21] The barrier (either energetic or dynamic) to the reaction must impede the $C_2H_3^+$ channel in the photoionization of C_2H_4. From these experiments, we believe that 265 ($^{+1}_{-2}$) kcal mol^{-1} is the correct value for the $C_2H_3^+$ heat of formation at 0 K. This value would then make reaction 3 0.5 kcal mol^{-1} endoergic and may explain the kinetic isotope effect, independent of a barrier on the surface. This heat of formation also requires the C-H bond energy of ethylene to be in excess of 104.9 kcal mol^{-1}.[22]

The observation of reaction 1 near 2 K is important to the C_2H_n chemistry observed in interstellar gas clouds.[23] The major production channel for C_2H^+ is photoionization of C_2H. This ion reacts rapidly with H_2 to produce $C_2H_2^+$. Previously, it was thought that the major loss channel of $C_2H_2^+$ was dissociative electron-ion recombination to produce CH or C_2H. This study suggests that in dense clouds the major loss channel may not be recombination, but reaction with H_2 to form $C_2H_3^+$, depending on the thermal conditions and the density of the cloud. This ion does not react with H_2 and will most likely recombine with electrons to produce neutral acetylene and possibly other radicals.

Tunneling is rarely a dominant mechanism in gas-phase chemistry, where collision times are usually extremely short. Dunn's group has suggested that tunneling plays an important role in the low-temperature reaction between NH_3^+ and H_2.[24,25] Their results, combined with the results reported in this communication, suggest that some reactions involving the transfer of H or H^+ may show dramatic increases in rate at low temperatures. This effect can have important consequences regarding the chemistry and isotopic balance in low-temperature environments such as the interstellar medium.

Acknowledgment. This work was supported through financial assistance provided by the Finnigan-MAT Corporation through the American Society for Mass Spectrometry and the National Science Foundation through Grant No. CHE-8820740. We thank Dr. P. A. M. Van Koppen and Prof. M. T. Bowers for providing us with a copy of their phase space codes.

(17) Hüber-Walchli, P.; Nibeler, J. W. *J. Chem. Phys.* **1982**, *76*, 273-279.
(18) Lee, T. J.; Schaefer, H. F., III *J. Chem. Phys.* **1986**, *85*, 3437-3443.
(19) Bass, L.; Chesnavich, W. J.; Bowers, M. T. *J. Am. Chem. Soc.* **1979**, *101*, 5493-5502.
(20) Stockbauer, R. *J. Chem. Phys.* **1973**, *58*, 3800-3815.
(21) Reinke, D.; Kraessig, R.; Baumgartel, H. *Z. Naturforsch., A* **1973**, *28*, 1021-1026.
(22) Berkowitz, J.; Mayhew, C. A.; Ruscic, B. *J. Chem. Phys.* **1988**, *88*, 7396-7404.
(23) Winnewisser, G.; Herbst, E. *Top. Curr. Chem.* **1987**, *139*, 119-172.
(24) Luine, J. A.; Dunn, G. H. *Astrophys. J.* **1985**, *299*, L67-L70.
(25) Barlow, S. E.; Dunn, G. H. *Int. J. Mass Spectrom. Ion Processes* **1987**, *80*, 227-237.

High-Resolution NMR in Cholesteric Medium: Visualization of Enantiomers

E. Lafontaine, J. P. Bayle, and J. Courtieu*

Laboratoire de Chimie Structurale Organique
I.C.M.O. Bat. 410, Université Paris Sud
91405 Orsay, France

Received March 14, 1989

The technique of NMR associated with liquid crystal solvents has been widely used for the past 20 years to study the structure and ordering of solute molecules. Most of the work has been realized in nematic phases. The reason is that nematics orientated themselves very rapidly and homogeneously in the magnetic fields commonly employed in NMR spectroscopy. On the other hand, much less work has been published which concerns experiments with cholesteric liquid crystal solvents. The latter are known as nematics twisted under the influence of chiral centers, and they give rise to a director field of the helical structure.[1,2] The response of a cholesteric phase to an external homogeneous magnetic field depends on the sign of its molecular anisotropic magnetic susceptibility. Collings et al.[3] have shown that when $\Delta\chi$ is positive,

* Author to whom correspondence should be addressed.

(1) Friedel, G. *Ann. Phys. (Paris)* **1922**, *18*, 273.
(2) Buckingham, A. D.; Ceasar, G. P.; Dunn, M. B. *Chem. Phys. Lett.* **1969**, *3*, 540.

0002-7863/89/1511-8294$01.50/0

Table I. Parameters of Spin Hamiltonian in Hz for the Nematic and the Cholesteric Solvents[a]

solvent	chemical shifts			dipolar couplings			RMS error
	δ_1	δ_2	δ_3	D_{12}	D_{13}	D_{23}	
nematic (ZLI 2806)	0.0	−22.4	130.8	48.5	272.5	−5.3	0.8
1.35/1 by weight mixture of cholesteryl propionate and ZLI 2806	0.0	−5.5	144.2	−135.1	221.0	−20.5	0.4
	0.0	−5.1	144.1	−123.9	216.4	−23.1	0.4

[a] The chemical shift of H_1 is taken as an arbitrary reference.

then the helix axis tends to align itself perpendicular to the magnetic field (B_0). In this situation the director is distributed in a plane which contains B_0. No high-resolution NMR is then possible as there is no homogeneous orientation of the director with respect to the magnetic field. The situation is more interesting if $\Delta\chi$ is negative, then the helix axis should orientate itself parallel to B_0 in such a way that the director should be distributed in a plane perpendicular to the magnetic field. The orientation of the director is then expected to be homogeneously orientated at 90° from B_0 and should provide a high-resolution NMR spectrum for small dissolved molecules. Unfortunately it has been shown[4] that iin this situation the director does not orientate homogeneously enough to provide high resolution NMR spectra, i.e., NMR lines 1–3 Hz wide. This has been attributed to existing textural defects and elastic forces that the magnetic field cannot overcome.[4] This is an unfavorable effect as these chiral phases are expected to orient different enantiomers.

In 1968 Snyder et al. performed a very clever experiment. Realizing that the helicity of the cholesteric phase was the origin of the low quality of the orientation, they made up a chiral nematic solvent from a compensated mixture of two different cholesteric compounds. By using racemic 1,2-epoxy-3,3,3-trichloropropane (Figure 1) as a guest solute, they announced that they obtained separate spectra for each enantiomer.[5] Several attemps have been made by us recently to reproduce the same effect without success. The orientation does not appear good enough, as can be seen in Figure 1a, even with a 6.2 T supercon magnet. The NMR lines still appear to be 30–40 Hz wide.

Some questions have been raised as to the reason why a cholesteric phase of negative $\Delta\chi$ does not orient homogeneously and whether it is possible to create a cholesteric phase which orients homogeneously enough to provide an orientated high-resolution NMR chiral solvent. One of the possible answers to the above is that the helicity is the main hindrance and that the higher the pitch, the easier the orientation will be as the textural defects are now less pronounced. The second remark results from the analyses of mobility and viscosity coefficients of the $\Delta\chi < 0$ nematics made of bicyclohexyl derivatives.[6] Also, it is well-known that mixing a nematic with a chiral compound results in an induced cholesteric phase. The above three remarks grouped together have guided us to realize a kind of induced cholesteric made from a mixture of nematic bicyclohexyl compounds and some cholesteryl derivatives known to induce a low pitch.[7]

In the course of such a systematic study, we had the chance to discover a cholesteric mixture made from a 1.35/1 by weight concentration of cholesteryl propionate in ZLI 2806 (a nematic mixture from Merck) which orients homogeneously in a macroscopic scale almost as easily as a pure nematic in a 6.2 T magnetic field. This can be checked first by the Bragg-type diffraction displayed by the sample.[8] More efficiently, the quality of the orientation can be assessed by the NMR spectrum of the racemic

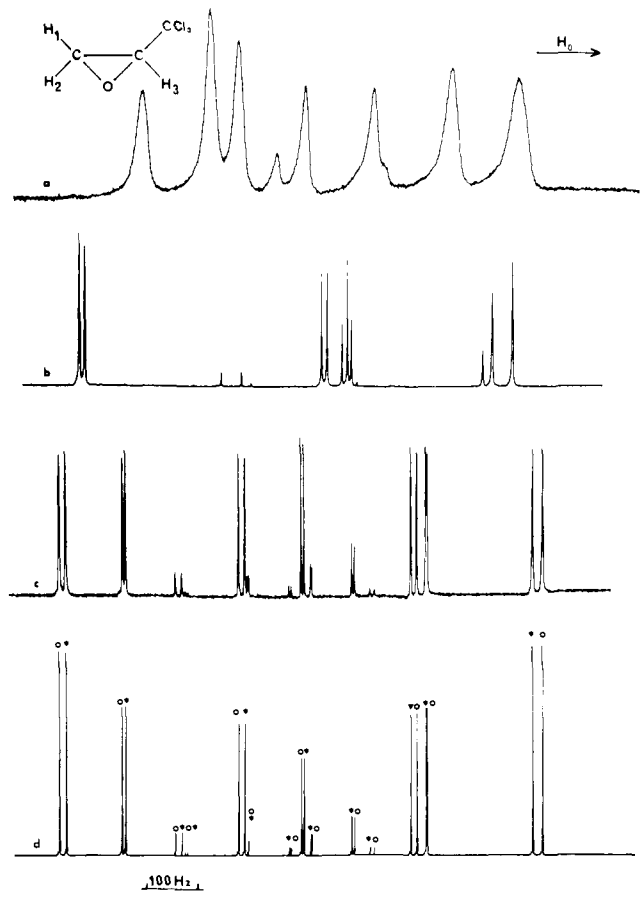


Figure 1. Spectra of the racemic 1,2-epoxy-3,3,3-trichloropropane in the following different liquid crystals solvents. (a) Compensated mixture of cholesteryl chloride and myristate (1.9/1 weight ratio). T = 313 K. (b) Pure $\Delta\chi < 0$ nematic (ZLI 2806). T = 323 K. (c) Cholesteric mixture of cholesteryl propionate and ZLI 2806 (1.35/1 weight ratio). T = 337 K. Note the doubling of this spectrum as compared to (b). (d) Simulated spectra of both enantiomers using the fitted parameters reported in Table I. Peaks due to each enantiomer are labeled by (▼) and (○).

1,2-epoxy-3,3,3-trichloropropane dissolved in such a mixture (Figure 1c). On this spectrum it can be noted first that the line width is of the order of 2 Hz for all transitions. This is a severe test of the quality of the orientation. Furthermore and nonetheless, this mixture also provides an extraordinarily wide separation of the dissolved enantiomers spectral lines that we primarily looked for (compare Figure 1 (parts c and b)).

In Table I are reported the chemical shifts and dipolar couplings obtained through spectrum simulation and iteration on the 14 experimental line positions of each enantiomer (Figure 1d). As it is well-known that the ABC spectrum cannot be iterated by using all of the nine spectral parameters, the scalar couplings have been assumed to have their isotropic values (J_{12} = 4.66 Hz, J_{13} = 2.15 Hz, J_{23} = 3.65 Hz). A crude analysis of the results shows that, within the experimental errors, the chemical shifts are the same for both enantiomers in a given solvent at a given temperature. Their only difference appears to be due to dipolar couplings. As the distances between proton nuclei are the same the origin of the spectral line separation of these enantiomers has to be ascribed

(3) Collings, P. J.; Goss, S. I.; McColl, J. R. *Phys. Rev. A.* **1975**, *11*, 684–689.
(4) Luz, Z.; Poupko, R.; Samulski, E. T. *J. Chem. Phys.* **1981**, *74(10)*, 5825–5837.
(5) Sackmann, E.; Meiboom, S.; Snyder, L. C. *J. Am. Chem. Soc.* **1968**, *90*, 2183–2185.
(6) Pohl, L.; Eidenschink, R.; Krause, J.; Weber, G. *Phys. Lett.* **1978**, *65A*, 169–172.
(7) Baessler, L.; Labes, M. M. *J. Chem. Phys.* **1970**, *52*, 631–637.
(8) Gray, G. *Molecular Structure and Properties of Liquid Crystals*; Academic Press: London, 1967.

to the difference between their average orientational parameters in the chiral medium.

The effect described here opens up a new and very wide field in the study of the geometry of chiral molecules through their dipolar spectra. Furthermore, following the work of Solladié et al.[9] regarding the sign of the pitch induced by a chiral molecule, it could be possible to relate the orientational parameters to the absolute configuration of the enantiomers in a given homologous compound series.

A systematic study is underway in our laboratory to optimize the different parameters such as temperature, relative concentration, and nature of the nematic and the cholesterogenic compounds as well as other NMR experimental conditions. On a more theoretical point of view, we are analyzing the effect of the pitch and the elastic constants of the twist[10] in these mixtures in order to be able to account for their interesting behavior in a magnetic field. There certainly exist other potential applications for these macroscopically, easily orientated cholesteric phases, to name a few—color display, light modulator in the visible and near-infrared range, etc.

(9) Solladié, G.; Zimmermann, R. G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 348-362, and references therein.
(10) De Gennes, P. G. *Solid State Commun.* **1968**, *6*, 163-165.

Very Strong Binding of Appropriate Substrates by Cyclodextrin Dimers

Ronald Breslow,* Noam Greenspoon, Tao Guo, and Ryszard Zarzycki

Department of Chemistry, Columbia University
New York, New York 10027

Received June 8, 1989

With the best substrates, a well-fitting cyclodextrin can achieve a binding constant, in water, of ca. 10^4 M^{-1}; this is not as strong as some enzymes and most antibodies, which typically bind several substrate segments. Many years ago we prepared dimeric cyclodextrin[1] **1**; other linked cyclodextrin dimers have also been made.[2] Recently dimer **2** has been reported,[3] and the finding that it shows reasonably strong (2×10^6 M^{-1}) binding of ethyl orange. However, only one segment of ethyl orange is significantly hydrophobic. We find that with substrates bearing two real hydrophobic segments the binding by dimeric cyclodextrins can be very strong.

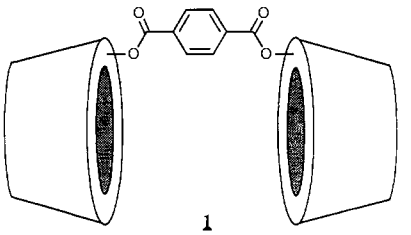
As binding hosts we examined dimers **2-4**. Compound **3** was prepared by opening our β-cyclodextrin 2,3-mannoepoxide[4] with benzyl mercaptan, then reduction (Na, NH_3) to the thiol, and air oxidation to the disulfide **3**.[5] It is thus the 2-epihydroxy 3-epidisulfide. It showed the expected ^{1}H NMR spectrum and a *m/e* (FAB) of 2323 (M + Na). Compound **4** was prepared by acylation of β-cyclodextrin at C-6 with thioxanthone-3,6-dicarbonyl dichloride. After purification by reverse-phase chromatography, it showed the expected ratios of aromatic and anomeric protons in the 400-MHz ^{1}H NMR spectrum.

We examined compounds **5-16**[6] as guests. Binding into the hosts led to an observable change in circular dichroism (CD), used to determine binding constants. Sometimes competition studies were used to establish or confirm binding constants. We have also synthesized BNS[7] (**17**),[8] an analogue of ANS that binds strongly to **2**, producing a fluorescent complex. Some binding constants were established by competition of **17** with other guests for binding into **2**.

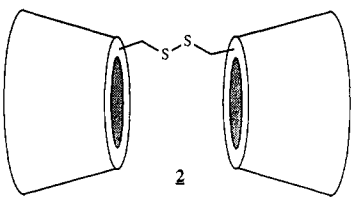
Table I. Binding Constants (25 °C)

guest	solvent	K_a,[a] M^{-1}
	To Host **2**	
acetylene **5**	glycol	$9 \pm 2 \times 10^3$
trans-stilbene **7**	glycol	$2 \pm 1 \times 10^4$
ester **8**	glycol	$1.3 \pm 0.01 \times 10^4$
dihydrostilbene **10**	glycol	1×10^4[b]
N-methylamide **15**	glycol	$9 \pm 3 \times 10^3$
cis-stilbene **6**	H_2O	$<3 \times 10^3$
ester **8**	H_2O	$1 \pm 0.8 \times 10^8$
amide **9**	H_2O	$2.4 \pm 0.4 \times 10^4$
disulfide **11**	H_2O	$1 \pm 0.3 \times 10^6$
fumarate **12**	H_2O	$<3 \times 10^3$
cyclopropene **13**	H_2O	3.5×10^8[c]
cyclopropane **14**	H_2O	1×10^8[c]
p-tert-butylphenol (**16**)	H_2O	$1.6 \pm 0.4 \times 10^4$
BNS (**17**)	H_2O	5×10^6[d]
	To Host **4**	
cyclopropene **13**	glycol	1.3×10^5
cyclopropene **13**	H_2O	7.0×10^8[e]

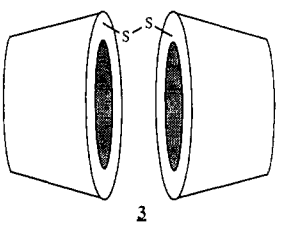
[a] From the change in circular dichroism intensity with varying concentrations of the guest, except where noted. [b] By competition with **5**, whose induced circular dichroism is significant. [c] By competition with the fluorescent guest **17**. [d] From the change in fluorescence intensity with varying concentrations of the host. [e] By competition with host **2** for the guest.



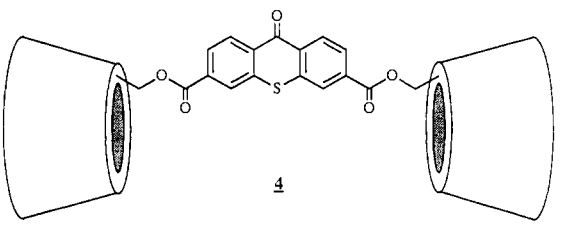
1



2



3



4

(1) Chao, Y. Ph.D. Dissertation, Columbia University, New York, 1972.
(2) (a) Harada, A.; Furue, M.; Nozakura, S.-I. *Polym. J.* **1980**, *12*, 29. (b) Tabushi, I.; Kuroda, Y.; Shimokawa, K. *J. Am. Chem. Soc.* **1979**, *101*, 1614. (c) Fujita, K.; Ejima, S.; Imoto, T. *Chem. Lett.* **1985**, 11.
(3) Fujita, K.; Ejima, S.; Imoto, T. *J. Chem. Soc., Chem. Commun.* **1984**, 1277.
(4) Breslow, R.; Czarnik, A. W. *J. Am. Chem. Soc.* **1983**, *105*, 1390.
(5) This compound was first prepared in our laboratories by Dr. Albrecht Berkessel.
(6) All were characterized by ^{1}H NMR and MS. The syntheses are straightforward; the cyclopropene and cyclopropane were prepared by reaction of ethyl diazoacetate with the appropriate acetylene or olefin.

0002-7863/89/1511-8296$01.50/0