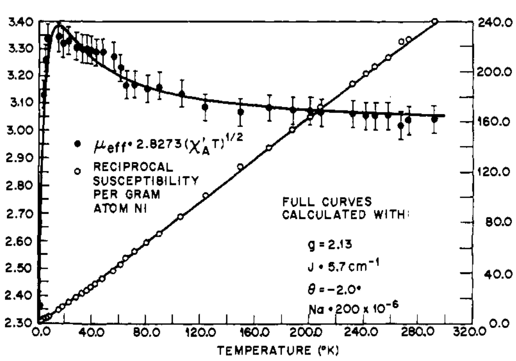

Figure 2. Temperature dependence of μ_{eff} (BM) per Ni atom and $1/\chi_A'$ for $[Ni_2(en)_4(SCN)_2]I_2$.

spins are coupled parallel, corresponds to a μ_{eff} of 3.46 BM per Ni atom for $g = 2$. Our results suggest that the dimer molecules are in a state of total spin $S' = 2$ below ~20°K, but the full value of μ_{eff} is not observed because of a lattice antiferromagnetic interaction which causes the observed decrease in moment at low temperatures. This conclusion is supported by comparison of the experimental results with the susceptibility equation for a nickel dimer

$$\chi_A' = \frac{3K}{T - \theta}\left[\frac{1 + 5e^{4J/kT}}{3 + 5e^{4J/kT} + e^{-2J/kT}}\right] + N\alpha$$

where J is the exchange integral, $N\alpha$ is the temperature-independent paramagnetism, $K = g^2N\beta^2/3k$, and θ is an effective Weiss constant included to take account of weak lattice interactions. The three sets of data were treated separately; the least-squares best fit to the susceptibility equation is obtained for $J = 7.4$–$8.1°$ ($\equiv 5.1$–5.6 cm^{-1}), $g = 2.08$–2.13, and $\theta = -2.2$ to $-2.0°$ with $N\alpha$ fixed at 200×10^{-6} cm^3 g-atom^{-1}. Figure 2 shows the comparison between experiment and theory; the agreement is satisfactory.

Further support for the conclusion that the two Ni atoms in $[Ni_2(en)_4(SCN)_2]I_2$ are ferromagnetically coupled to give an $S' = 2$ molecular ground state, and that the dimer molecules in this ground state engage in a lattice antiferromagnetic interaction, is provided by the magnetization curve ($\langle\mu\rangle$ dimer *vs.* H) determined at 1.65°K. The curve is linear and may be fitted to the molecular field theory equation

$$\langle\mu\rangle_{\text{dimer}} = \frac{g^2\beta S'(S' + 1)H}{3k(T - \theta)}$$

for $g = 2.10$, $\theta = -2.7°$, and $S' = 2$, in agreement with the results described above.

In view of the long Ni–Ni distance in $[Ni_2(en)_4(SCN)_2]I_2$, it is clear that the exchange coupling must take place *via* the bridging thiocyanate groups. By analogy with the molecular orbital description of the isoelectronic molecule CO_2,[9] the ground state of NCS^- may be written as $(2s_N)^2(3s_S)^2(\sigma_s{}^b)^2(\sigma_z{}^b)^2(\pi_{x,y}{}^b)^4(\pi_{x,y})^4$, where the π orbitals are of the form $\pi_y{}^b = c_12p_{yN} + c_22p_{yC} + c_33p_{yS}$ and $\pi_y = c_42p_{yN} - c_53p_{yS}$, and the σ orbitals are $\sigma_s{}^b = c_62s_C + c_72p_{zN} + c_83p_{zS}$ and $\sigma_z{}^b = c_92p_{zN} + c_{10}2p_{zC} + c_{11}3p_{zS}$. From the point of view of Anderson's expanded-orbital theory,[10] assuming an idealized geometry with linear thiocyanate bridges and 90° N–Ni–S angles, the pathways for ferromagnetic coupling may be written $e_g(Ni_I)||\sigma_z{}^b \perp \pi_y{}^b||e_g(Ni_{II})$, $e_g(Ni_I)||\sigma_z{}^b \perp \pi_y||e_g(Ni_{II})$, $e_g(Ni_I)||\sigma_s{}^b \perp \pi_y{}^b||e_g(Ni_{II})$, and $e_g(Ni_I)||\sigma_s{}^b \perp \pi_y||e_g(Ni_{II})$, where || symbolizes overlap and ⊥ represents orthogonality. The first of these pathways is exactly analogous to the principal pathway for ferromagnetic coupling in a monatomic 90° Ni–X–Ni bridge where a $2p_y$ atomic orbital is used instead of the three-center $\pi_y{}^b$ orbital.[11] The other pathways are not present in a monatomic bridge, but occur here because the thiocyanate bridge is polynuclear.

It is particularly interesting to compare the exchange coupling in $[Ni_2(en)_4(SCN)_2]I_2$ with that in $[Ni_2(en)_4Cl_2]Cl_2$. The latter compound has a dimeric cation[12] with two Cl bridging atoms. The Ni–Cl–Ni angle was not reported in ref 12, but is not likely to deviate much from 90°. As expected, magnetic measurements show the molecular ground state to have $S' = 2$. From the susceptibility *vs.* temperature curve we find $J = 13°$ ($\equiv 9$ cm^{-1}), $g = 2.15$, and $\theta = -2.2°$.

We conclude that the essential requirement for ferromagnetic coupling between Ni atoms is the availability of connecting orbitals of proper symmetry. If the connecting orbitals are multicenter molecular orbitals, the coupling can take place over long distances and through polyatomic bridges.

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Received July 13, 1971

Induced Circular Dichroism in Cholesteric Liquid Crystals

Sir:

During the past decade or so, there have been several reports of induced optical activity in inactive molecules either complexed to polypeptides while in a helical conformation[1-4] or noncomplexed in chiral solvents,[5,6] or as aggregated dyes.[7] This phenomenon has also been used for determining optical purities and absolute configurations.[8,9]

We wish to report that optically inactive molecules become chiral when dissolved in cholesteric liquid crystals, as detected by circular dichroism in

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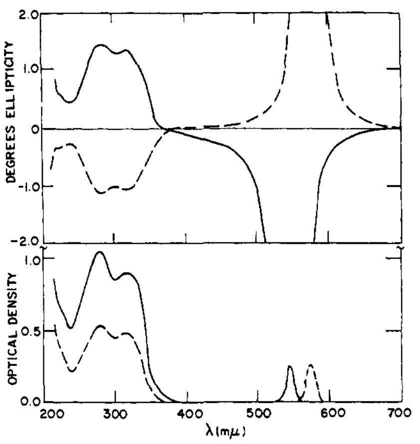

Figure 1. Circular dichroism (upper) and absorption spectrum (lower): ---, 6.3-μ film of *N*-(*p*-methoxybenzylidene)-*p*-butylaniline (**1**) (52.5 mg) in 10.0 g of 27.7:72.3 wt % cholesteryl chloride (**2**)–cholesteryl nonanoate (**3**) (right-hand helix); —, 11.7-μ film of **1** (63.19 mg) in 10.0 g of 90.6:9.4 wt % **2**:**3** (left-hand helix).

their electronic transitions, and that potentially chiral molecules show a helical stacking preference.

Cholesteric liquid crystals are known to form macroscopic helical structures by molecular association which can be either left or right handed.[10] This helical sense can be deduced from the sense of optical rotation at a wavelength small in comparison to the critical inversion wavelength λ_0 in deVries' equation.[11,12] While investigating the optical activity associated with liquid crystalline mixtures of *N*-(*p*-methoxybenzylidene)-*p*-butylaniline (**1**), a room temperature nematic,[13] in cholesteryl chloride (**2**) with a polarizing microscope, anomalous wavelength behavior from that predicted by deVries was observed in the vicinity of the anil absorption bands. We have extended our observations to clarify this behavior. Figure 1 shows the circular dichroism (CD) and absorption spectrum of left- and right-handed cholesteric mesophases in which **1** has been dissolved. Selective reflection of circularly polarized light of one sense at the cholesteric pitch band[14] occurs between 500 and 600 mμ while anil absorption lies between 220 and 390 mμ. Spectroscopy was performed on thin films of the mesophases between 1 in. × 1/8 in. quartz disks using a Cary 60 spectropolarimeter and a Cary 14 spectrophotometer for the circular dichroism and absorption spectra, respectively. It is apparent from Figure 1 that induced circular dichroism (ICD) is present, and that the sign of the ICD bands in the anil is opposite to that of the pitch-band CD of the cholesteric liquid crystal. The sign of the ICD bands has been found to be always opposite to the pitch-band CD and appears entirely independent of solute molecular structure. A variety of chemical structures (*i.e.*, azo compounds, aromatic ketones, anils) all show this effect, even though the solutes are not liquid crystalline themselves. The sign of the ICD bands of **1** is dependent upon the sense of the cholesteric helix, being positive for a left-hand helix, and negative for a right-hand helix. When the cholesteric environment is converted to an inactive nematic mesophase either by use of a compensated mixture of cholesteryl compounds[10] or by conversion to a nematic mesophase with an electric field,[15] ICD no longer exists, indicating that a macroscopic helical structure, not just a chiral solvent, must be present for the induced effect. Molecular ellipticity [θ] values for the 280-mμ electronic transition in **1** are +55,270 and −89,421° for the solid and dashed lines. The difference in molecular ellipticity values is tentatively attributed to a variation in pitch of the cholesteric mesophase. This conclusion is supported by the observation that the ICD band intensity increased as the pitch of a cholesteric mesophase was increased by thermal means in a separate experiment. Such a relationship between pitch and ICD band intensity cannot continue indefinitely, however, since the intensity must go to zero when the pitch increases to infinity. This dependence requires further investigation.

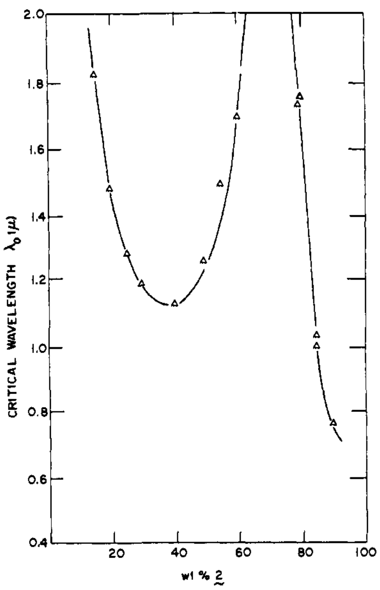

Figure 2. Plot of critical wavelength λ_0 (μ) *vs.* weight per cent cholesteryl chloride (**2**) in mixture with *N*-(*p*-methoxybenzylidene)-*p*-butylaniline (**1**).

It was also observed that compound **1** prefers to stack in a right-hand helix, and when added to **2**, which preferentially forms a left-hand helix, compensation results at approximately 70 wt % **2** (see Figure 2) and a nematic mesophase results. Preferential stacking of **1** suggests that chiral conformations are important in their effect on the helical structure of cholesteric mesophases. Interestingly, it was found that naphthalene which is not potentially chiral does not affect, in this fashion, the pitch of a cholesteric mesophase composed of cholesteryl-2-propyn-1-yl carbonate or cholesteryl bromide. This is another ramification of our work which we intend to pursue. This mechanism of induced optical activity could possibly have functional importance in biological processes.

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Received July 26, 1971

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