absorb between 550–590 mμ and are either blue or bluish-violet, they are predominantly planar or at the most 'pseudo-octahedral with weakly co-ordinated drug anion.

All the Cu $(en)_2D_2$ complexes are normal paramagnetic and the μ_{eff} lies between 1·80–2·10 BM in agreement with the observed values for one unpaired electron in Cu (II) complexes[8].

Infrared spectra of the complexes show several bands in the 3500–3000 cm^{-1} due to ν NH from drug and *en* molecules. Although one of the series of the complexes has been prepared from copper (II) hydroxide but the close similarity of i.r. spectra of copper (II) chloride complexes indicates absence of OH group. When ν NH, δNH_2, phenyl ring, SO_2 asym., SO_2 Sym. and τNH_2 vibrational modes of the sulfanilamide part[9] (appearing in the regions 3500–3000, 1660–1620, 1600–1500, 1350–1300, 1150–1120 and 680–670 cm^{-1} respectively) in the sulfadrugs and Cu $(en)_2D_2$ complexes are compared, after eliminating the bands due to ethylenediamine, no significant changes are observed. It appears that the electron density has uniformly distributed itself over the entire drug molecule. In the case of sulfamerazine and sulfadiazine complexes, however, the SO_2 asymmetric band shows lowering of ~ 10 cm^{-1}, which may be due to the slight decrease of electron density over-SO_2-group.

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EFFECT OF SUBSTITUTION AND ITS LOCATION ON LIQUID CRYSTALLINE PROPERTIES OF CHOLESTERYLBENZOATE AND CHOLESTERYL CINNAMATE

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ABSTRACT

Cholesteryl 2- and 3-methoxybenzoates are non-mesomorphic, cholesteryl 2-nitrobenzoate is monotropic smectic and enantiotropic cholesteric. Cholestery 4-nitrocinnamate exhibits enantiotropic smectic and cholesteric mesophases, whereas cholesteryl 4-chlorocinnamate is only cholesteric. The mesomorphic properties are explained by comparing these compounds with other related compounds.

THE detailed study of many mesogenic homologous series has helped to evolve some general rules for the effect of chemical constitution in the nematogenic and smectogenic compounds[1]. The effect of chemical constitution on cholesteric mesophase has been also reported recently[2,3]. Dave and Vora[4] and Barral *et al.*[5], have reported *ortho*, *meta*, and *para* substituted benzoates of cholesterol and some substituted benzoates and cinnamates of cholesterol, respectively. From the study of substituted benzoates of cholesterol[4] it was observed that effect of same substituent at different locations is quite interesting. Generally the order of thermal stability is para > parent compound > meta > ortho. All the substituted benzoates of cholesterol reported exhibit mesomorphism. Some more substituted benzoates and cinnamates of cholesterol are reported here which are compared with other known compounds. Transition temperatures of these compounds are recorded in Table I.

Reference to Table I shows that methoxy group in the 4-position of cholesteryl benzoate, enhances cholesteric thermal stability quite appreciably but

TABLE I

Name of the Compound	Transition temperatures (°C)		
	Smectic	Cholesteric	Isotropic
1. Cholesteryl 4-methoxy benzoate[6] ..		180·0	268·0
2. Cholesteryl 3-methoxy-benzoate ..		..	153·0
3. Cholesteryl 2-methoxy-benzoate ..		..	122·0
4. Cholesteryl 2-nitro-benzoate[a]	(98·5)*	147·5	155·0
5. Cholesteryl 4-nitro-benzoate[4,7] ..		191·5	260·0
6. Cholesteryl 4-chloro-benzoate[4,5] ..		170·0	257·0
7. Cholesteryl 4-nitro-cinnamate	174·5	185·0	280·0 (decomp.)
8. Chalesteryl 4-chloro-cinnamate[b] ..		150·0	274·0
9. Cholesteryl benzoate[4] ..		150·0	178·0
10. Cholesteryl cinnamate[8] ..		160·5	215·0

* Values in the parenthesis indicate monotropy.
[a] Sandquist and Gorton report 150·9, 156·9[7].
[b] Barrall *et al.* report 146·0, 262·0[5].

in the 2- and 3- positions, the same group destroys the mesomorphism. This is quite interesting. Substituted benzoates of cholesterol so far reported, irrespective of the location of the substituent exhibit mesomorphism. Arora *et al.*[9], and Barrall *et al.*[5], have suggested with the help of molecular models that in the aromatic esters, due to the steric factors, twist would occur which would be dependent on the size of the substitutent in the adjoining phenyl ring. It would be reasonable to assume that the methoxy group due to its size and position would create steric hindrance in the molecule. Due to the steric hindrance, the benzene ring may not be able to assume any position in the plane of cholesterol molecule which ultimately destorys the mesomorphism.

Cholesteryl 2-nitrobenzoate exhibits monotropic smectic and enantiotropic cholesteric mesophases. Sandquist and Gorton report only cholesteric mesophase for this compound[7]. Cholesteryl 4- and 3-nitrobenzoates exhibit only cholesteric mesophase. The solid-cholesteric transition temperatures of cholesteryl 3- and 2-nitrobenzoates do not differ much. The smectic mesophase is observed in the 2-substituted compound as it could be supercooled sufficiently without crystallization to exhibit smectic mesophase. Compared to methoxy substituent, nitro substituent behaves differently in the 2- and 3-positions. This behaviour of nitro group is not surprising. Nitro group is known to enhance the thermal stability and the enantiotropy due to very high polarity of the group. Similar behaviour is exhibited by nitro group in other mesomorphic compounds[1,10].

Cholesteryl 4-nitrocinnamate exhibits smectic and cholesteric mesophases whereas cholesteryl 4-nitrobenzoate is only cholesteric. This is quite an interesting observation as difference between the two compounds is only a trans- —CH=CH— group. It would be difficult to postulate the appearance of smectic mesophase in a single compound by different modifications. $—NO_2$ group is known to promote smectogenic tendencies of a compound and more so when it does not increase the breadth of a compound[1]. Cholestericisotropic transition temperature of cholesteryl 4-nitrocinnamate is higher than that of cholesteryl 4-nitrobenzoate. This is due to the increased length and polarizability of the molecules in the cinnamate ester due to the presence of trans —CH=CH— group.

Cholesteryl 4-chlorocinnamate exhibits cholesteric mesophase. Thermal stability of this compound is more than that of cholesteryl 4-chlorobenzoate. However the smectic tendency is not promoted even-though chloro group is also known to promote smectic tendencies in other compounds[1].

Above discussion shows that it would require some more data to evolve general rules for the effect of chemical constitution on cholesteric mesophase.

The compounds were prepared by the method reported earlier[4,8].

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