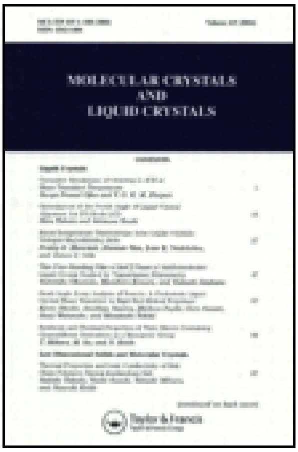

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Inositol Liquid Crystals, X-Ray Diffraction Studies of Their Hydrogen-Bond Supported Supramolecular Mesophases[1]

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Inositol Liquid Crystals, X-Ray Diffraction Studies of Their Hydrogen-Bond Supported Supramolecular Mesophases[1]

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Results of x-ray measurements on the various columnar mesophases of multi-ethers of the naturally occurring stereoisomers *myo*- and *scyllo*-inositol are presented. Depending on the number of alkyl substituents at their inositol cores such derivatives show interesting kinds of molecular organization in their liquid-crystalline states. Thus, to the best of our knowledge, the first thermotropic mesophase of tetragonal symmetry exhibited by a low-molecular weight system is described. Vicinal diols and a tetrol of this new group of liquid crystals are coupled within their mesophases by hydrogen bonding networks. In case of *scyllo*-inositol it could be shown that the number of functionalizations determines the size of this network or the degree of multimerization; columnar mesophases composed of dimers or pentamers were observed. A comparison of stereoisomeric inositol tetraethers (vicinal *cis*- and *trans*-diols) clearly revealed stereochemical influences on their liquid-crystalline properties.

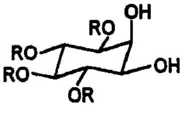
Keywords: inositols natural product, derivatives, 2H-NMR, mesogens, x-ray diffraction

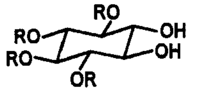
INTRODUCTION

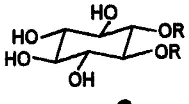
Although the formation of mesophases by molecules not only rod-shaped in structure was discussed[2] as early as in 1923 and explained theoretically by different authors[3] since 1938 it took over fifty more years until—in the late seventies—the first example of a mesophase of a disc-shaped[4] material was described.[5] Also this form of thermomesomorphism results from a spontaneous self-organization of such molecules to mainly columnar, but in few cases[6] to nematic (N_D) phases, too.

Studies on the thermotropic liquid-crystalline behavior of the di-isobutylsilanediol[7] as well as of carbohydrate, inositol, inosose and phloroglucitol liquid crystals[8a–d] show that columnar mesophases can also be composed of disc-like units consisting of *hydrogen-bonded multimers* rather than of *monomers* as in the case of conventional discotic liquid crystals.

In this paper we present results of x-ray investigations on supramolecular mesophases exhibited by partially alkylated inositols, novel types of liquid crystals.[8b]


1a–e


2a–e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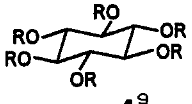
4[9]

1,**2** : R = $-C_nH_{2n+1}$

	a	b	c	d	e
n	4	5	6	7	8

3,**4** : R = $-C_6H_{13}$

RESULTS AND DISCUSSION

In addition to polarizing optical microscopy and differential scanning calorimetry, applied to inositol multi-ethers **1a–e**,[8b] **2a–e**,[8b] **3**,[8b] and **4**[9] we used x-ray diffraction for the characterization of the mesophase structures of **1c** and **e**, **2c–e**, **3**, and **4**.[9] As a result of these investigations the phase sequences shown in Table I could be established.†

The two representatives **1c** and **e** of the *cis*-series were selected and investigated exemplarily by x-ray scattering in two of our laboratories, see Experimental. These measurements revealed the hexagonal columnar phase type for both compounds as anticipated by polarizing microscopy.[8b]

The inter- and intracolumnar distances deduced from the scattering patterns of these D_h -phases are a = 21.78 Å and c = 4.6 Å for an oriented sample of **1c** or a = 23.3 Å and c = 4.5 Å for a non-oriented one of **1e**, cf. Table II.

In case of the *cis*-diol **1c**, we determined an intracolumnar correlation length of about five molecules indicating a very low intracolumnar order compared to values of typically ten to fifteen molecules in ordered hexagonal columnar phases (D_{ho}) as usual.[11] Therefore, no further indication is given here with respect to a distinction between a D_{ho}- or a D_{hd}-phase.‡

Based on these x-ray data it is possible to deduce that the mesophases of the *cis*-diols **1c** and **e** are composed of *dimers*.

The density ρ of a columnar phase can be calculated according to $\rho = MZ/$

---

† Dynamical processes in the liquid-crystalline states of **1e** and **2e**, each a representative of the *cis*- and *trans*-diol series, respectively, were studied by deuterium NMR spectroscopy, but published elsewhere.[12]

‡ Also polarizing optical microscopy gave no further information on this point. Even on slow cooling from the isotropic liquids of the *cis*-diols **1a–e** and tempering just below their clearing points, we could not obtain textural domains large enough to distinguish between D_{ho}- and D_{hd}-textures.

TABLE I

Temperatures of the enantiotropic (one monotropic exception: **1a**) phase transitions [°C] and types of mesophases found for various new inositol multi-ethers. The two non-mesomorphic scyllitol tetraethers **2a** and **b** melt at 137.3°C and 117.5°C, respectively. The temperature values were obtained by differential scanning calorimetry (d.s.c.) using a Mettler TA 3000/DSC 30 S with GraphWare TA 72, heating rate 5 K/min. As exceptions, the transitions $D_{sq,o} \rightarrow D_{ro}$ (**2d**) and $D_1 \rightarrow D_2 \rightarrow D_3 \rightarrow D_{ho}$ (**2e**) could only be seen in the polarizing microscope (Leitz Laborlux 12 Pol equipped with a hot stage Mettler FP 82, heating rate 0.2 K/min.); the same is true for the monotropic transition of **1a**. (**Cr**: crystalline, **D**: discotic, H_x: hexagonal columnar, **I**: isotropic liquid; the indices **h**, **m**, **sq**, **o**, **ro** and **ho** stand for **h**exagonal, **m**onoclinic, **sq**uare **o**rdered, **r**ectangular **o**rdered and **h**exagonal **o**rdered, respectively. D_1, D_2, and D_3 represent columnar phases of hexagonal symmetry similar to D_{ho}, but with different textural features.)

Compound		Phase Transitions					
		Cr	⟶	D_h	⟶	I	
myo-inositol tetraethers 1	**1a**	●	44.8	(●	≈ 15.0)	●	( ) : monotropic transition
	b	●	≈20.0	●	29.9	●	
	c	●	27.7	●	35.8	●	
	d	●	34.5	●	40.7	●	
	e	●	37.1	●	44.1	●	
scyllo-inositol tetraethers 2	**2c**	$Cr \xrightarrow{48.9} D_m \xrightarrow{104.4} I$					
	d	$Cr \xrightarrow{39.6} D_{sq,o}^{*)} \xrightarrow{82.2} D_{ro} \xrightarrow{96.9} I$					
	e	$Cr \xrightarrow{44.3} D_1 \xrightarrow{55.8} D_2 \xrightarrow{69.5} D_3 \xrightarrow{78.1} D_{ho} \xrightarrow{92.7} I$					
scyllo-inositol di-ether	**3**	$Cr \xrightarrow{111.5} H_x \xrightarrow{167.1} I$					
scyllo-inositol hexaether	**4**[9]	$Cr \xrightarrow{18.4} D_{ho} \xrightarrow{90.8} I$					

*) To our knowledge the tetra*heptyl*ether **2d** seems to be the first thermotropic liquid crystal of *low-molecular weight* which exhibits a mesophase of *tetragonal* symmetry; similar phases were found recently in liquid-crystalline CT complexes of polymers with 2,4,7-trinitrofluorenone, too.[10]

$A_0 c N_A$ with M = molar mass, Z = number of molecules being at the same level in a column, i.e. located in a column slice of the thickness c, A_0 = area of one column (area of the lattice divided by the number of columns per lattice), c = intracolumnar molecular spacing, and N_A = Avogadro constant. A rough estimation of ρ is only needed for the knowledge of Z unless Z is not a small integer.

Thus, we calculated for the density of the D_{ho}-phase of the *scyllo*-inositol hexaether **4**[9] $\rho = 0.91$ g/cm^3 using the x-ray parameters measured for this dicogen of conventional type with $Z = 1$. Corresponding density values, i.e. $\rho = 0.9 - 1.0$ g/cm^3, were obtained for the columnar phases of both *myo*-inositol tetraethers **1c** and **e**, only when we set $Z = 2$ (*two* molecules per level of columns). In other words, the D_h-phases of these two *cis*-diols are composed of *dimers*.

Because of our consistent findings that both *cis*-diols **1c** and **e** exist as dimers in their mesophases, we assume analogous behavior for the other synthesized *cis*-diols **1a**, **b**, and **d**, but not studied by x-ray diffraction.

Our x-ray diffraction measurements performed for the only thermomesomorphic

TABLE II

X-ray parameters of the inositol multi-ether derivatives **1c** and **e**, **2c–e**, **3**, and **4**.[9] Regarding the lattice spacings of **2c** and of the LT* mesophase of **2d** see Table III.

Compound		Array Symmetry and Parameters	Period along Columns	Molecules per Column Slice
myo-inositol tetaethers **1**	**1c**	hexagonal *a* = 21.78 Å	*c* = 4.6 Å	2
	e	hexagonal *a* = 23.30 Å	*c* = 4.5 Å	2
scyllo-inositol tetraethers **2**	**2c**	monoclinic (3d C2/m) *a* = 32.86 Å *b* = 23.25 Å *α* = 91.4°	*c* = 4.91 Å	2
	d	centered rectangular (C2/m); [HT]*) *a* = 36.22 Å *b* = 24.26 Å	*c* = 4.8 Å	2
		tetragonal; [LT]*) *a* = 28.45 Å	*c* = 4.8 Å	2
	e	hexagonal *a* = 23.08 - 23.29 Å	*c* = 4.6 Å	2
scyllo-inositol di-ether	**3**	hexagonal *a* = 26.55 Å	*c* = 4.5 Å	≈ 5
scyllo-inositol hexaether	**4**[9]	hexagonal *a* = 17.73 Å	*c* = 4.55 Å	1

*) [HT]: High-temperature mesophase, [LT]: Low-temperature mesophase

TABLE III

Measured and calculated Bragg reflexes of the (**a**) monoclinic and (**b**) tetragonal mesophase of the *trans*-diols **2c** and **2d**, respectively.

(a)

Indices	X-Ray Reflections (Å)	
	Measured	Calculated
110	18.86	18.98
200	16.40	16.43
020	11.58	11.63
310	0.02	0.01
400	8.23	8.22
130	7.54	7.54
330	6.33	6.327
001	4.883	4.861
201	4.734	4.752
021	4.482	4.485

(b)

Indices	X-Ray Reflections (Å)	
	Measured	Calculated
110	20.10	20.12
200	14.39	14.23
210	12.71	12.73
310	9.02	9.00
400	7.13	7.11
420	6.32	6.36
520	5.24	5.28
440	5.027	5.031
001	4.795	- -
610	4.639	4.678
620	4.448	4.499
540	4.428	4.444
630	4.276	4.242
550, 710	4.096	4.024

representatives **2c–e** of the series of the five *trans*-diols clearly show different columnar arrangements in their mesophases. The lattice parameters found for oriented samples of **2c–e** are given in Table II, see also Table III.

As described above for the two *cis*-diols **1c** and **e**, we analogously calculated the densities of the columnar phases exhibited by the three *trans*-diols **2c–e** using their corresponding x-ray data. Assuming that their mesophases also consist of dimers ($Z = 2$), we got density values ranging from 0.9 to 1.0 g/cm^3 as found for the *cis*-diols **1c** and **e**.

This result clearly shows that both the columnar phases of the *cis*- and *trans*-diols under consideration consist of dimers.

Based on the diffraction pattern we identified a three-dimensional lattice of monoclinic symmetry with a centered face in the *a,b*-plane for the mesophase of the *trans*-diol **2c**, cf. Figure 1. The deduced lattice parameters are $a = 32.86$ Å, $b = 23.25$ Å, $c = 4.91$ Å, and $\alpha = 91.4°$.

There are two columns in the *a,b*-plane and this section shows a very anisometric molecular arrangement. Thus, the dimers are all oriented in the same direction and the columnar axis is not perpendicular to the planes of these pairs of molecules. In addition, there is a weak correlation between positions of molecules belonging to different columns.

Obviously, the molecular order of this columnar phase corresponds neither to a normal crystal nor to a conventional mesophase. However, the fluidity of this phase observed in the polarizing microscope is more characteristic of a mesophase than of a solid.§

According to our pol-microscopic investigations,[8b] the *trans*-diol **2d** forms *two* types of mesophases. X-ray diffraction studies show that the high-temperature

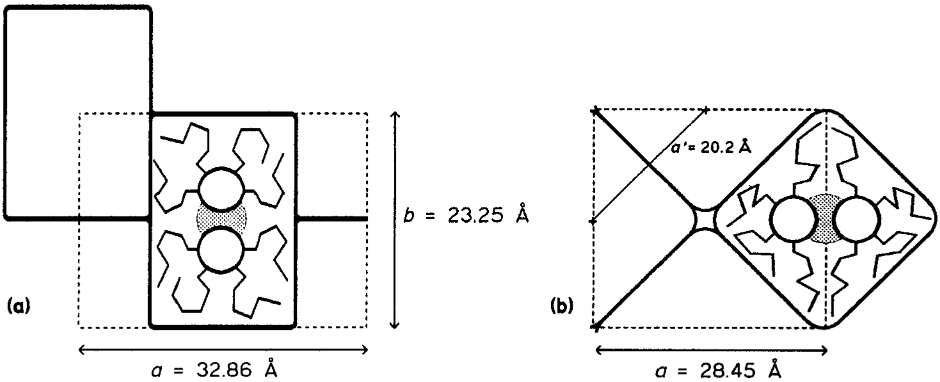

FIGURE 1 Scheme of the (a) monoclinic and (b) tetragonal lattice identified for the mesophases of the *trans*-diols **2c** and **2d** (LT mesophase), respectively, cf. Tables II and III. The diol dimers in these sketches are shown in an abstract manner: the circles symbolize cyclohexane rings, the shaded areas mark the hydrogen bonding networks, and the zigzags indicate the OR-groups (cf. structural formulas).

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§ In our opinion, the high clearing enthalpy (18.0 kJ/mol) measured for the *trans*-diol **2c** [8b] does not indicate a phase transition solid/isotropic-liquid,[14] since the mesophase of the *trans*-diol **2d** and **e** present similar values for their clearing processes.[8b] In addition, the clearing points of all these three *trans*-diols can (almost) not be supercooled.

phase (between 82.2 and 96.9°C) of **2d** has the same kind of lattice as the mesophase of the *trans*-diol **2c**, but is only of two-dimensional, i.e., centered rectangular symmetry. The mean distance between two dimers is c = 4.80 Å and the correlation length is of about ten molecules. The lattice dimensions are a = 36.22 Å and b = 24.26 Å. However, we cannot determine the angle between the columnar axis and the molecular plane.

On cooling below about 82°C, we still find a two-dimensional columnar network, but with a tetragonal symmetry (cf. Figure 1). In this low-temperature mesophase we deduce a = 28.45 Å and the mean distance between two dimers is c = 4.80 Å. If we neglect diffraction rings of weak intensity, there is a smaller square lattice with a' = 20.2 Å. According to literature,[13] we propose $D_{sq,o}$ (square, ordered) as abbreviation for the tetragonal mesophase of *trans*-diol **2d**. In fact, it seems to us that this mesophase transforms slowly into a crystalline phase with nearly the same lattice dimensions at room temperature: a 28.79 Å, b = 28.38 Å, and c = 4.80 Å.

To our knowledge the *trans*-diol **2d** seems to be the first thermotropic liquid crystal of *low-molecular weight* which exhibits a mesophase of tetragonal symmetry. However, it was found recently that mixtures of triphenylene main-chain polymers with 2,4,7-trinitrofluorenone form similar two-dimensional orthorhombic (a = b) columnar phases.[10]

In case of the *trans*-diol **2e** we reproducibly observed three reversible textural changes in its liquid-crystalline state by polarizing microscopy what we interpreted in terms of three mesophase/mesophase transitions.[8b] Unfortunately, this polymesomorphism could not be confirmed yet by other physical methods (e.g. differential scanning calorimetry or deuterium NMR spectroscopy). Therefore, these four putative mesophases of the *trans*-diol **2e** were investigated individually by x-ray diffraction in both a spontaneously oriented and a non-oriented specimen. The low angle lattice reflections of the oriented sample were always in a plane perpendicular to the axis of the sample capillary. The packing reflection was continually oriented on an axis parallel thereto. The phases D_1, D_2, and D_{ho} (cf. Table I) all gave reflections consistent with those from a two-dimensional hexagonal lattice of a = 23.08 – 23.29 Å.

The packing reflection occurred at an average spacing of 4.6 Å.

The weight of evidence favors the same hexagonal structure for the D_3-phase as well. In the case of the D_3-phase the first experiment, on the oriented specimen, gave evidence for several diffraction lines which could not be identified with the simple hexagonal lattice, but they additionally could not be indexed on any of a number of other lattices tested either. Furthermore, the repeat experiment on the unaligned sample did not show these additional lines. Therefore, while we really do not have any satisfactory explanation for the appearance of these weak extra lines, the stronger lines are still in accordance with the hexagonal lattice and we would tentatively make the same assignment for D_3.

Various questions concerning the phases D_1, D_2, and D_3 of this particular multimesomorphic *trans*-diol **2e** are still open. Hopefully, they will be answered in the future, probably by applying other and more sensitive methods.

Our x-ray scattering experiments on the mesophase of an aligned sample of the *scyllo*-inositol di-ether **3** revealed a hexagonal columnar lattice presenting a similar type of diffraction pattern as found for dithioacetals of D-glucose.[8a] Thus, a unique large angle diffuse ring corresponding to a mean distance of about 4.5 Å has been detected and there is no evidence of a specific intracolumnar core ordering and a fortiori of a helicoidal array in a column. The hexagonal lattice constant of this H_x-phase is $a = 26.55$ Å (cf. Table II). Assuming a specific gravity of 1 g/cm^3 one finds in average five molecules (calculated 4.75) per column slice of 4.5 Å thickness.

Based mainly on the x-ray diffraction investigations (cf. Table II and Figure 2) we suggest the following models for the molecular organisation of the inositol multi-ethers in their mesophases:

1. The D_{ho} phase of the scyllitol hexaether **4** is formed by covalently structured disc-shaped units consisting of single molecules, which are regularly stacked up to columns yielding a hexagonal network.
2. The columnar phases of the *myo*- and *scyllo*-inositol tetraethers of type **1** and **2** are made up by hydrogen bridged *dimers*, i.e., crescent-shaped diol monomers couple and form discoid (elliptical) aggregates. Whereas the different

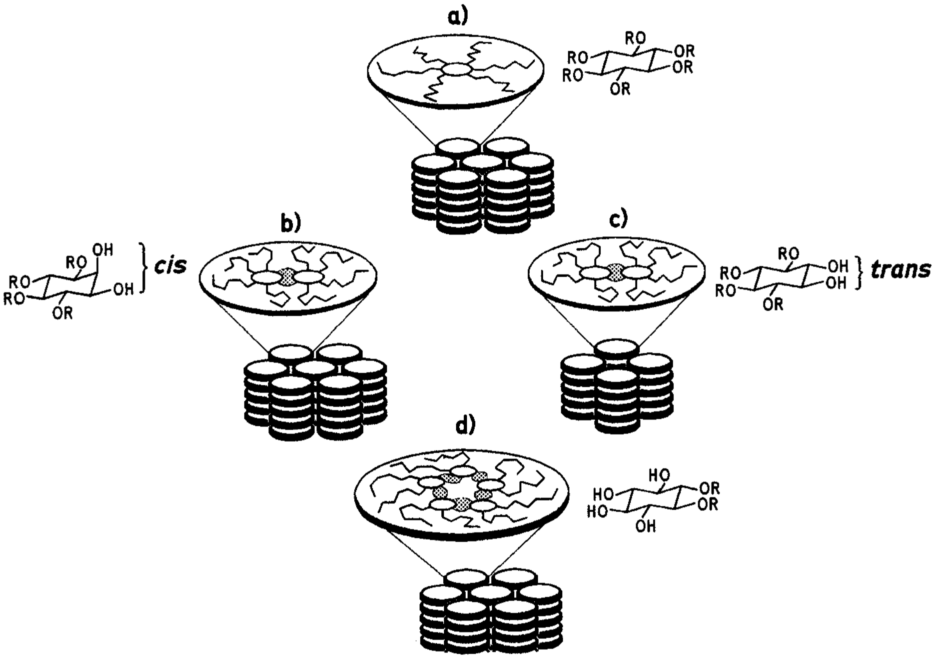

FIGURE 2 Models of the molecular organizations of the studied inositol multi-ethers of types **1**, **2**, **3**, and **4** in their columnar liquid-crystalline phases. The blown-up parts represent slices of single columns showing the differences of their compositions. The regions of hydrogen bonding among hydroxyl groups located between the small ellipses (symbols for cyclohexane) inside these simplified cuts are shaded; the zigzags symbolize OR-groups (cf. structural formulas): **a**) the monomeric *scyllo*-inositol **hexa**ether[9] **4** (D_{ho}), **b**) and **c**) the hydrogen-bridged vicinal diol dimers of *myo*- and *scyllo*-inositol **tetra**ethers of type **1** (D_h) and **2d** ($D_{sq,o}$), respectively, and **d**) the hydrogen-bridged pentamer of the *scyllo*-inositol **di**-ether **3**, an all-*trans*-tetrol (H_x, cf. exposition above).

stereochemistry of the vicinal diol situation in **1** and **2** is not affecting their mode of aggregation, the symmetry in their columnar arrays strongly is.

3. In the H_x mesophase [8a, c] of the scyllitol di-ether **3** about five molecules are found per slice of the columns. Thus, one can assume a model of partially non-covalently structured building units ("supramolecular discs") in average consisting of pentamers of such tetrols via hydrogen bonding.

It should be noted that the identified hexagonal columnar phase of the neat scyllitol di-ether **3**—assigned here H_x—shows structural similarities 8[c] to corresponding (inverted) lyotropic mesophases. Therefore, our presented model showing *distinct discs* of aggregated molecules of the scyllitol di-ether **3** (cf. Figure 2) is certainly idealized; it goes without saying that intracolumnar molecular fluctuations are possible.

Previous studies[15] on the relation between structure and properties of discotic molecules revealed certain criteria (1. perfect space filling and 2. optimal coverage of the area in the periphery of the core) which obviously have to be fulfilled by such compounds to exhibit discotic thermomesomorphism.

In this context, a comparison of the molecular organisation of the inositol multiethers of type **1**, **2**, **3**, and **4** within their mesophases shows the following particularities: According to the structural requirements for discogens[15] mentioned above the formation of discotic mesophases in case of the radialsymmetric, disc-shaped hexaether **4**[9] is understood.

In contrast, the formation of mesophases by the non-radialsymmetric multi-ethers **1**, **2**, and **3** is unexpected since these compounds as such show no optimal coverage of the peripheral area of their inositol cores. In terms of classical conditions,[15] the numbers of lateral alkyl chains are not sufficient in these cases. Nevertheless, the thermomesomorphic properties of these inositol di- and tetraethers are comprehensible and in agreement with earlier statements[15] if the following alternative is given. As deduced from x-ray results the mesophases of such compounds are composed of supramolecular disc-like units based on hydrogen bonding networks. Thus, the diols of type **1** and **2** form dimers and the tetrol **3** pentamers. The lack of covalently bonded side chains in these monomers is compensated by such multimerizations, i.e. the necessary optimal coverage in the periphery is achieved, here, in this manner.

We hope that our findings will stimulate further work in the field of natural product mesogens, in particular the research on the relation between structure and properties of molecules which might be able to form thermotropic (and lyotropic) mesophases by hydrogen bond supported self-organizations. A progress in this field is of additional interest with respect to the understanding of membrane processes in biological systems.

EXPERIMENTAL

The x-ray experiments were performed using different local devices in the labs of (**a**) Dr. A.-M. Levelut (studies of **1c**, **2c**, **d**, and **3**) and (**b**) Dr. E. Wachtel (examinations of **1e** and **2e**).

(**a**) Here, the powder pattern of the mentioned four inositol multi-ethers were obtained using a Guinier camera. The x-ray beam was issued from a fine focus linear source 8 × 0.05 mm with a copper target and reflected on a Johannson quartz crystal which selected the Cu $K\alpha_1$ radiation. The sample was held in a Lindemann glass tube of 1 mm diameter rotating along a vertical axis parallel to the linear source. The temperature of the sample was maintained within ±1 K. The diffraction pattern was recorded on a photographic film. With this device, the accuracy for the measurement of the scattering angle was ±0.02°. The orientation of each of these materials was achieved by stretching the samples on a Lindemann glass wall.

(**b**) In this lab the two inositol tetraethers **1e** and **2e** were studied (each non-oriented, but **2e** also spontaneously aligned) using an Elliott GX 6 rotating anode generator with a 200 μm focus, to which was affixed a Searle camera with Franks mirror optics. The Cu radiation was Ni-filtered. Samples were held in 1.5 mm diameter x-ray capillaries (Li or quartz glass) and their temperature was regulated within a precision of ±0.5 K. The scattering patterns were detected using Direct Exposure Film (Kodak) during an exposure time of about 16 h. The sample to film distance was calibrated with powdered calcite, which coated both the front and back surfaces of the x-ray capillary, thereby giving rise to a double calibration ring on each photograph. The simple average spacing was taken. The reflection spacings were measured (at least twice) directly on the films with a Stoe comparator.

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