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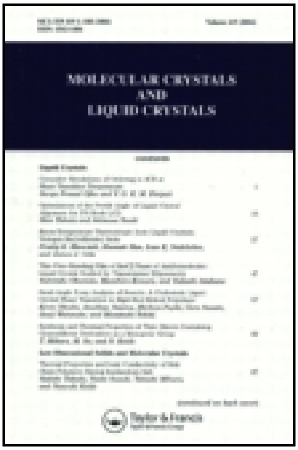

Molecular Crystals and Liquid Crystals

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Solid State Polycondensation of Precursors of Phenolic Resins

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SOLID STATE POLYCONDENSATION OF PRECURSORS OF PHENOLIC RESINS

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Abstract Twelve substances derived from phenol or 4-alkylphenol, six of which are precursors of phenolic resins, have been prepared by condensation of the phenol with paraformaldehyde or by further reaction of one of these with the starting phenol. Two cyclic oligomers belonging to the class of calixarenes or cyclophanes have been isolated and characterized. Single crystals of some precursors have been obtained and their crystalline structures have been determined. The thermal decomposition of precursors of phenolic resins has been investigated. Their solid state behaviour and their relative reactivities in acidic and basic conditions have been evaluated. The obtained substances can be considered as important intermediates. They are both sufficiently stable and highly reactive.

INTRODUCTION

Although, phenolic resins have interesting properties[1,2,3,4] such as high thermal stability, excellent resistance to combustion, high dimensional stability, good mechanical properties and high chemical stability, the development of these materials is not taken into account probably because of the complexity of the precondensation mixtures. This complexity results from the fact that the starting materials, phenol and formaldehyde,

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present 3 ans 2 reactive positions respectively leading to a great number of substitution possibilities[5]. Contrary to the polymerization reactions of olefins, for example, in which only one monomer is present and which gives directly the final polymers, in the case of phenolic resins formaldehyde combines with phenol in many ways leading to a mixture of precursors (monomers) capable of polycondensation and forming resins. In addition, phenol-formaldehyde condensations are sensitive to pH, temperature and molar ratio (R) of formaldehyde to phenol[5]. Finally, a number of patents on phenolic resins show that their production and properties are still achieved by empirical and somewhat questionable considerations. It seems therefore that a basic knowledge of precursors present in the initial mixture of these materials would allow us to establish correlations between, the initial composition of precursors and the properties of final products.

With respect to solid state chemistry, we decided to investigate phenolic precursors as follows.

1) Preparation and characterization.
2) Crystallization and determination of crystalline structure.
3) Thermal and chemical stability of solids.

PREPARATION AND CHARACTERIZATION OF PHENOLIC PRECURSORS

Initially we studied the preparation of 2,4,6 trihydroxymethylphenol, 1, and 3,5,3',5'-tetrahydroxymethyl-4,4'-dihydroxydiphenylmethane, 2. 1 and 2 were prepared in large quantities, isolated and stabilized. It was shown that the use of lithium hydroxide monohydrate and a reaction temperature of 20°C are the best conditions to produce 1[6].

We also prepared substances derived from 4-isopropylphenol, four of which, precursors of phenolic resins, were prepared by condensation of the phenol with paraformaldehyde in aqueous media under basic conditions, the others by reacting one of these with the starting phenol under acidic conditions. By successive stages the following products have been obtained :

3, 2-hydroxymethyl-4-isopropylphenol.

4, 2,6-dihydroxymethyl-4-isopropylphenol.

5, 2,2'-dihydroxy-5,5'-diisopropyl diphenylmethane.

6, 2,6-di (2-hydroxy-5-isopropylbenzyl)-4-isopropyl phenol.

7, 2,6 bis (2-hydroxy-5-isopropylphenol)-4-isopropylphenol.

8, 2,6 bis (2-hydroxy-3-hydroxymethyl-5-isopropylbenzyl)-4-isopropylphenol.

9, Cyclohexa (2-hydroxy-5-isopropyl-1,3-phenylene) methylene.

10, Cycloocta (2-hydroxy-5-isopropyl-1,3 phenylene) methylene.

These last two products are cyclic oligomers belonging to the class of calixarenes or cyclophanes[7,8]. Their characterization was done by proton and carbon NMR (Table I and Table II).

In addition in the series of 4-phenylphenol derived compounds, 2,6-dihydroxymethyl-4-phenylphenol, 11, 2,6-di (2-hydroxy-5-phenylbenzyl)-4-phenylphenol, 12, and 2,6 -bis (2-hydroxy-5-phenylphenol)-4-phenylphenol, 13, were synthesized, isolated and characterized.

Recently we isolated 1,3-dihydroxy-4-dihydroxymethyl benzene, 14, which is one of a series of a compounds derived from resorcinol.

This substance was prepared by condensation of

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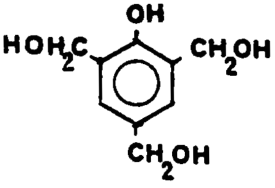

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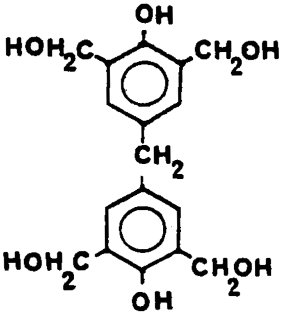

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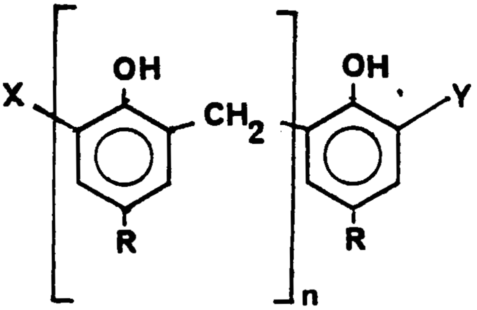

R = isopropyl

3 n = 0 ; X = -H ; Y = $-CH_2OH$

4 n = 0 ; X = Y = $-CH_2OH$

5 n = 1 ; X = Y = -H

6 n = 1 ; X = Y = $-CH_2OH$

7 n = 2 ; X = Y = -H

8 n = 2 ; X = Y = $-CH_2OH$

FIGURES 1 a,b,c. Compounds prepared for this study.

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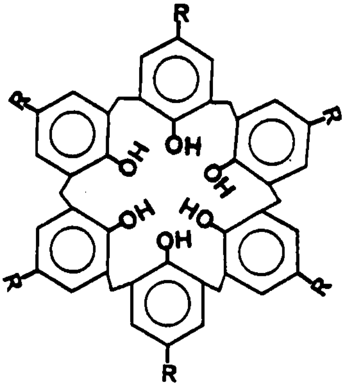

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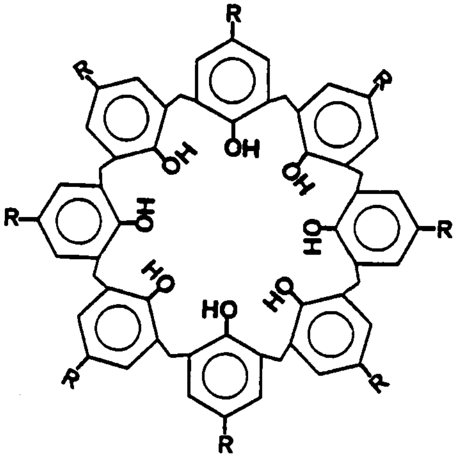

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FIGURE 1b.

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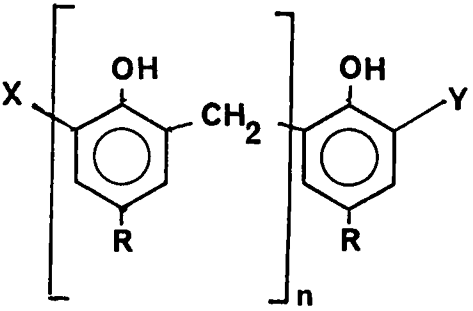

R = phenyl

11 n = 0 ; X = Y = $-CH_2OH$

12 n = 1 ; X = Y = $-CH_2OH$

13 n = 2 ; X = Y = -H

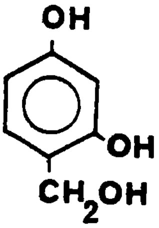

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FIGURE 1c.

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TABLE I. ^{1}H nmr* for compounds 9 and 10.

Compounds	Aliphatics	Benzylics	Aromatics
9	1.18(d,6H,J=7Hz)	2.79 (sept.,1H) 3.65(broad s,1H) 4.17(broad s,1H)	7.00 (s,2H)
10	1.17(d,6H,J=7Hz)	2.79(sept.,1H) 3.85(s,2H)	6.98 (s,2H)

* Chemical shifts δ in ppm from tms. 0.1 M in $CDCl_3$.

TABLE II. ^{13}C nmr* for compounds 9 and 10.

Compounds	Aliphatics	Benzylics	Aromatics
9	24.18 (42)	31.96 (12) 33.28 (34)	126.31 (37) 128.79 (101) 192.26 (51) 146.70 (53)
10	24.19 (176)	32.61 (37) 33.30 (87)	127.01 (200) 141.77 (60) 147.34 (47)

* Chemical shifts δ in ppm from tms. 100-200 mg of compounds 9 and 10 in ~ 3mL of $CDCl_3$.

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resorcinol with paraformaldehyde in a methanol medium with an amine as catalyst. Compound 14 is very unstable in the reaction mixture and can only be stored when it is highly pure and crystallized.

CRYSTALLIZATION AND DETERMINATION OF CRYSTALLINE STRUCTURE

We were able to obtain single crystals of different compounds.

Pure crystals of 1 were obtained by slow evaporation of solutions of 1 in diethylether or ethylacetate. Solutions of 1 in diethylether were obtained by shaking a chosen volume of this solvent with the same volume of an aqueous solution containing large amounts of 1.

Single crystals of pure 2 were obtained by recrystallizing from solutions of pure 2 in a mixture of ethylacetate-methanol, 50-50. Slow evaporation of the solution at room temperature yields needle-like crystals or lozenge shaped plates, which have the same melting point.

The crystalline structure of 1 and 2 were resolved by x-ray diffraction.

Compound 1 crystallizes in the monoclinic system[9]. As shown on Figure 2, the oxygen of one hydroxymethyl group in ortho position lies in the benzene ring plane. The two other oxygen atoms of the hydroxymethyl groups are out of the ring plane and on the same side.

Compound 2 crystallizes in the triclinic system[9]. As shown in Figure 3, on one benzene ring the oxygen atom of one hydroxymethyl group is in the ring plane, the other is out of it. On the other benzene ring the two oxygen

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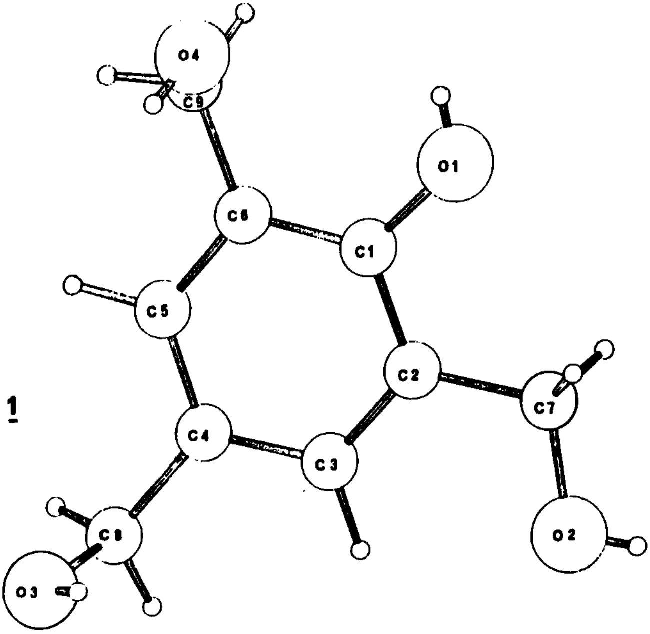

FIGURE 2. View perpendicular to the aromatic ring.

2

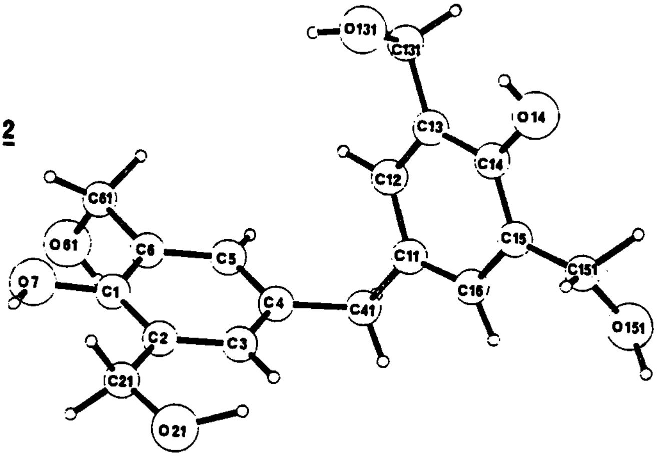

FIGURE 3. View perpendicular to [100].

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atoms of the hydroxymethyl groups are out of the plane and on both sides. The dihedral angle between the two benzene rings has a value of 80.7°.

Notice that the values of the calculated densities, $D_c = 1.365\ mg.m^{-3}$ for 1, and $D_c = 1.46\ mg.m^{-3}$ for 2 are high for substances containing only C,H and O atoms. The high degree of packing of 1 and 2 can be explained by the great number of intermolecular H-bonds arrays which constitute a two dimensional network for 1 and a three dimensional network in the crystal 2. The great number of intermolecular H-bonds found in 1 and 2 explains their high densities. On the other hand it is noticed that intramolecular H-bonds are not found.

In the series derived from 4-isopropylphenol the crystalline structure of compounds 3, 4, and 6, were determined. The crystalline structures of the other compounds are currently under investigation.

Compound 3, Figure 4, crystallizes in the tetragonal system, space group $I4_1/a$, with sixteen molecules in the unit cell. The molecules are bonded by H-bonds forming tetramers.

Compound 4 crystallizes in the orthorombic system[10]. There are 8 molecules in the unit cell. The molecules are held together by H-bonds forming sheets interrelated by Van der Waals contacts and there are no intramolecular H-bonds. As shown in Figure 5 the oxygen of one hydroxymethyl group lies in the benzene ring plane, the other oxygen atom of hydroxymethyl group is out of the plane.

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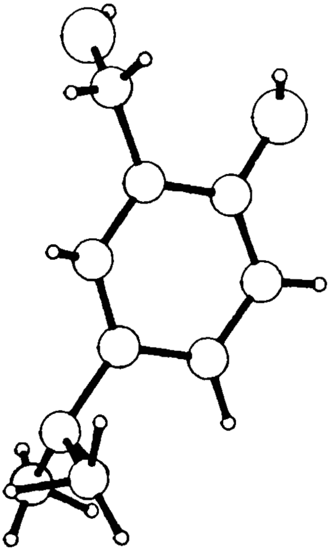


FIGURE 4. View along [010].

4

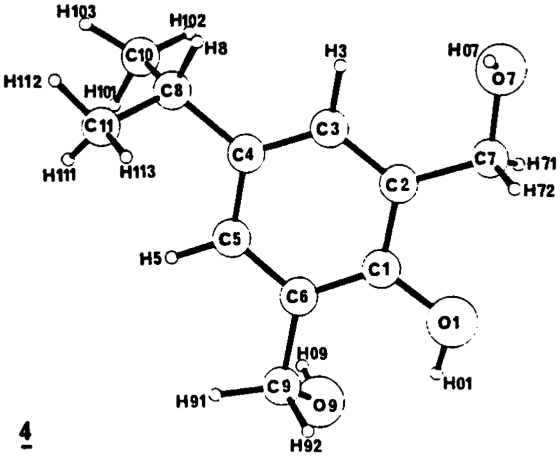
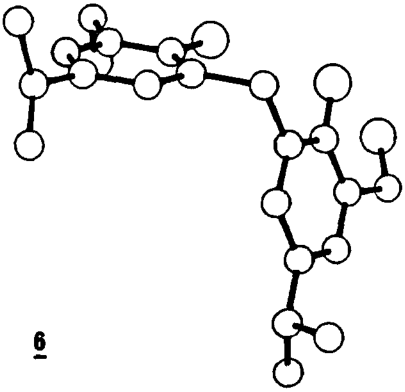


FIGURE 5. View along [100].

Compound <u>6</u>, Figure 6, crystallizes in the tetragonal system, group $P42_1c$, with eight molecules in the unit cell a = b = 20.452 A, c= 9.167 A.



<u>6</u>

FIGURE 6. View along [010].

The crystalline structure of these five precursors show that no intramolecular H-bond are exhibited. In all cases intermolecular H-bonds are found and explain the high degree of packing of these substances and their density. For these substances the oxygen of one hydroxymethyl group in the ortho position lies in the benzene ring plane the other oxygen is out of the plane.

THERMAL AND CHEMICAL STABILITY OF SOLID PRECURSORS

Thermal decomposition of precursors of phenolic resins has been the subject of a detailed study reviewed in the book by Megson[3]. Thermal decomposition is schematized as follows with 2-hydroxymethylphenol as model.

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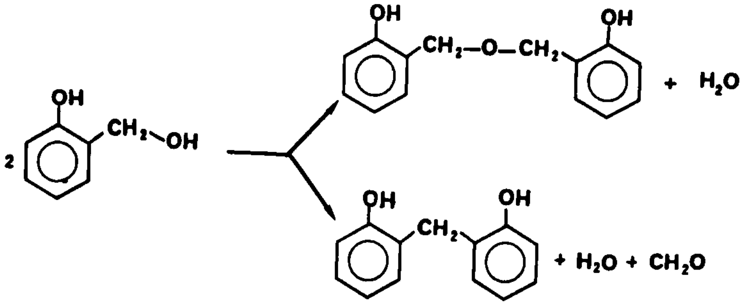

Compounds 1 and 2 are precursors of resins manufactured in large quantities over the world. Consequently it was of great interest to investigate the stabilities of compounds 1 and 2 in order to evaluate their thermal behaviour.

The thermal analysis curves figures 7 and 8, which we obtained[11] in air in alumina and silica vessels, show that pure compounds 1 and 2 are stable until 80°C. Above this temperature a loss of weight is registered. Compound 2 starts to decompose in the solid state between 80 and 145°C. As is shown by the derived curve of the function giving the loss of weight versus temperature for compounds 1 and 2 there are two temperature ranges in which two different reactions are occuring. Experiments at 130°C and 250°C show that the first range corresponds mainly to a loss of water, determined by measuring the index of refraction, the second by a loss of formaldehyde, determined by gas chromatography. It is concluded that the polycondensation reactions of 1 and 2 as solid pure compounds the occur above 80°C chiefly with the formation of water and the formation of ether bonds. Above 230°C

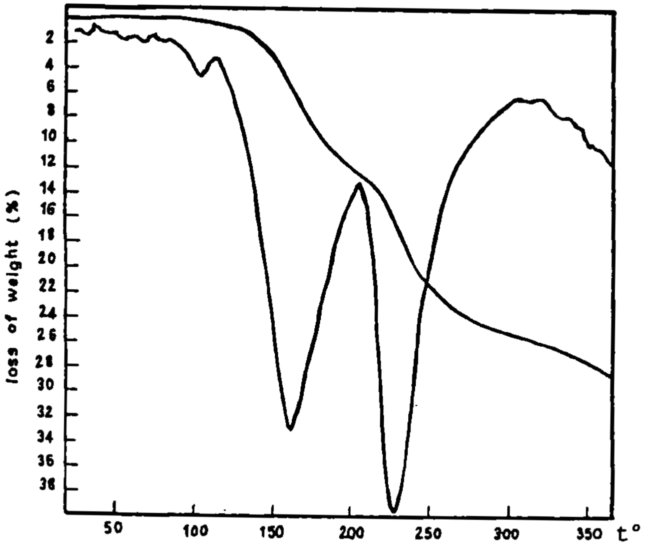

FIGURE 7. Thermal analysis of 1 loss of weight in percent vs. temperature °C.

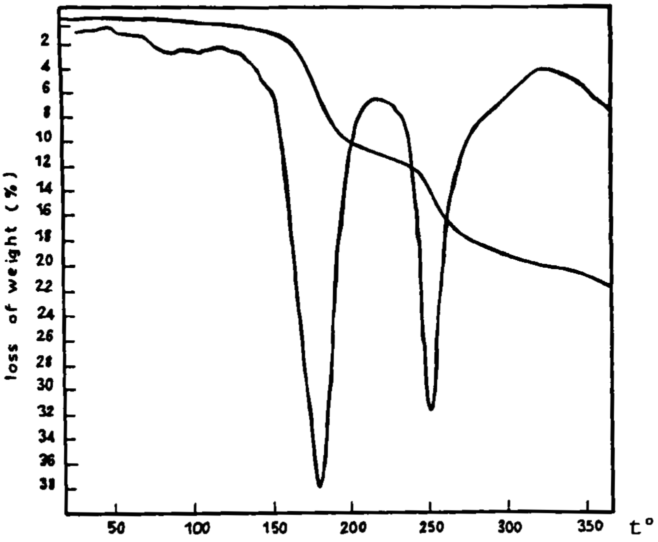

FIGURE 8. Thermal analysis of 2 loss of weight in percent vs. temperature °C.

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formaldehyde is evolved and methylene bridges are formed.

In the field of organic solid state chemistry we have studied the polycondensation reaction of crystals of 1 and 2 in order to evaluate their behaviour and their relative reactivities under acidic and basic conditions.

a -Behaviour of single crystals of 1 : in the presence of air, an increase in temperature of crystals of 1 from room temperature to 88°C does not give any observable modification. This result is in agreement with the thermal analysis already given showing no loss of weight in this range of temperature. Between 88 an 89°C one observes a true melting of the crystal.

When single crystals of 1 are placed at room temperature on a microscope slide in the presence of air saturated with concentrated hydrochloric acid, one observes an immediate transformation. In a few seconds a liquid phase is formed which has the consistency of a resin and in which neither compound 1 nor precursors with 1,2 or 3 aromatic rings are present.

b -Behaviour of single crystals of 2 : a slow increase in temperature of the crystals of 2 from 20 to 150°C during 40 minutes, in the presence of air shows a modification of the shiny appearence of the crystalline faces. No change in the crystal habit is observed. There is a slight bubbling, the crystals turn brown and the colour becomes darker as the temperature is increased. No true melting is observed until 250°C. Contrary to the preceeding experiment, abrupt heating from 20 to 145°C provokes true melting. From this, one concludes that during a slow

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increase of the temperature, the polycondensation reaction in the solid state is developed and the macroscopic form of the crystal is conserved. The thermogravimetric analysis, previously given, confirms this conclusion as shown by the weight loss above 80°C.

When microcrystals of 2 were exposed to air saturated with hydrochloric acid at room temperature on a microscope slide, a transformation was observed. They decomposed within 4 days to give an amorphous product. Larger crystals slowly transformed within 15 to 20 days for instance. The slow transformation allowed microscopic observation of reacting zones on the different faces as is shown by the black lines in figure 9.

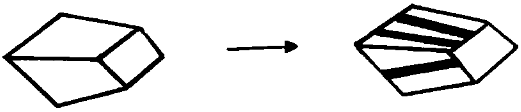

FIGURE 9. Anisotropic polycondensation of single crystal of 2.

The reacting zones correspond to amorphous substance. Until now we have not been able to find relationships between the crystalline structure of 2 and the reacting zones on the faces of the crystal.

These results show that in presence of hydrochloric acid, in the gaseous phase, the crystals of 1 and 2 have different reactivities. Compound 1 is much more reactive than compound 2. In all these cases, by changing the temperature, it is possible from these

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precursors to obtain phenolic polymers even in the solid state. We also noticed that in presence of vapours of basic catalysts as solid diazabicyclooctane and N,N-dimethylaminopyridine no transformation occurs even after one week. In order to appreciate the differences in behaviour of precursor 1 in the solid state and in solution its polycondensation has been investigated in the methanol in the presence of hydrochloric acid. It is apparent that the rate of polycondensation is lower in solution than in the solid phase. Of course methanol is a solvent which is known to slow down the rate of polycondensation. It has been chosen because of the difficulties of dissolving compound 1 in othen solvents. Moreover it is shown that in this case it is preferable to perform the polycondensation in the solid state. The different rates observed for the solution and the solid phase reactions may be due to different arrangements of hydrogen-bonds in the two phases.

CONCLUSION.

In conclusion, we have shown that phenol-alcohols, precursors of phenolic resins, can be isolated as very pure products and could be stored when they are highly pure and crystallized. With single crystals, we have determined the crystalline structures and studied the thermal and chemical behaviour. At room temperature with hydrochloric acid, crystals of 1 are more reactive than crystals of 2. Precursor 1 reacts more rapidly in the solid state than in solution in methanol. Lastly crystals of 2 give anisotropic polycondensation reactions.

It is to be noticed that precursors of phenolic resins constitute substances which are important because they are highly reactive but relatively stable under certain conditions. In fact they constitute starting materials able to produce phenolic resin in the solid state and also they are intermediates leading to products which are in great demand in industry.

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