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LINEAR CHAIN MODELS AND SOUND VELOCITIES IN MOLECULAR ORGANIC CRYSTALS

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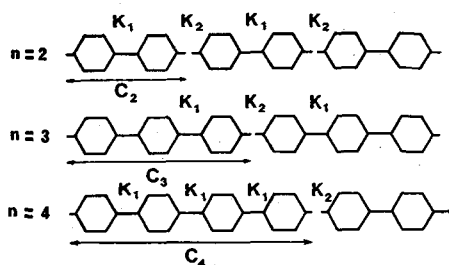
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**Abstract** Longitudinal sound velocities in crystals of elongated aromatic molecules have been measured by Brillouin scattering and are found to be faithfully described by a simple linear chain model, whereas a similar behaviour is observed for compressibility and thermal expansion. A particular attention has been paid to the p-polyphenyls and polyacenes series.

**1. INTRODUCTION** Despite the width of the aromatic rings ; p-polyphenyls and polyacenes are good examples of chain-like molecules which crystallizes in parallel stacks, themselves parallel to the molecular long axis. This kind of stacking is far from being unusual in molecular and specially in flat molecules crystals which most of the time belong to the monoclinic  $P 2_1/a$  symmetry group. This is exactly what happens for naphthalene, biphenyl, dibenzyl and many others.

We will consider here a simple chain model for crystals of molecules composed of a various number of aromatic rings and look at the sound longitudinal velocities along the stacking direction, intra and intermolecular bonds will be represented by springs of force constants resp.  $K_1$  and  $K_2$ .

**2. LONGITUDINAL SOUND VELOCITIES IN p-POLYPHENYLS and POLYACENES** Let us



consider first the p-polyphenyls which are represented on Fig.1 as a function of the molecular ring number ; the  $C_n$  parameter being the length of the crystallographic period.

It can be shown very easily that the longitudinal sound velocity along the molecular long axis can be written for a molecule with n rings as :

$$v_n = \frac{C_n}{\sqrt{M_n \left( \frac{1}{K_2} + \frac{n-1}{K_1} \right)}}$$

Fig. 1 Polyphenyls chain model for longitudinal wave propagation.

Where  $M_n$  is the mass of the molecule.

The  $K_1$  value can be obtained from I.R. experiments on biphenyl which frequency mode is about  $334 \text{ cm}^{-1}$  this gives  $K_1 \approx 450 \text{ N/m}$ . We report in Table 2 the  $K_2$  values

obtained at 300 K and 5 K of the 3 first elements of the polyphenyls series from sound velocities obtained by Brillouin scattering <sup>(1)</sup>.

n	2	3	4	
$C_n(\text{Å})$	9.51	13.62	17.85	
$N_{A_n} M_n(\text{g})$	154	230	306	
300 K	$V_n(\text{m/s})$	3940	4730	5210
	$K_2(\text{N/m})$	4.49	4.60	4.32
5 K	$V_n(\text{m/s})$	4650	5440	6010
	$K_2(\text{N/m})$	6.11	6.08	5.75

Table 1 Intermolecular force constant  $K_2$  for biphenyl p-terphenyl, p-quaterphenyl at room temperature and near liquid helium temperature.

We see on this table an excellent agreement at low temperature when vibrations are more harmonic, it is also noticeable that the effect of  $K_1$  is negligible and it should only be detectable for  $n > 10$ .

n	2	3	
$C_n(\text{Å})$	8.66	11.16	a) TESLENKO } (2) b) AFANASSIEVA }
$N_{A_n} M_n(\text{g})$	130	178	
$V_n(\text{m/s})$	3540 <sup>a</sup> 3620 <sup>b</sup>	3860 <sup>c</sup>	c) HUNTINGTON (3)
$K_2(\text{N/m})$	3.55 3.71	3.54	

Table 2 Intermolecular force constant  $K_2$  for naphtalene and anthracene at room temperature.

Table 2 give the same results taken from ultrasonic measurements previously reported in the litterature for the 2 first elements of the polyacenes at room temperature.

From these data one can clearly see that these organic crystals which look rather complicated can be surprisingly well described by simple chain models ; moreover these models also describe the effect of deuteration and the absence of sound velocity variation in directions perpendicular to the chains when  $n$  varies.

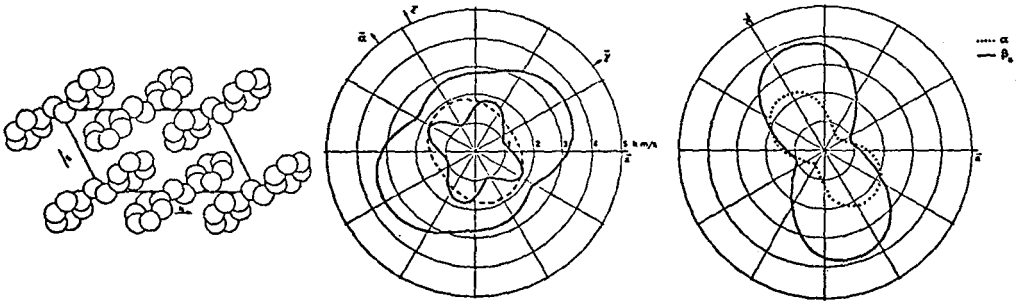
3. COMPRESSIBILITY and THERMAL EXPANSION ANISOTROPIES The linear compressibility  $\beta$  which can be expressed as a function of the elastic compliance moduli  $S_{ik}$  writes down for monoclinic crystals

$$\beta = A_1 n_x^2 + A_2 n_y^2 + A_3 n_z^2 + A_5 n_x n_z$$

where  $A_i = \sum_k S_{ik}$

For all the crystals studied here experimental data show the same anisotropy for compressibility and thermal expansion. A counter example found in the littera-

ture was dibenzyl and it motivates a new determination of its elastic properties, for the maximum of compressibility found along the molecular long axis looked rather unrealistic. Structure, sound velocities compressibility and thermal expansion in the  $(\vec{a}, \vec{c})$  plane can be seen on figure 2.



**Fig. 2** Structure, sound velocities, linear compressibility and thermal expansion (left to right) of dibenzyl. The dashed curve in the center diagram is related to the transverse mode polarized along  $\vec{b}$ , whereas the dotted line in the right diagram corresponds to the thermal expansion  $\alpha$  ( $.25 \cdot 10^{-3} \text{ K}^{-1}$  per division) and the other curve to the linear compressibility  $\beta_G$  ( $15 \cdot 10^{-12} \text{ m}^2 \text{ N}^{-1}$  per division)

This is a typical example of the results we can expect for such kind of crystals where the forces have a short range nature.

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