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Dynamic Mechanical Behaviour of Organic Molecular Crystals. II. Elastic Constants of Single-Crystal Anthracene

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The thirteen elastic constants, C_{ij}, and the elastic compliances, s_{ij}, of monoclinic single-crystal anthracene were determined from sound velocities measured by the ultrasonic pulse method at room temperture. The observed elastic constants were $C_{11}=8.92$, $C_{12}=4.63$, $C_{13}=4.49$, $C_{15}=-2.58$, $C_{22}=13.8$, $C_{23}=8.45$, $C_{25}=-2.59$, $C_{33}=17.0$, $C_{35}=-2.88$, $C_{44}=2.42$, $C_{46}=1.14$, $C_{55}=2.84$ and $C_{66}=3.16$ (in units of 10^{10} dyn/cm^2). The hydrostatic linear compressibilities, β, of the anthracene molecular crystal were then calculated from these elastic constants and compliances; the β along [100] was 12.7×10^{-12} cm^2/dyn, $\beta_{[010]}=4.41\times10^{-12}$ cm^2/dyn, and $\beta_{[001]}=3.59\times10^{-12}$ cm^2/dyn.

It is well known that the general forces of the cohesion, or van der Waals forces, between the polycyclic aromatic molecules play an important part in the building up of organic crystals. The dynamic mechanical properties of these organic molecular crystals provide a sensitive test of the forces, but those studies on this problem have scarcely been undertaken.[1]

In a preceding paper,[2] the dynamic elastic moduli and losses of organic crystals, perylene, anthracene, coronene, 1, 2, 3, 4-dibenzanthracene, and their complexes with trinitrobenzene were observed by a forced-resonance vibration method. By this method, however, only information on the dynamical mechanical properties of the crystals along the longest axis, mainly the b-axis, was obtained.

Since the crystal structures of polycyclic aromatic crystals belong to the monoclinic or the triclinic system, thirteen elastic constants for the monoclinic system and twenty-one constants for the triclinic system must be measured if we are to ascertain all their dynamic mechanical properties exactly.

This paper will present experimental results of acoustic velocity measurements in monoclinic single-crystal anthracene, $C_{14}H_{10}$, by the ultrasonic pulse technique, and the thirteen elastic constants calculated from them.

1) J. C. W. Heseltine, D. W. Elliott and E. B. Wilson, Jr., *J. Chem. Phys.*, **40**, 2584 (1964).

2) T. Danno, T. Kajiwara and H. Inokuchi, This Bulletin, **40**, 2793 (1967).

Experimental Procedures

Sample Preparation. Anthracene, purified by means of zone-refining, was grown by the Bridgman method. The sample, a clump composed of a moderately large single crystal, 20 mm×20 mm×10 mm, was cut along the cleavage plane with a razor blade. The cleavage plane lies parallel to the ab crystalline axes. Further, the direction of the b-axis was decided on the cleavage plane by means of the double refraction method.[3]

Then, four parallelepipeds of anthracene crystals, about 5 mm×5 mm×5 mm, as shown in Fig. 1, were cut out and rubbed on benzene-soaked leather until the surface became clear. The ultrasonic pulse technique requires a pair of plane parallel faces for transmitter and receiver mounting. Therefore, two surfaces of the crystal specimen were polished on benzene-soaked deer leather. This procedure was repeated until the desired parallelism and smoothness of the end surfaces of the crystal were obtained.

The crystal structure of anthracene is of the monoclinic symmetry, with a $P2_1/a$ space group, and with $a=8.56$ Å, $b=6.04$ Å, $c=11.16$ Å, and

3) I. Nakada, "Organic Semiconductors," (H. Inokuchi, I. Nakada and M. Hatano ed.), Kyoritsu Publ., Tokyo (1966), p. 92.

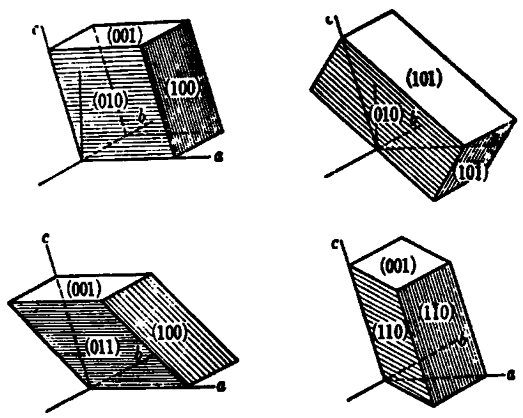

Fig. 1. Four parallelepipeds used for sound velocity measurement.

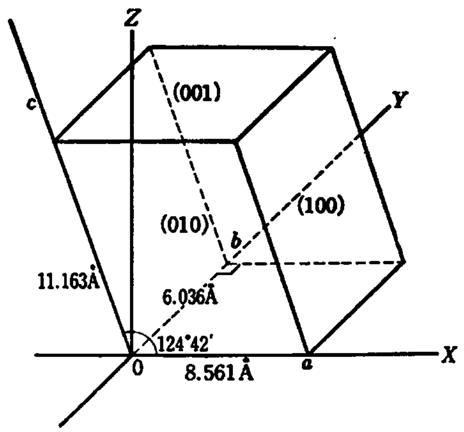

Fig. 2. The relation between XYZ orthogonal system and crystal axes.

$\beta=142°40'$.[4,5] The formulation of the strain-energy function for a monoclinic crystal results in thirteen independent elastic constants. The XYZ orthogonal system of coordinates was used for calculation in the following way: The Y-axis is the monoclinic b-axis of the crystal, the X-axis, the a-axis, and the Z-axis is perpendicular to the ab cleavage plane, as is shown in Fig. 2. The thirteen elastic constants may be shown, in accordance with Cady,[6] as:

$$\begin{vmatrix} C_{11} & C_{12} & C_{13} & 0 & C_{15} & 0 \\ C_{12} & C_{22} & C_{23} & 0 & C_{25} & 0 \\ C_{13} & C_{23} & C_{33} & 0 & C_{35} & 0 \\ 0 & 0 & 0 & C_{44} & 0 & C_{46} \\ C_{15} & C_{25} & C_{35} & 0 & C_{55} & 0 \\ 0 & 0 & 0 & C_{46} & 0 & C_{66} \end{vmatrix}. \quad (1)$$

Using the observed values of the velocities of

4) A. M. L. Mathieson, J. M. Robertson and V. C. Singlar, *Acta Cryst.*, **3**, 245 (1950).
5) J. M. Robertson, *Rev. Mod. Phys.*, **30**, 155 (1958).
6) W. G. Cady, "Piezoelectricity," McGraw-Hill Book Co., New York (1946).

TABLE 1. THE WAVE DIRECTIONS USED AND THE VELOCITIES MEASURED FOR DETERMINING THREE DIAGONAL CONSTANTS

Direction of propagation	Direction of particle displacement	Measured velocity	Constants determined
[010]	[010]	v_{YY}	$C_{22}=\rho v_{YY}^2$
[100]	[010]	v_{XY}	$C_{66}=\rho v_{XY}^2$
[001]	[010]	v_{ZY}	$C_{44}=\rho v_{ZY}^2$

TABLE 2. THE WAVE DIRECTIONS USED AND THE VELOCITIES MEASURED FOR DETERMINING THE REMAINING THREE DIAGONAL AND SEVEN OFF-DIAGONAL CONSTANTS

Direction cosines of propagation direction l	m	n	Measured velocity	Related constants
0	1	0	$v_{YX}v_{YZ}$	$C_{44}C_{66}C_{46}$
1	0	0	$v_{XX}v_{XZ}$	$C_{11}C_{55}C_{15}$
0	0	1	$v_{ZZ}v_{ZX}$	$C_{33}C_{55}C_{35}$
0.254	0	0.852	v_{t_1}	$C_{44}C_{66}C_{46}$
			$v_{NN}v_{t_2}$	$C_{11}C_{33}C_{55}$ $C_{13}C_{15}C_{35}$
$1/\sqrt{2}$	$1/\sqrt{2}$	0	$v_l v_{t_1} v_{t_2}$	$C_{11}C_{22}C_{44}C_{55}$ $C_{66}C_{12}C_{15}C_{25}$ C_{46}
0	$1/\sqrt{2}$	$1/\sqrt{2}$	$v_l v_{t_1} v_{t_2}$	$C_{22}C_{33}C_{44}C_{55}$ $C_{66}C_{23}C_{25}C_{35}$ C_{46}

longitudinal and transverse sound waves along the three principal axes, the three diagonal terms of elastic constants, that is C_{22}, C_{44}, and C_{66}, may be calculated easily; the results are shown in Table 1.

However, the calculation of the remaining three diagonal terms and the seven off-diagonals is somewhat complicated. In order to determine these diagonal and off-diagonal terms of C_{ij}, it is necessary to carry out the acoustic velocity measurements along other than the principal axes of the crystal. We chose to make velocity measurements along the following three directions: [110], [011] and [101]. Adopting the method of calculation which was used by Aleksandrov[7] for the monoclinic crystal, the remaining three diagonal constants and seven off-diagonal terms were obtained from the measurement of the transversal and longitudinal velocities along each direction, assuming that the density of anthracene $\rho=1.25\ g/cm^3$.[*1] Table 2 summarizes the wave directions and the velocities measured in determining these constants.

Velocity-measurement Apparatus. The ultrasonic pulse technique was used in this work; the pulse duration time was less than 1 μ sec. Figure 3 shows a schematic diagram of the ultrasonic pulse apparatus. The pulsed high-frequency generator was triggered by a negative pulser, which was similar to that described by Shimoda.[8] Further,

7) K. S. Aleksandrov, *Soviet Phys. Cryst.*, **3**, 630 (1958).
*1 See Appendix 2.
8) K. Shimoda, *J. Appl. Phys. Japan*, **27**, 346 (1958).

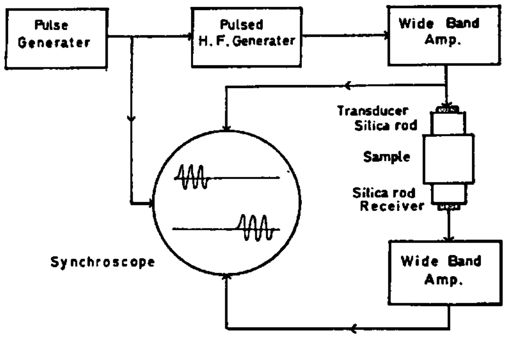

Fig. 3. The schematic diagram of the measurement of ultrasonic velocity across the anthracene crystal.

the synchroscope was triggered by a negative pulse simultaneously. Figure 4 shows the circuit of the high-frequency generator.

The anthracene specimen was sandwiched between two fused silica rods, 5 mm in diameter. A pair of Pb-Zr-titanate ceramics, 4 mm in diameter and 0.6 mm thick, having a fundamental resonance at 3 Mc/sec, were used as the transmitter and the receiver respectively. The transducers were cemented to the fused silica rods using silicone grease. After the transmitter and the receiver had been attached, the assembly was mounted in a holder which contained conductive rubber electrodes pressed against the transducers by a micrometer screw, as is shown in Fig. 5. The micrometer screw permitted a precise control of the acoustic path length.

The signal, transmitted through the specimen, was received by the ceramic receiver and was then amplified by a wide-band amplifier. After the signals from both the specimen and the delayed line had been led to a dual-beam synchroscope, the sound velocity in the specimen was calculated.

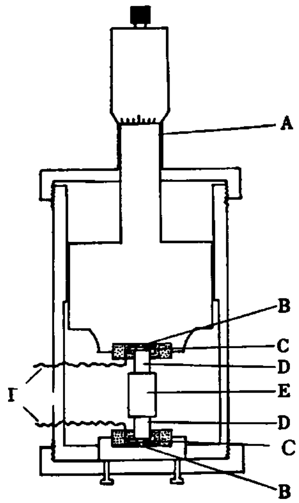

Fig. 5. The assembly for sound velocity measurement across organic crystal. A micrometer screw, B conductive rubber electrodes, C tansmitter, D fused silica rods, E sample, F lead wire and receiver.

Results and Discussion

The measured sound velocities along each direction of crystal are summarized in Table 3, while Table 4 shows the calculated elastic constants of the anthracene crystal.

The elastic compliances, s_{ij}, were calculated from the elastic constants, C_{ij}, by the following equation:

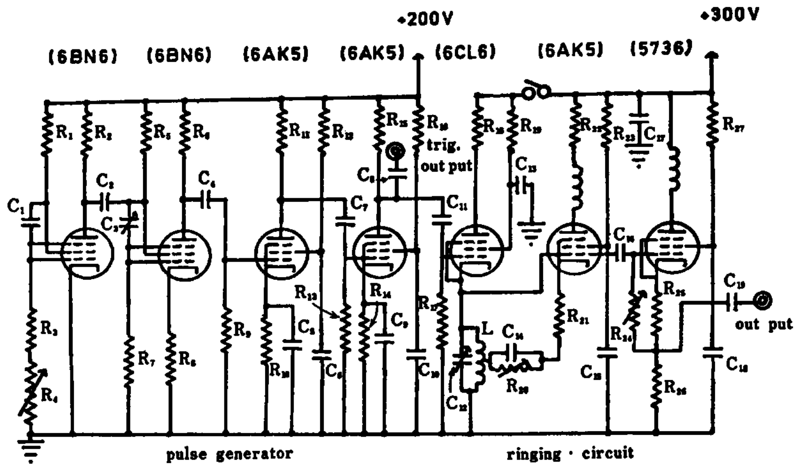

Fig. 4. The circuit of the pulsed high frequency generator, where R_1, R_5 30 kΩ; R_2, R_6 2 kΩ; R_3, R_{11}, R_{15} 1 kΩ; R_4, R_{24} 500 kΩ; R_7, R_{22}, R_{27} 20 kΩ; R_8 500 kΩ; $R_9, R_{12}, R_{13}, R_{16}$ 10 kΩ; R_{10}, R_{14} 180 Ω; R_7 250 kΩ; R_{18}, R_{26} 2 kΩ (20 W); R_{20} 5 kΩ; R_{21} 100 Ω; R_{23} 70 kΩ; R_{25} 150 Ω; C_1, C_{14} 50 pF; C_2 30 pF; C_3 100 pF; C_4, C_{16} 0.01 μF; C_5, C_9, C_{11}, C_{18} 0.1 μF; $C_6, C_{10}, C_{13}, C_{15}$ 0.5 μF; C_7, C_8, C_{16}, C_{19} 0.01 μF; C_{17} 5 μF and C_{12} 400 pF.

TABLE 3. SOUND VELOCITY IN ANTHRACENE CRYSTAL (in 10^5 cm/sec)

Direction of propagation of wave	Direction displacement in wave	Velocity of sound
[001]	[001]	3.75
	[100]	1.35
	[010]	1.39
[010]	[010]	3.32
	[001]	1.15
	[100]	1.75
[100]	[100]	2.81
	[010]	1.59
	[001]	1.32
[101]	[101]	2.91
	[010]	1.76
	$[10\bar{1}]$	1.32
[011]	[011]	2.99
	$[0\bar{1}1]$	1.42
	[100]	1.53
[110]	[110]	3.33
	$[1\bar{1}0]$	1.49
	[001]	1.43

TABLE 4. ELASTIC CONSTANTS OF ANTHRACENE (in 10^{10} dyn/cm^2)

C_{11}	C_{12}	C_{13}	C_{15}	C_{22}	C_{23}	C_{25}
8.92	4.63	4.49	−2.58	13.8	8.44	−2.59

C_{33}	C_{35}	C_{44}	C_{46}	C_{55}	C_{66}
17.0	−2.88	2.42	1.14	2.84	3.16

TABLE 5. ELASTIC COMPLIANCES OF ANTHRACENE (in 10^{-12} cm^2/dyn)

s_{11}	s_{12}	s_{13}	s_{15}	s_{22}	s_{23}	s_{25}
16.5	−2.75	−1.05	11.4	11.6	−4.41	−3.58

s_{33}	s_{35}	s_{44}	s_{46}	s_{55}	s_{66}
9.05	4.19	49.9	−18.0	53.1	38.2

$$s_{ij}=\bar{D}_c\binom{i}{j}\Big/D_c, \qquad (2)$$

The calculated elastic compliances are summarized in Table 5.

When a monoclinic crystal anthracence is compressed under hydrostatic pressure, the linear compressibility, β, is related to the elastic compliance and the direction cosine as follows:

$$\beta=(s_{11}+s_{12}+s_{13})l^2+(s_{21}+s_{22}+s_{23})m^2 \\ +(s_{31}+s_{32}+s_{33})n^2+(s_{15}+s_{25}+s_{35})ln. \qquad (3)$$

Therefore, the linear compressibility along [100], [010] and [001] are calculated by means of Eq. (3); that is:

$$\beta_{[100]}=12.7\times10^{-12}\ \text{cm}^2/\text{dyn}$$
$$\beta_{[010]}=-4.41\times10^{-12}\ \text{cm}^2/\text{dyn}$$
$$\beta_{[001]}=3.59\times10^{-12}\ \text{cm}^2/\text{dyn}.$$

The elastic constants of anthracene are one-tenth or one-hundredth those of valence crystals, ionic crystals, or metals, because of the van der Waals coupling between molecules. The facts that the s_{11} elastic compliance, is the largest and s_{33} is the smallest seem reasonable in view of the packing of the molecules in the monoclinic anthracene crystal.

Further, the pressure-dependence of the electrical properties of the anthracene single crystal is consistent with the results of the compressibility reported here; the electron-drift mobility in the crystal along the direction perpendicular to the ab plane is approximately constant up to a pressure of 6.6 kbar, but the drift mobilities at 6.6 kbar along the a and b axes increase to 1.3 times the atmospheric pressure-value.[9]

In an X-ray investigation of some organic monoclinic molecular crystals, linear polyphenyls, the linear compression was reported to be a 5.4% contraction along the c axis under a pressure of 10 kbar.[10] Our results tend to support this.

Appendix

1) In general, when a plane wave propagates along a direction of which the direction cosine is (lmn), the velocity of this wave is given as the root of the next equation[11]:

$$\begin{vmatrix} \lambda_{11}-\rho v^2 & \lambda_{12} & \lambda_{13} \\ \lambda_{12} & \lambda_{22}-\rho v^2 & \lambda_{23} \\ \lambda_{13} & \lambda_{23} & \lambda_{33}-\rho v^2 \end{vmatrix}=0 \qquad \text{(A-1)}$$

where ρ is the density, and λ is the function of both the direction cosine (lmn) and the elastic constants, C_{ij}, as follows:

$$\begin{aligned} \lambda_{11}&=l^2C_{11}+m^2C_{66}+n^2C_{55}+2mnC_{56} \\ &\quad +2nlC_{15}+2lmC_{16} \\ \lambda_{22}&=l^2C_{66}+m^2C_{22}+n^2C_{44}+2mnC_{24} \\ &\quad +2nlC_{46}+2lmC_{26} \\ \lambda_{33}&=l^2C_{55}+m^2C_{44}+n^2C_{33}+2mnC_{34} \\ &\quad +2nlC_{35}+2lmC_{45} \\ \lambda_{12}&=l^2C_{16}+m^2C_{26}+n^2C_{45}+mn(C_{25}+C_{46}) \\ &\quad +nl(C_{14}+C_{56})+lm(C_{12}+C_{66}) \\ \lambda_{13}&=l^2C_{15}+m^2C_{46}+n^2C_{35}+mn(C_{36}+C_{45}) \\ &\quad +nl(C_{36}+C_{55})+lm(C_{14}+C_{56}) \\ \lambda_{23}&=l^2C_{56}+m^2C_{24}+n^2C_{34}+mn(C_{23}+C_{44}) \\ &\quad +nl(C_{36}+C_{45})+lm(C_{25}+C_{46}) \end{aligned} \qquad \text{(A-2)}$$

2-a) Solving the above determinant (A-1), three equations related to wave propagation along the Y axis to the elastic constants are obtained:

$$C_{22}=\rho v_{YY}^2 \qquad \text{(A-3)}$$
$$C_{44}+C_{66}=\rho v_{YX}^2+\rho v_{YZ}^2 \qquad \text{(A-4)}$$
$$C_{44}C_{66}-C_{46}^2=\rho^2 v_{YX}^2 v_{YZ}^2 \qquad \text{(A-5)}$$

9) T. Kajiwara, H. Inokuchi and S. Minomura, This Bulletin, **40**, 1055 (1967).
10) S. S. Kabalkina, *Soviet Phys. Solid State*, **4**, 2288 (1963).
11) M. J. P. Musgrave, *Proc. Roy. Soc.*, **A 226**, 339 (1954).

The six analogous equations are obtained from the wave propagations along the X and Z axes respectively:

$$C_{66}=\rho v_{XY}^2 \quad \text{(A-6)}$$
$$C_{11}+C_{55}=\rho v_{XX}^2+\rho v_{XZ}^2 \quad \text{(A-7)}$$
$$C_{11}C_{55}-C_{15}^2=\rho^2 v_{XX}^2 v_{XZ}^2 \quad \text{(A-8)}$$

and

$$C_{44}=\rho v_{ZY}^2 \quad \text{(A-9)}$$
$$C_{33}+C_{55}=\rho v_{ZZ}^2+\rho v_{ZX}^2 \quad \text{(A-10)}$$
$$C_{33}C_{55}-C_{35}^2=\rho^2 v_{ZZ}^2 v_{ZX}^2 \quad \text{(A-11)}$$

2-b) As for the propagation along the [101] direction, of which the direction cosine is $l=0.254$, $m=0$, and $n=0.852$, the following three equations are derived from Eqs. (A-1) and (A-2).

$$0.274\,C_{66}+0.726\,C_{44}+0.893\,C_{46}=\rho v_{t_1}^2 \quad \text{(A-12)}$$
$$0.274\,C_{11}+C_{55}+0.726\,C_{33}+0.893(C_{15}+C_{35})=\rho v_{NN}^2+\rho v_{t_2}^2 \quad \text{(A-13)}$$
$$\{0.274\,C_{15}+0.726\,C_{35}+0.446(C_{13}+C_{55})\}^2-(0.274\,C_{11}+0.726\,C_{55}+0.893\,C_{15})\times(0.274\,C_{55}+0.726\,C_{33}+0.893\,C_{35})=\rho^2 v_{NN}^2 v_{t_2}^2 \quad \text{(A-14)}$$

where v_{NN}, v_{t_1}, and v_{t_2} are the velocities of one longitudinal and two transverse waves respectively.

2-c) As for the propagation along the [110] direction, the next determinant is obtained when the direction cosine is $l=1/\sqrt{2}$, $m=1/\sqrt{2}$ and $n=0$.

$$\begin{vmatrix} C_{11}+C_{66}-2\rho v^2 & C_{12}+C_{66} & C_{15}+C_{46} \\ C_{12}+C_{66} & C_{22}+C_{66}-2\rho v^2 & C_{25}+C_{46} \\ C_{15}+C_{46} & C_{25}+C_{46} & C_{55}+C_{44}-2\rho v^2 \end{vmatrix}=0 \quad \text{(A-15)}$$

2-d) Analogously with the propagation along the [110] direction, the determinant for the propagation along the [011] direction is:

$$\begin{vmatrix} C_{66}+C_{55}-2\rho v^2 & C_{25}+C_{46} & C_{46}+C_{35} \\ C_{25}+C_{46} & C_{22}+C_{44}-2\rho v^2 & C_{23}+C_{44} \\ C_{46}+C_{35} & C_{23}+C_{44} & C_{44}+C_{33}-2\rho v^2 \end{vmatrix}=0 \quad \text{(A-16)}$$