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Dynamic Mechanical Behaviour of Organic Molecular Crystals. I

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The forced resonance vibration method was applied to several needle-like organic crystals, triphenylene (I), 1, 2, 3, 4-dibenzanthracene (II), coronene (III), anthracene-trinitrobenzene (TNB) complex (IV), perylene-TNB (V), coronene-TNB (VI), acridine-iode (VII), and acetylacetone-Cu (VIII), and their elastic constants were obtained. The observed Young's moduli, E_1, of these organic crystals were $E_1(\mathrm{I})=1.19\times10^{10}$ dyn/cm^2, $E_1(\mathrm{II})=2.81\times10^{10}$, $E_1(\mathrm{III})=1.10\times10^{10}$, $E_1(\mathrm{IV})=1.24\times10^{11}$, $E_1(\mathrm{V})=7.77\times10^{10}$, $E_1(\mathrm{VI})=9.99\times10^{10}$, $E_1(\mathrm{VII})=1.67\times10^{11}$ and $E_1(\mathrm{VIII})=2.87\times10^{10}$ dyn/cm^2. These values are consistent with the E_1-values of some aromatic hydrocarbons, as obtained from the acoustic velocity.

The dynamic mechanical properties of crystals provide a sensitive test of the nature of bonds and so have been studied by a large number of workers. However, the properties of organic molecular crystals have been scarcely studied at all. The reason for this may be the difficulty of single-crystal preparation and the complexity of their crystal structures.

On the other hand, several experimental studies of the electrical and the optical properties of organic crystals under atmospheric and also under high pressure[1,2] have been made. Consequently, when the dynamic mechanical properties of these organic molecular crystals are studied, their electrical and optical properties may be analysed quantitatively in relation to the mechanical properties.

In this paper, we will report on our work on the elastic constants and losses of some condensed aromatic hydrocarbons[*1] and their complexes by means of the vibrating-reed method.

Experimental

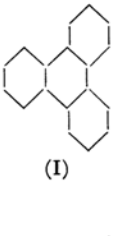
Sample. Three condensed aromatic hydrocarbons were applied to the measurement of elastic constants.

Triphenylene (I). The crude hydrocarbon, obtained from the Rütgerswerke A. G., Germany, was purified by recrystallization from xylene, followed by chromatographing on alumina.

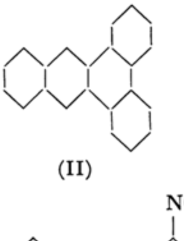
Coronene (II). This seven-ring polycyclic aromatic compound was provided by the Badish Anilin Soda Fabrik A. G., Germany. A fairly pure hydrocarbon was obtained by repeated recrystallizations from 1, 2, 4-trichlorobenzene. When this material was chromatographed under argon, it yielded pale yellow needles, which were then sublimed at 250°C under a vacuum of 10^{-5} mmHg.

1, 2, 3, 4-Dibenzanthracene (III). This pale yellow hydrocarbon, also furnished by the Rütgerswerke A. G., was purified by recrystallization from benzene, followed by sublimation *in vacuo*. Through this sublimation, fine needle-like single crystals of several millimetres in length were obtained.

Further, three kinds of complexes between the aromatics and trinitrobenzene (TNB) (anthracene-TNB (IV), perylene-TNB (V), and coronene-TNB (VI)) were prepared: When the hot carbon tetrachloride solution which dissolved equivalent amounts of the purified aromatic hydrocarbon, anthracene,[*2] perylene,[*2] or coronene, and TNB, was cooled, the complex was precipitated as needle-like crystallites. The acridine-iode (VI) and acetylacetone-copper (VII) complexes were kindly supplied by Dr. Tokiko Uchida.



(I)



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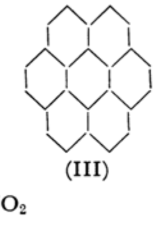

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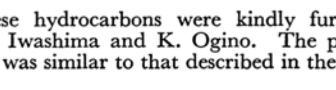

(IV)

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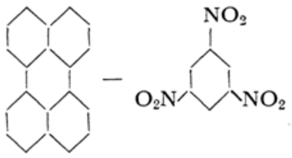
1) H. Inokuchi, I. Shirotani and S. Minomura, This Bulletin, **37**, 1234 (1964); **39**, 386 (1966); **40**, 2277 (1967); T. Kajiwara, H. Inokuchi and S. Minomura, *ibid.*, **40**, 1055 (1967).

2) H. Ohigashi, I. Shirotani, H. Inokuchi and S. Minomura, *J. Phys. Soc. Japan*, **19**, 1966 (1964); *J. Chem. Phys.*, **43**, 314 (1965); *Mol. Cryst.*, **1**, 463 (1966).

[*1] As has been mentioned above, the preparation of large single crystals is generally difficult. Therefore, in this experiment, long and fine needle-like single crystals were used to observe their elastic constants along the longest side, usually the b-axis.

[*2] These hydrocarbons were kindly furnished by Messrs. S. Iwashima and K. Ogino. The purification procedure was similar to that described in the preceding section.



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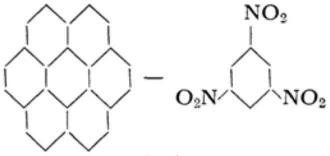

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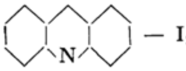

(VII)

$CH_3 \cdot CO \cdot CH_2 \cdot CO \cdot CH_3 - Cu$

(VIII)

Apparatus. The forced resonance vibration method[3] was applied to the needle-like organic crystals in order to measure their Young's moduli. Figure 1 shows a schematic diagram of the resonance vibration method. The needle-like specimen was attached to the moving coil of a modified loud-speaker with an appropriate adhesive.

The amplitude of the free end (1 in Fig. 1) was measured by visual observation with a cathetometer. The whole vibrating-reed system was mounted in a bell jar, which was then evacuated to 10^{-2} mmHg in order to avoid any air-damping of the vibration.

All the experiments were carried out at room temperature. The density of the samples was determined by a pycnometer.

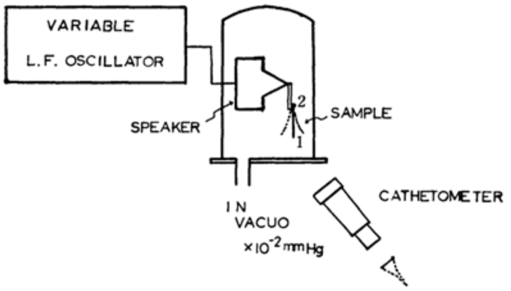

Fig. 1. The schematic diagram of the vibrating-reed method.

Results and Discussion

The methods of the calculation of the modulus of elasticity, E_1, and the viscosity coefficient, η, have already been reported by Horio *et al.*:[3]

$$E^* = E_1 + jE_2 \qquad (1)^{*3}$$

$$E_1 = \frac{4\pi^2}{a_0{}^4 k^4} \cdot \rho \cdot l^4 \left\{ \nu_r{}^2 + \frac{1}{8} (\varDelta\nu)^2 \right\} \qquad (2)^{*3}$$

$$\eta = \frac{E_2}{\omega} = \frac{2\pi}{a_0{}^4 k^2} \cdot \rho \cdot l^4 \cdot \varDelta\nu \qquad (3)^{*3}$$

The dimensions and the densities of the specimens used in this study are summarized in Table 1.

TABLE 1. THE DIMENSION AND THE DENSITY OF SPECIMENS

Substance	Length mm	Thickness mm	Density g/cm³
Triphenylene	9.68	5.71×10^{-3}	1.30
1, 2, 3, 4-Dibenzanthracene	9.39	1.07×10^{-2}	1.30
Coronene	4.53	2.63×10^{-2}	1.38
Coronene-TNB	2.61	4.24×10^{-3}	1.67
Anthracene-TNB	4.69	0.71×10^{-2}	1.40
Perylene-TNB	5.10	2.14×10^{-2}	1.55
Acridine-I₂	6.85	8.29×10^{-2}	2.40
Acetylacetone-Cu	2.36	1.43×10^{-2}	1.62

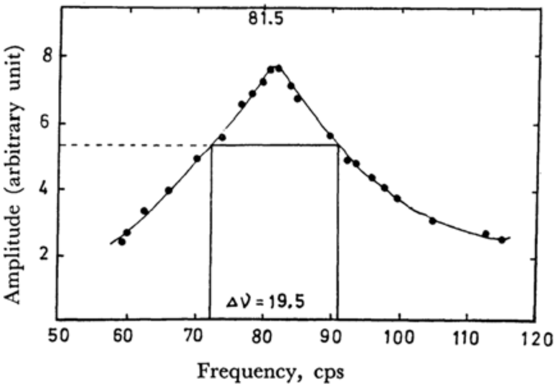

Fig. 2. The resonance curve of triphenylene.

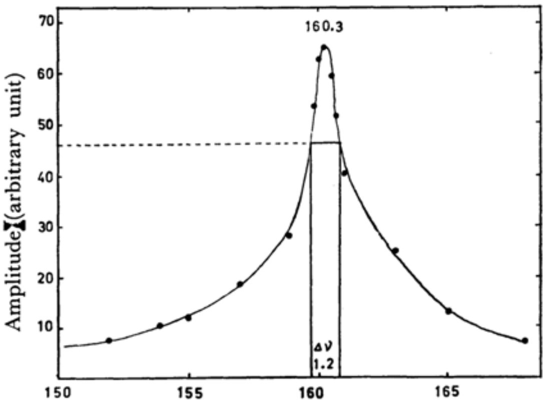

Fig. 3. The resonance curve of coronene.

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3) J. W. Ballon and J. C. Smith, *J. Appl. Phys.*, **20**, 493 (1949); M. Horio and S. Onogi, *ibid.*, **22**, 977 (1951) and S. Newman, *J. Appl. Polymer Sci.*, **2**, 333 (1959).

[*3] In these equations, ρ is the density of the compound, k^2, the moment of inertia, ν_r, the resonance frequency at the free end of the specimen, $\varDelta\nu$, the band width of the resonance curve, and l, the length of the specimen. Further, for a fundamental vibration, $a_0 = 1.875$.

The Condensed Aromatic Hydrocarbons. Figure 2 shows the resonance curve of the triphenylene single crystal. From the curve, the resonance frequency, $\nu_r = 8.15\times 10$ cycle/sec, and the half-value width, $\Delta\nu = 1.95\times 10$ cycle/sec, were obtained. Moreover, similarly shaped resonance curves were found for coronene and 1, 2, 3, 4-dibenzanthracene: $\nu_r = 1.60\times 10^2$ cycle/sec and $\Delta\nu = 1.2$ cycle/sec for coronene, and $\nu_r = 25$ cycle/sec and $\Delta\nu = 1.0$ cycle/sec for 1, 2, 3, 4-dibenzanthracene. Figure 3 shows the resonance curve for coronene.

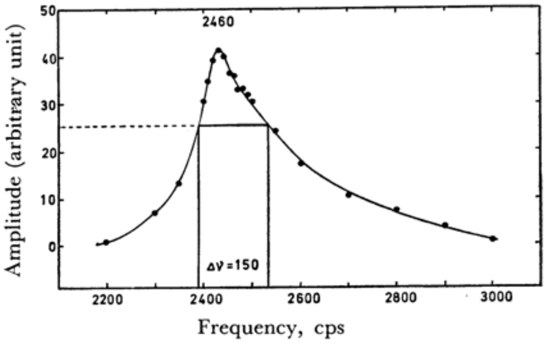

Fig. 4. The resonance curve of coronene-TNB.

The Charge Transfer Complexes. Figure 4 shows the resonance curve for the coronene-TNB complex; it has a resonance frequency of 2.46×10^3 cycle/sec and a half-width frequency of 1.50×10^2 cycle/sec. The resonance frequencies of the two other complexes, anthracene-TNB and perylene-TNB, were 1.55×10^3 cycle/sec and 2.98×10^2 cycle/sec respectively, while the $\Delta\nu$ value for perylene-TNB was 1.9×10 cycle/sec.

A similar procedure was carried out for different types of complexes: $\nu_r = 4.86\times 10^2$ cycle/sec $\Delta\nu = 3.4$ cycle/sec for the acridine-I_2 complex, and $\nu_r = 5.52\times 10^2$ cycle/sec and $\Delta\nu = 3.2\times 10$ cycle/sec for the acetylacetone-Cu complex.

On the basis of these results, the dynamic elastic moduli and the losses are listed in Table 2, these values were obtained by applying Eqs. (2) and (3).

TABLE 2. THE ELASTIC MODULI AND LOSSES OF SOME MOLECULAR ORGANIC CRYSTALS AND CHARGE-TRANSFER COMPLEXES

Substance	E_1 dyn/cm^2	E_2 dyn/cm^2
Triphenylene	1.19×10^{10}	2.29×10^9
1, 2, 3, 4-Dibenzanthracene	2.81×10^{10}	1.13×10^9
Coronene	1.10×10^{10}	8.21×10^7
Coronene-TNB	9.99×10^{10}	6.10×10^9
Anthracene-TNB	12.4×10^{10}	—
Perylene-TNB	7.77×10^{10}	4.96×10^9
Acridine-Iode	16.7×10^{10}	4.82×10^8
Acetylacetone-Cu	2.87×10^{10}	2.55×10^9

Since the growth of these organic single crystals takes place along the b-axis, the observed modulus, E_1, corresponds approximately to Young's modulus along the b-axis. The elastic moduli of these simple molecular crystals are very small in comparison with those of other kinds of crystals, ionic crystals, valence crystals, and metals, and are of an order similar to that of organic polymers.3) These results are acceptable in view of the fact that these crystals are built up with weak van der Waals' forces. Recently, the elastic moduli of the anthracene single crystal have been observed by the ultrasonic method.4) Those results also are consistent with the present data.

The elastic moduli of the charge-transfer complexes were ten times larger than those of the simple aromatic hydrocarbons. This increment may be interpreted in terms of the contribution of a partially ionic character to the dispersion force.

The vibration-reed method is simple and is useful for observing the elastic constants of the molecular crystals. However, the observation by this method is limited to one axis. Therefore, the measurement of the velocity of ultrasonic waves in the large single crystals is now in progress in order to obtain detailed information on their dynamic mechanical characteristics along all their axes.

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4) T. Danno, to be published.