

Elastic Constants of Acenaphthene Determined from Studies of Thermal Diffuse Scattering of X-rays

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Abstract

The absolute values of all the nine elastic constants of acenaphthene single crystals, $C_{12}H_{10}$, belonging to the orthorhombic system, have been determined by the photographic method from the measurement of the intensities of thermal diffuse scattering observed in a series of Laue photographs taken with monochromatized Cu $K\alpha$ radiation having no higher harmonics of $\lambda_{K\alpha}$. The direct beam was recorded photographically after being absorbed through nickel foils of known thickness, its intensity being reduced by a factor of 10^6 . Diffuse scattering domains near the reciprocal-lattice nodes 400, 080, 004, 105, 014 and 072 were investigated extensively. The diffusely scattered intensities were corrected for the general scattering, polarization and skew factors. Corrections for absorption, divergence and second-order diffuse scattering were found negligible. The values of the elastic constants in units of GN m^{-2} , with e.s.d.'s in parentheses, are $C_{11} = 11.05$ (50); $C_{22} = 10.26$ (30); $C_{33} = 9.40$ (23); $C_{44} = 4.25$ (08); $C_{55} = 3.69$ (07); $C_{66} = 4.87$ (10); $C_{12} = -1.93$ (20); $C_{13} = 3.34$ (12); $C_{23} = 2.34$ (13). The accuracy of experimentally determined values of the elastic constants is discussed.

Introduction

From the study of thermal diffuse scattering (TDS) of X-rays from single crystals, Ramchandran & Wooster (1951*a, b*), Prince & Wooster (1951, 1953), Prasad & Wooster (1955*a, b, c*, 1956*a*), by the counter diffractometer method, and Prasad & Wooster (1956*b, c*), by the photographic method, determined the ratios of the elastic constants of a number of crystals belonging to high-symmetry classes; from the corresponding compressibility data, the absolute values of the elastic constants were computed. Chakraborty (1958; Chakraborty & Sen, 1958) developed a photographic photometric method for a quantitative study of TDS and the method was successfully applied for the first time to the determination of absolute values of all the elastic constants of benzil ($C_{14}H_{10}O_2$), a trigonal

crystal, from X-ray measurements only. The outstanding feature of this method is its simplicity, high angular resolution and practicability for studying TDS owing to the low values of q for which the theory is correct. The other marked advantage of the method is that only very small crystals are required for such an investigation and these can be easily obtained free from any static defect. Further, the stabilization of the output of the X-ray tube, which is essential for the counter diffractometer method, is not essential for this method. This specially developed photographic method has been used by a number of investigators (Srivastava & Chakraborty, 1962; Joshi & Kashyap, 1964; Chandra & Hemkar, 1973) to determine absolute values of elastic constants of a number of molecular crystals. In the present investigation a similar method has been applied to determine the elastic constants of crystals of acenaphthene belonging to the orthorhombic system.

Theory

In the long-wave approximation, the first-order diffusely scattered X-ray intensity, I_d , in the direction ϕ from a thermally vibrating crystal of volume δV containing N unit cells, is given by

$$I_d = I_0 \varepsilon^2 \frac{NkT}{\tau} F_T^2 \frac{Q^2}{q^2} K[uvw]_{lmn} \quad (1)$$

$$= I_0 \varepsilon^2 \frac{kT}{\tau^2} \delta V F_T^2 \frac{Q^2}{q^2} K[uvw]_{lmn},$$

where I_0 = intensity of an incident X-ray at the crystal; ε^2 = intensity scattered by a free electron under identical conditions,

$$\varepsilon^2 = \left(\frac{e^2}{mc^2} \right)^2 \frac{1}{r^2} [A^2 + B^2 \cos^2 \phi];$$

e , m = electronic charge and mass respectively; c = velocity of light; r = the distance of the scattering volume from the point of observation; A , B = amplitude components normal and parallel to the plane of incidence for unit incident intensity; k = Boltzmann

constant; T = absolute temperature of the crystal; F = crystal structure factor at the temperature T for the plane (hkl) giving rise to the diffuse reflection; \mathbf{Q} = reciprocal-lattice vector corresponding to the node hkl ; \mathbf{q} = thermal wave vector; τ = volume of the unit cell of the crystal;

$$K[uvw]_{lmn} = P^2 A_{11}^{-1} + Q^2 A_{22}^{-1} + R^2 A_{33}^{-1} + 2PQA_{12}^{-1} \\ + 2QRA_{23}^{-1} + 2PRA_{13}^{-1}.$$

P , Q , R , and u , v , w are the direction cosines of \mathbf{Q} and \mathbf{q} respectively with respect to the orthogonal axes that are used to define the elastic properties, and A_{11}^{-1} , A_{22}^{-1} , etc. are the elements of the matrix inverse to the matrix A_{ij} whose elements for an orthorhombic crystal are given by

$$A_{11} = C_{11}u^2 + C_{66}v^2 + C_{55}w^2 \\ A_{22} = C_{66}u^2 + C_{22}v^2 + C_{44}w^2 \\ A_{33} = C_{55}u^2 + C_{44}v^2 + C_{33}w^2 \\ A_{23} = (C_{44} + C_{23})vw \\ A_{31} = (C_{55} + C_{13})wu \\ A_{12} = (C_{66} + C_{12})uv.$$

The values of \mathbf{q} and φ for a particular direction of propagation of the thermal wave are calculated from the known orientation of the crystal with respect to the incident rays. \mathbf{Q} and τ are known from the axial parameters. The crystal structure factor F_T is known from the intensity of the Bragg reflections. The volume δV is calculated from the measured weight of the crystal and its density. Hence, from a measurement of I_d/I_0 in the direction φ , the value of $K[uvw]_{lmn}$ can be evaluated from (1) and from it the elastic constants.

Experimental

Crystals of acenaphthene were grown by slow evaporation of the solution of the compound in ether with a mixture of ethyl acetate and carbon tetrachloride at room temperature (298–303 K). Well defined single crystals thus obtained were tested for any static defect. A single crystal of suitable dimensions (about 0.5 mm long) was weighed by means of a semimicrobalance. Because the crystal sublimates very slowly a special technique had to be adopted for the experimental study. A weighed crystal free from any strain was introduced inside a thin-walled Lindemann-glass capillary tube sealed at one end with the desired axis of the crystal approximately lying along the axis of the tube. Aluminium powder in the form of a small globule was placed on the top of the crystal. The capillary tube was then sealed and placed vertically on the goniometer head. In order to increase the re-

solution, the Laue photographs were taken with a Universal Unicam camera fitted with a specially fabricated film holder of diameter 100 mm and a modified collimator of suitable dimensions. Al powder diffraction lines were used for (i) determination of the correct orientation of a particular plane with respect to the incident beam; (ii) standardization of the camera radius; and (iii) calibration of the angle of diffraction to a high degree of accuracy. In certain cases, however, the Al powder lines were found to superpose on the selected diffuse spot under study. In such cases a sharp metallic knife edge was used instead of Al powder to achieve the same objective.

The monochromatized X-ray beam (Cu $K\alpha$), obtained by reflection from a lithium fluoride plane crystal, was collimated and allowed to fall on the crystal at the correct orientation, known from the Laue photograph taken earlier with white radiation. The direct beam was recorded on the film after reduction in intensity by a factor of about 10^6 by interposing nickel foils of known thickness between the experimental crystal and the film so that the intensity of the recorded transmitted beam and that of the diffuse reflection became comparable. The average time of exposure varied from 20 to 40 h. The X-ray unit was operated at 18 kV and 25 mA so that $\lambda/2$ and higher harmonics were practically absent. Each photograph thus obtained contained the diffuse spot, the impression of the direct beam and Al powder lines (or image of the sharp knife edge). A large number of such photographs for various diffuse reflections with different angles of misset ($\pm\Delta\theta$) from the Bragg position were taken. As we were interested in long-wave approximation, photographs for small values of $\pm\Delta\theta$ were considered. Each photograph was developed in fresh developer solution at a controlled temperature together with a calibration strip, cut from the same sheet of film as used to record the diffuse spot with the monochromatic beam.

For the distribution of the intensity of the diffuse spot along φ , the angle of diffraction was used, and for intensity of the direct beam, a recording microphotometer was used. Photographs were scanned by an exploring spot of light with appreciably high intensity and small size along an equatorial line passing through the diffuse spot and the direct beam image, and the photometric curves were thus recorded. The intensities were computed from the ordinates of the photometric curve by comparison with the calibration wedge, following the method of Robinson (1933). The measured intensities were corrected for general scattering, polarization, and skew factors. Corrections for divergence, absorption and second-order diffuse scattering were, however, not taken into consideration because contributions from such effects towards the intensity were found to lie well below the limits of accuracy of measurement of the intensities by the photographic method.

Results

Acenaphthene, $C_{12}H_{10}$, belongs to the orthorhombic system with axial parameters $a = 8.92$ (1), $b = 14.00$ (1) and $c = 7.22$ (1) Å and space group $Pcm2_1$. There are four molecules per unit cell and $\rho_{\text{calc}} = 1.22$ and $\rho_{\text{obs}} = 1.20$ Mg m^{-3} . The melting point of the substance is 368 K.

For the determination of all the nine elastic constants of this crystal, a series of Laue photographs were taken with monochromatized Cu $K\alpha$ radiation to record 004, 080, 014 and 072 diffuse spots with the [100] crystal axis coinciding with the axis of the camera; 004, 400 and 014 diffuse spots with the [010] crystal axis coinciding with the axis of the camera; and 080, 400 diffuse spots with the [001] crystal axis coinciding with the axis of the camera.

The value of the wave vector \mathbf{q} for any particular direction of propagation for the thermal wave and the corresponding angle of diffraction φ was calculated by establishing trigonometrical relations from the consideration of the geometrical position of the sphere of reflection in the reciprocal-lattice net for a particular

setting of the crystal with respect to the incident X-ray beam. The uncorrected diffuse intensity corresponding to this value of φ was determined from the ordinate of the microphotometric record of the diffuse spot and from this a corrected value of I_d/I_0 was calculated. For a particular direction of propagation of a thermal wave, corrected values of diffuse intensity in terms of incident intensity, i.e. I_d/I_0 , were plotted against $\lambda_t^2 = 1/q^2$ for the different orientation photographs taken to record a particular diffuse spot. The mean curve was a straight line passing through the origin. A few such graphical representations showing the dependence of I_d/I_0 on λ_t^2 obtained for different directions of propagation of thermal waves for three diffuse spots are shown in Fig. 1.

The value of $K[uvw]_{hkl}$ in general depends in a complex way on elastic constants and the direction of propagation of the wave. The values of $K[uvw]_{hkl}$ as functions of C_{ij} , which were utilized in the present study, are given in Table 1.

Table 1 shows that for some simple directions of propagation of thermal waves, $K[uvw]_{hkl}$ depends on one constant only and corresponding to these directions

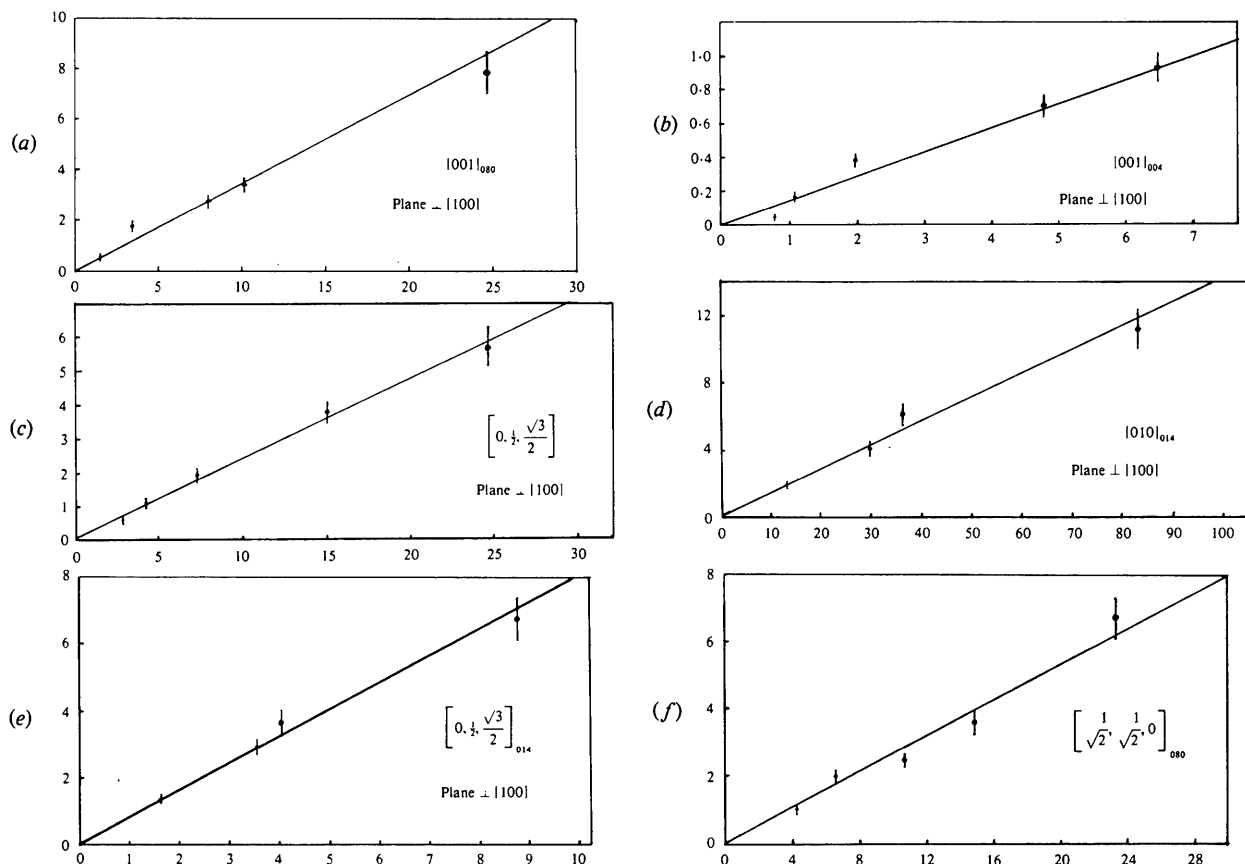


Fig. 1. Variation of TDS intensity ($I_d/I_0 \times 10^6$ along ordinate) with the square of the wavelength of thermal waves ($\lambda_t^2 \times 10^{-3}$ Å along abscissa) for different directions of propagation vector and various reciprocal-lattice points, plotted with possible error in intensity measurement of up to 5%.

Table 1. $K[uvw]_{hkl}$ in terms of elastic constants

$K[010]_{004}$	$\frac{1}{C_{44}}$	$K[010]_{014}$	$\frac{Q^2}{C_{44}} + \frac{R^2}{C_{33}}$
$K[001]_{004}$	$\frac{1}{C_{33}}$	$K[001]_{072}$	$\frac{Q^2}{C_{22}} + \frac{R^2}{C_{33}}$
$K[010]_{080}$	$\frac{1}{C_{22}}$	$K[100]_{105}$	$\frac{P^2}{C_{11}} + \frac{R^2}{C_{55}}$
$K[001]_{080}$	$\frac{1}{C_{44}}$	$K[001]_{105}$	$\frac{P^2}{C_{55}} + \frac{R^2}{C_{33}}$
$K[100]_{004}$	$\frac{1}{C_{55}}$		
$K[100]_{400}$	$\frac{1}{C_{11}}$		
$K[100]_{080}$	$\frac{1}{C_{66}}$		
$K[0, 1/\sqrt{2}, 1/\sqrt{2}]_{004}$	$\frac{2(C_{22} + C_{44})}{C_{22}(C_{33} + C_{44}) + C_{33}C_{44} - 2C_{23}C_{44} - C_{23}^2}$		
$K[0, 1/\sqrt{2}, 1/\sqrt{2}]_{080}$	$\frac{2(C_{33} + C_{44})}{C_{22}(C_{33} + C_{44}) + C_{33}C_{44} - 2C_{23}C_{44} - C_{23}^2}$		
$K[1/\sqrt{2}, 0, 1/\sqrt{2}]_{004}$	$\frac{2(C_{11} + C_{55})}{C_{11}(C_{33} + C_{55}) + C_{33}C_{55} - 2C_{13}C_{55} - C_{13}^2}$		
$K[1/\sqrt{2}, 0, 1/\sqrt{2}]_{400}$	$\frac{2(C_{33} + C_{55})}{C_{11}(C_{33} + C_{55}) + C_{33}C_{55} - 2C_{13}C_{55} - C_{13}^2}$		
$K[1/\sqrt{2}, 1/\sqrt{2}, 0]_{080}$	$\frac{2(C_{11} + C_{66})}{C_{11}(C_{22} + C_{66}) + C_{22}C_{66} - 2C_{12}C_{66} - C_{12}^2}$		

the related values of I_d/I_0 were used in (1) to determine the values of C_{ij} for $i = j$. The absolute values of C_{11} , C_{22} , C_{33} , C_{44} , C_{55} and C_{66} were thus determined independently from the TDS of X-rays in different sections around the reciprocal-lattice nodes 400, 080 and 004. The values of these elastic constants thus determined were also redetermined by considering TDS about the reciprocal-lattice nodes of the type $h0l$, $0kl$, where the K values are functions of two elastic constants as shown in Table 1.

The remaining three elastic constants, C_{12} , C_{13} and C_{23} , were determined by considering thermal waves travelling in complex directions. The value of C_{12} was determined by considering TDS along $[1/\sqrt{2}, 1/\sqrt{2}, 0]$ for the 080 diffuse spot, where

$$K[1/\sqrt{2}, 1/\sqrt{2}, 0]_{080} = \frac{2(C_{11} + C_{66})}{C_{11}(C_{22} + C_{66}) + C_{22}C_{66} - 2C_{12}C_{66} - C_{12}^2}$$

involves the values of constants C_{11} , C_{22} , C_{66} and C_{12} . It gives

$$C_{12} = -C_{66} + C_{66} + C_{11}(C_{22} + C_{66}) + C_{22}C_{66} - \frac{2(C_{11} + C_{66})^{1/2}}{K[1/\sqrt{2}, 1/\sqrt{2}, 0]_{080}}$$

Thus, the value of C_{12} was determined with $K[1/\sqrt{2}, 1/\sqrt{2}, 0]_{080}$ and known values of C_{11} , C_{22} and C_{66} .

Similarly, the value of the constant C_{13} was determined from two separate sets of values of K , namely $K[1/\sqrt{2}, 0, 1/\sqrt{2}]_{004}$ and $K[1/\sqrt{2}, 0, 1/\sqrt{2}]_{400}$, and the value of C_{23} from values of $K[0, 1/\sqrt{2}, 1/\sqrt{2}]_{004}$ and $K[0, 1/\sqrt{2}, 1/\sqrt{2}]_{080}$.

The absolute values of all nine elastic constants of acenaphthene could thus be determined from measured intensities of TDS in various directions around different reciprocal-lattice nodes. The mean values of the elastic constants obtained from various measurements of TDS for different settings of the crystal with respect to the incident beam are given in the *Abstract*.

Discussion

The accuracy of the absolute values of the constants determined is limited owing to normal errors in the measurement of intensities, the error in the absolute values of the crystal structure factors used and the linear absorption factor for the nickel foils used to attenuate direct-beam intensities. The values of the constants are reliable within 5%. This may be seen if we compare the expected values of I_d/I_0 computed by utilizing the experimentally determined values of the constants with the experimental value of

$$K[0, \sqrt{3}/2, 1/2]_{080} = \frac{4(C_{33} + 3C_{44})}{C_{33}3C_{22} + C_{44} + 9C_{22}C_{44} - 3C_{33}^2}$$

The experimental value is $13.7 \mu\text{m}^2 \text{N}^{-1}$ as obtained from the I_d/I_0 vs λ_l^2 curve, whereas the calculated value for this direction of propagation is $13.5 \mu\text{m}^2 \text{N}^{-1}$. The agreement is excellent. Similarly, the observed and calculated values of $K[0, \sqrt{3}/2, 1/2]_{004}$ are 19.5 and $23.0 \mu\text{m}^2 \text{N}^{-1}$ respectively.

Once again these values lie within the limits of accuracy of the experimental results. Further, an examination of the packing of the acenaphthene molecules (Ehrlich, 1957) in the unit cell shows that the intermolecular separation is largest along **c**. Thus, the van der Waal type of interaction, which is the principal interaction between any two molecules for this type of structure of organic crystals, will be of lower magnitude along **c** than that along **a** and **b**. This obviously would indicate lower values of force constants in the **c**

direction. Consequently, the longitudinal deformation along **c** will be more compared with that along **a** and **b** for the same magnitude of longitudinal stress in the three directions. Thus, from the structural point of view one would expect that $C_{33} < C_{11}$ or $< C_{22}$ and the experimentally determined values of the elastic constants are thus consistent with the structure of the crystal. Magnitudes of the shearing deformation are expected to be larger in comparison with the longitudinal deformation. Consequently, the values of C_{44} , C_{55} and C_{66} should be much lower than the values of C_{11} , C_{22} and C_{33} . This has actually been obtained in the present investigation. The values of the constants are thus estimated to be accurate within 5% for the constants C_{ij} when $i = j$ and 10% for the constants where $i \neq j$.

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Des Dangers d'Utiliser sans Précaution des Tables de Sous-Groupes Maximum; Retour au Théorème d'Hermann*†

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Abstract

Most tables of space subgroups of space groups are devoted to maximal subgroups. Although available tables of maximal subgroups are complete with regard to *translationgleich* subgroups, they are inaccurate concerning *klassengleich* subgroups. As a matter of fact, these tables do not show that several *klassengleich* subgroups relevant to the same set of basis vectors may be distinguished by non-congruous origins.

Moreover, these tables do not give any information about isosymbolic subgroups. These failures are prejudicial to phase-transition applications. The paper is illustrated by several examples. For instance, *thirteen intermediate subgroups* between space group $Pm\bar{3}m$ (A, B, C) and its subgroup $P4/m$ (A – B, A + B, 2C) result from repeated use of maximal-subgroup tables; actually there are *four distinct subgroups* $P4/m$ (A – B, A + B, 2C) with origins $(0,0,0)$, $(\frac{1}{2}, \frac{1}{2}, 0)$, $(0, 0, \frac{1}{2})$, $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (referred to the standard setting of $Pm\bar{3}m$) and *forty-six intermediate subgroups*. Another example is connected with perovskite-derivative structures: the tilt system $a^0a^0c^-$ of Glazer [*Acta Cryst.* (1972), **B28**, 3384–3392] is not the only model associated with the subgroups $I4/mcm$ (A – B, A + B, 2C) of $Pm\bar{3}m$; there are three other models.

* English translations, not 'refereed' may be obtained from the author on request.

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