

DETERMINATION OF ELASTIC CONSTANTS OF *m*-DINITROBENZENE FROM DIFFUSE REFLECTIONS OF X-RAYS

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The absolute values of all the nine elastic constants of orthorhombic *m*-dinitrobenzene have been determined at room temperature (293 K—295 K) from the measurement of intensities of thermal diffuse scattering (TDS) of X-rays using photographic-photometric method. A series of Laue photographs were taken with a monochromatic CuK_α radiation obtained by reflection from a fluorite crystal. Diffuse scattering domains near the reciprocal lattice nodes 600, 040, 081, 101 and 520 were extensively studied. The values of elastic constants in units of 10^9 Nm^{-2} are: $C_{11} = 10.70$ (05), $C_{22} = 11.30$ (03), $C_{33} = 20.27$ (19), $C_{44} = 4.37$ (04), $C_{55} = 2.04$ (05), $C_{66} = 5.31$ (03), $C_{12} = 6.30$ (18), $C_{13} = 1.95$ (14), $C_{23} = 3.19$ (16). The accuracy of the experimentally determined values of the constants is discussed.

1. Introduction

From the study of the thermal diffuse scattering of X-rays from crystals Rammachandran and Wooster¹⁾ for the first time studied the elastic properties of crystals. Prince and Wooster²⁾ and Prasad and Wooster³⁾ determined the ratios of elastic constants for a number of inorganic crystals belonging to cubic and tetra-

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gonal classes from the quantitative measurement of intensities of diffuse spots by Geiger Counter spectrometry. Prasad and Wooster, Hoerni and Wooster⁴), also determined the ratios of elastic constants using a photographic method by measuring the intensities of diffuse reflection. Chakraborty and Sen⁵) developed and standardised a method for the quantitative study of TDS by photographic-photometric method where the values of both the incident intensity and diffuse intensity were obtained in the same scale and thus they determined the values of the elastic constant of benzil directly. The outstanding feature of this method is its simplicity, high angular resolution and practicability for studying TDS owing to the low q values for which the theory is correct. The advantage of the method is that only very small crystals are required for such an investigation and these can easily be obtained free from any static defect. Furthermore 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 method has been successfully employed by a number of investigators e. g. Srivastava and Chakraborty⁶), Joshi and Kashyap⁷), Chandra and Hemkar⁸), Chakraborty and Chatterjee⁹) to determine the absolute values of elastic constants of a number of molecular crystals. In the present study a similar method has been employed to determine the elastic constants of *m*-dinitrobenzene¹⁰) of orthorhombic symmetry. The crystal-data are given in Table 1.

TABLE 1.

Chemical formula	$C_6H_4N_2O_4$; D_M — 1.570 g/cm ³
Crystal system	Orthorhombic; D_C — 1.583 g/cm ³
Axial parameters	$a = 13.257 \times 10^{-10}$ m, linear absorption $b = 14.048 \times 10^{-10}$ m, coefficient (μ_c) for $CuK\alpha$ — 13.5 mm ⁻¹ $c = 3.806 \times 10^{-10}$ m,
Space group	Pbn 2 ₁
No. of molecules per cell	4
Vol. of unit cell	708.80×10^{-30} m ³ ,

Crystal data on *m*-dinitrobenzene (room temp.).

2. Theory

The ratio (σ') of the intensity of diffuse X-rays I'_d (after all corrections) to that of the incident beam I_0 , corresponding to a thermal wave vector q (where $|q| \rightarrow 0$), is given by the relation (Laval¹¹); Wooster¹²)

$$\sigma' = I'_d/I_0 = \frac{\varepsilon^2 kT}{V^2} F_T^2 \frac{|Q|^2}{|q|^2} K [uvw]_{hkl} \delta V \dots \quad (1)$$

where ε^2 is the intensity scattered by a free electron and is given by

$$\varepsilon^2 = (e^2/mc^2)^2 \frac{1}{R^2} (P_1^2 + P_2^2 \cos^2 \varphi) \tag{2}$$

e , m are the electronic charge and mass, respectively, c is the velocity of light, R is the distance of the scattering volume from the point of observation, P_1 and P_2 are the amplitude components normal and parallel to the plane of incidence for unit incident intensity, k is the Boltzmann's constant, F_T is the structure factor of the reflection hkl at temperature T , Q is the reciprocal lattice vector corresponding to hkl , q is the thermal wave vector, δV is the volume of the crystal immersed in the beam and V is the volume of the unit cell, $K [uvw]_{hkl}$ is given by

$$K [uvw]_{hkl} = L^2 A_{11}^{-1} + M^2 A_{22}^{-1} + N^2 A_{33}^{-1} + 2MN A_{23}^{-1} + 2NL A_{13}^{-1} + 2ML A_{12}^{-1} \tag{3}$$

where L , M , N and u , v , w are the direction cosines of Q and q , respectively w. r. t, orthogonal elastic axes, A_{ij}^{-1} are the elements of the inverse of the matrix A_{ij} which for orthorhombic crystals is given by Wooster,

$$\begin{matrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ & C_{22} & C_{23} & 0 & 0 & 0 \\ & & C_{33} & 0 & 0 & 0 \\ & & & C_{44} & 0 & 0 \\ & & & & C_{55} & 0 \\ & & & & & C_{66} \end{matrix}$$

The values of q and φ for a particular direction of propagation of the thermal wave are calculated from the known orientation of the crystal w. r. t. the incident rays. Q and V are known from the axial parameters of the crystal, F_T from the intensity of the Bragg reflections. The volume δV is calculated from the measured weight of the crystal and its density. Hence from the measurement of I_d/I_0 in the direction φ , the value of $K [u v w]_{hkl}$ can be calculated from (1) and from it the elastic constants.

The value of $K [u v w]_{hkl}$ in general depends in a complex way on the elastic constants and the direction of propagation of the wave. The values of $K [u v w]_{hkl}$ as functions of C_{ij} which were utilised in the present study is given in Table 2.

TABLE 2.

$$K [100]_{600} = \frac{1}{C_{11}}$$

$$K [010]_{040} = \frac{1}{C_{22}}$$

$$K [001]_{040} = \frac{1}{C_{44}}$$

$$K [010]_{600} = \frac{1}{C_{66}}$$

$$K [100]_{040} = \frac{1}{C_{66}}$$

$$K [001]_{600} = \frac{1}{C_{55}}$$

$$K [011]_{101} = \frac{L^2}{C_{55}} + \frac{N^2}{C_{33}}$$

$$K [100]_{520} = \frac{L^2}{C_{11}} + \frac{M^2}{C_{66}}$$

$$K [010]_{520} = \frac{L^2}{C_{66}} + \frac{M^2}{C_{22}}$$

$$K [1/\sqrt{2} \ 1/\sqrt{2} \ 0]_{040} = \frac{2(C_{11} + C_{66})}{C_{11}(C_{22} + C_{66}) + C_{22}C_{66} - 2C_{12}C_{66} - C_{12}^2}$$

$$K [1/\sqrt{2} \ 1/\sqrt{2} \ 0]_{600} = \frac{2(C_{22} + C_{66})}{C_{11}(C_{22} + C_{66}) + C_{22}C_{66} - 2C_{12}C_{66} - C_{12}^2}$$

$$K [1/\sqrt{2} \ 0 \ 1/\sqrt{2}]_{600} = \frac{2(C_{33} + C_{55})}{C_{11}(C_{33} + C_{55}) + C_{33}C_{55} - 2C_{13}C_{55} - C_{13}^2}$$

$$K [0 \ 1/\sqrt{2} \ 1/\sqrt{2}]_{040} = \frac{2(C_{22} + C_{44})}{C_{22}(C_{33} + C_{44}) + C_{33}C_{44} - 2C_{23}C_{44} - C_{23}^2}$$

$$K [0 \ 1/\sqrt{2} \ 1/\sqrt{2}]_{081} = \frac{2M^2(C_{33} + C_{44}) + N^2(C_{22} + C_{44}) - 2MN(C_{23} + C_{44})}{(C_{22} + C_{44})(C_{33} + C_{44}) - (C_{23} + C_{44})^2}$$

$$K [1/\sqrt{2} \ 0 \ 1/\sqrt{2}]_{101} = \frac{2L^2(C_{55} + C_{33}) + N^2(C_{11} + C_{55}) - 2MN(C_{13} + C_{55})}{(C_{11} + C_{55})(C_{33} + C_{55}) - (C_{13} + C_{55})^2}$$

Relation between $K [u \ v \ w]_{hkl}$ and the elastic constants for the reciprocal lattice points used.

3. Experimental

Yellow crystals of *m*-dinitrobenzene were obtained by slow evaporation of the solution of the compound in ethanol at room temperature (293–295 K). Well defined single crystals thus obtained were tested for any static defect. A single crystal of suitable dimension (about 0.5 mm long) was weighed by means of a microbalance. Aluminium powder in the form of small globule was placed on top of the crystal. The crystal was then placed vertically on the goniometer head. In order to increase the resolution the Laue photographs were taken with a Universal Unicam camera fitted with a specially fabricated film holder of diameter 100 mm and modified collimator of suitable dimensions. Aluminium powder diffraction lines were used for i) determination of the correct orientation of a particular plane w. r. t. incident beam, ii) standardization of the camera radius, iii) calibration of the angle of diffraction with high degree of accuracy.

The monochromatized X-ray beam (CuK_α) obtained by reflection from a fluorite 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 of the intensity by a factor of about 10^6 by interposing nickel foil of known thickness between the experimental crystal and the film so that the intensity of the recorded transmitted beam and that of the diffuse reflections become comparable (Fig. 1). The average time of exposure varied from 20–40 hours depending on the structure factor of the plane considered. The X-ray tube 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 direct beam and aluminium powder lines. A large number of such photographs for various diffuse reflections with different angles of ($\pm \Delta\theta$) from the Bragg position were considered. Each photograph was developed in fresh developer solution at a controlled temperature together with a calibration strip, out 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 the intensity of the direct beam, recording microphotometer was used (Carl-Zeiss, Germany). Photographs were scanned by an exploring spot of light with appreciably high intensity and small size along an equatorial line

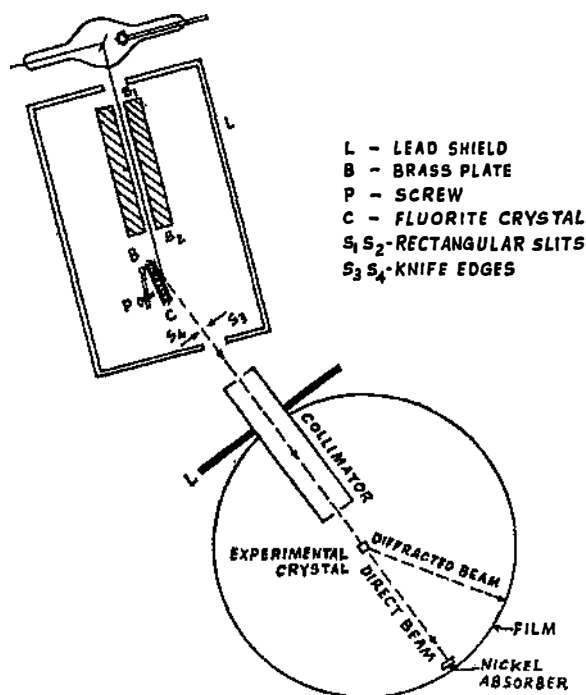


Fig. 1. Experimental arrangements of taking Laue photograph with monochromatic radiation.

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 Robinson¹³⁾. The observed diffuse intensity I_d for each q was corrected for skew, polarisation, divergence and background correction following Ramachandran and Wooster¹⁾ and Amoros and Amoros¹⁴⁾. The absorption corrections was determined by the method of Albrecht¹⁵⁾. The corrections for second order TDS for all elastic constants were made by the method of successive approximation following Ramachandran and Wooster¹⁾ and Lucas¹⁶⁾.

4. Results

The structure factor data for different planes studied in each crystal setting is given in Table 3.

TABLE 3.

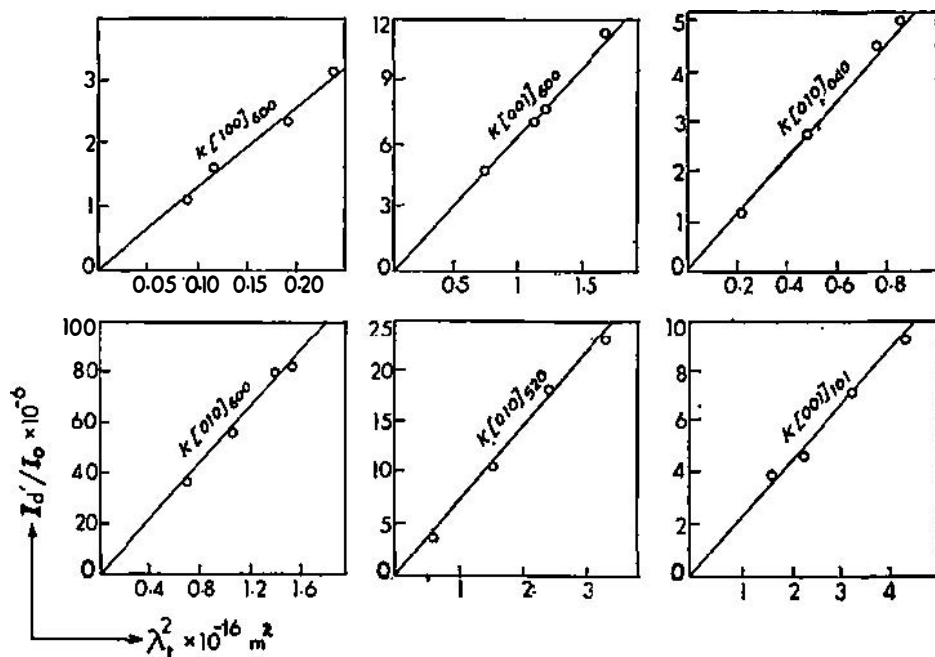
Planes studied	Axis of rotation	Structure factors	Volume of the crystal studied in cm^3
600	010	56.8	30.2×10^{-6}
600	001	56.8	5.7×10^{-5}
040	001	34.1	8.83×10^{-5}
520	001	38.3	42.8×10^{-5}
101	010	84.2	68.1×10^{-5}
081	100	15.4	39.4×10^{-5}
101	001	84.2	68.1×10^{-5}

Structure factor data or different planes of *m*-dinitrobenzene.

For the determination of all the nine elastic constants of *m*-dinitrobenzene crystal, a series of Laue photographs were taken with monochromatized CuK_α radiation to record 600, 040, 520 and 101 diffuse spots with the [100] crystal axis coinciding with the axis of the camera; 600, 101, 081 with the [010] crystal axis coinciding with the axis of the camera; and 600, 040, 101 nodes with [001] crystal axis coinciding with the camera axis, respectively.

The value of wave vector 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 w. r. t. the incident X-ray beam. The uncorrected diffuse intensity corresponding to the 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 value of diffuse intensity, i. e. I'_d/I_0 , were plotted against $\lambda_i^2 = 1/q^2$ for the different orientation photograph 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_i^2 obtained for different directions of propagation of thermal waves for few diffuse spots are shown in Fig. 2.

Fig. 2. Intensity vs. λ_1^2 graph.

5. Discussion

The absolute values of the elastic constants determined are reliable within 10% due to the following normal errors:

- i) in the measurement of intensities,
- ii) in the absolute value of the structure factors used,
- iii) in the linear absorption factors for the Ni-foil used to attenuate the direct beam intensities.

It is evident from Table 2 that elastic constants C_{11} , C_{22} , C_{44} , C_{55} and C_{66} can be determined independently from the studies of TDS intensities. As for instance, C_{66} is evaluated from the values of I_d/I_0 for (600) node in different photographs taking the wave vector along [010]. But in the evaluation of C_{11} and C_{22} the TDS intensity is measured in the same direction as the reciprocal lattice vector and hence, for the slightest missetting from the Bragg angle, the value of q becomes very large. Consequently, a small error in the measurement of angle of missetting introduces a large error in q . Moreover for larger q , the low values I_d/I_0 become less accurate. As such C_{11} and C_{22} were also evaluated from the studies of $K[100]_{520}$ and $K[010]_{520}$ before the results were finalized. The value of C_{66} obtained from $K[010]_{600}$ was also checked up from the study of $K[100]_{040}$. Since no (001) node was available, C_{33} can not be evaluated independently. So it was obtained from the studies of the node (101). $K[001]_{101} = g_1^2/C_{55} + g^2/C_{33} =$

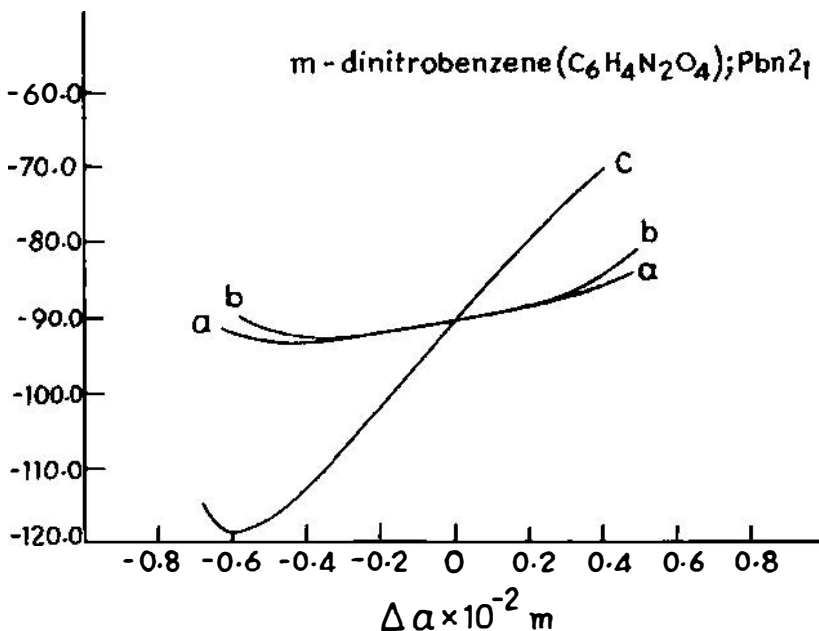
$= 0.076/C_{55} + 0.924/C_{33}$. Now substituting the value of K obtained from the appropriate I'_d/I_0 vs. λ_i^2 curve and using the evaluated value of C_{55} , C_{33} is obtained.

For the constant C_{12} we used the following equation $K [1/\sqrt{2} \ 1/\sqrt{2} \ 0]_{040} = 2(C_{11} + C_{66})/C_{11}(C_{22} + C_{66}) + C_{22}C_{66} - 2C_{12}C_{66} - C_{12}^2$. On substituting the appropriate K value and other values of elastic constants we get a second degree equation in C_{12} .

The solution yields two values, +6.3 and -17.9 in units of 10^9 Nm^{-2} . The correct value of C_{12} was ascertained by substituting these values in the equation

$$K [1/\sqrt{2} \ 1/\sqrt{2} \ 0]_{600} = 2(C_{22} + C_{66})/C_{11}(C_{22} + C_{66}) + C_{22}C_{66} - 2C_{12}C_{66} - C_{12}^2.$$

The value of C_{13} was found from the study of the node (600) along $[1/\sqrt{2} \ 0 \ 1/\sqrt{2}]$ and was finalized from the study of the node (101) along $[1/\sqrt{2} \ 0 \ 1/\sqrt{2}]$. The constant C_{23} needed the study of (040) and (081) before the final result was obtained. The estimated accuracy of C_{11} , C_{22} , C_{44} , C_{55} , C_{66} is 5% as they were obtained independently, constant C_{33} depends on the value of another constant so its accuracy is 8% and C_{12} , C_{13} , C_{23} depend on the value of two other constants and so have lower accuracy of about 10%.



One dimensional energy cross-section

Fig. 3. One dimensional energy cross-sections of m-dinitrobenzene $U(a)$, $U(b)$ and $U(c)$ (in kJ/mole).

Further investigation on the packing of m-dinitrobenzene in the unit cell shows that molecule lie along *c*-axis (*c*-axis being shortest). So Van der Waals interaction which is the predominating force between molecules for this type of crystals will be of higher magnitude in *c* than along *a* and *b*. This obviously would indicate higher values of force constant along *c* than along *a* and *b*. Consequently the longitudinal deformation along *c* will be less compared to that along *a* and *b* for the same magnitude of longitudinal stress in the three directions. Thus from structural point of view one would expect $C_{33} > C_{11}$ or $> C_{22}$, which is consistent with the experimental findings.

The lattice energy of m-dinitrobenzene evaluated on the basis of empirical non-bonded atom-atom potentials and the subsequent computation of Young's moduli¹⁷⁾ from one dimensional energy cross-sections (Fig. 3) (Kitaigorodskii¹⁸⁾) enabled us to compare the experimental values with the theoretical ones. The theoretical values are not likely to differ much from the real values, because, using the same potential parameters Scheraga et al.¹⁹⁾ obtained good agreement between the calculated lattice energy and the experimental heat of sublimation for a number of molecular crystals.

TABLE 4.

C_{11}	11.52	10.70
C_{22}	12.54	11.30
C_{33}	22.99	20.27

Elastic constants in units of 10^9 Nm^{-2} .

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ODREĐIVANJE ELASTIČNIH KONSTANTI *m*-DINITROBENZENA IZ
DIFUZNIH REFLEKSA X-ZRAKA

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Određene su apsolutne vrijednosti devet elastičnih konstanti ortorompskog *m*-dinitrobenzena na sobnoj temperaturi na temelju mjerenih intenziteta termičkog raspršenja (TDS) X-zraka, koristeći fotografsko-fotometrijsku metodu. Niz Laueovih fotografija snimljeno je monokromatskim Cu K_{α} zračenjem, dobivenim refleksijom na monokristalu fluorita. Proučavana su područja difuznog raspršenja blizu čvorova recipročne rešetke 600, 040, 081, 101 i 520. Dobivene su ove vrijednosti elastičnih konstanti u jedinicama 10^9 Nm^{-2} : $C_{11} = 10.70 (05)$, $C_{22} = 11.30 (03)$, $C_{33} = 20.27 (19)$, $C_{44} = 4.37 (04)$, $C_{55} = 2.04 (05)$, $C_{66} = 5.31 (03)$, $C_{12} = 6.30 (18)$, $C_{13} = 1.95 (14)$, $C_{23} = 3.19 (16)$. Diskutirana je točnost dobivenih eksperimentalnih vrijednosti.