

## X-RAY ANALYSIS OF THE STRUCTURE OF BENZENE AT DIFFERENT PRESSURES

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X-ray diffraction patterns of benzene were obtained at room temperature and at different pressure up to 2kbar. The radiation was Mo  $K_{\alpha}$ , monochromated by a graphite crystal. Radial distribution curves at four different pressures were obtained by a Fourier analysis of the X-ray intensity data. Intensities and radial distribution functions have been computed for a model structure and compared to those derived from experiment. The coordination numbers and the bond lengths of the intramolecular  $C_1-C_2$ ,  $C_1-C_3$ , and  $C_1-C_4$  are pressure independent. The temperature factor, which is a measurable quantity for the linewidth is affected by pressure. It decreases with increase in pressure.

**Key Words:** X-ray Analysis; Benzene; Graphite; Diffraction

### INTRODUCTION

The first diffraction pattern and structure of liquid benzene was obtained by Katzoff.<sup>1</sup> He concluded that benzene molecules might be oriented as in solid. Pierce<sup>2</sup>, however, was not convinced of the correctness of this conclusion. Narten<sup>3</sup> obtained X-ray diffraction data for liquid benzene at 25°C. It extends and improves upon Katzoff's results, and also confirm his guess about the structure of liquid benzene.

The aim of this work is to present and discuss the results of the X-ray diffraction investigation for benzene at room temperature and at pressures of 0.001, 0.5, 1 and 2kbar.

### EXPERIMENTAL

The experimental arrangement for studying the diffraction from liquids require a diffractometer with monochromatic X-rays, well-defined direction of the incidence and scattering beam. Accurate intensity data over a large angular range is required for the calculation of the radial distribution function.

Data were taken with an automatic Enraf Nonius single crystal diffractometer<sup>4</sup> modified to suit the liquid state. The sample was contained in a pressure cell<sup>5</sup> which was mounted vertically along the axis around which the counter arm was rotated. A graphite crystal monochromator was set in the diffracted beam to isolate the  $K_{\alpha}$  (0.7107 Å) radiation of the source. The data were obtained by operating the diffractometer in the step-scan mode, a certain number of counts were accumulated in pre-set time at a given angle  $2\theta$ . After the preset time was completed and the number of counts printed on a paper tape, the scattering angle  $2\theta$  was changed automatically by a fixed increment and the counting cycle was started again.

In our experiments, an increment of one-tenth was used in all the available observable range  $2^{\circ} \leq \theta \leq 35^{\circ}$  which corresponds to  $0.617 \text{ Å} \leq S \leq 10.14 \text{ Å}$  where the scattering variable  $S = 4\pi/\lambda \sin \theta$ .  $\lambda$  is the wavelength of the target and  $\theta$  half the scattering angle. The count time was four minutes at each given scattering angle, equivalent to a total counting time of about one day for each run. The scattered intensities were measured for the empty cell and the cell filled with sample. The whole angular region was scanned from two to three times for each sample at each different pressure in order to examine the reproducibility of the results. The intensities measured at the same angle agreed within 2% and the intensities measured at each angle were averaged.

The pressurizing system was hydraulic and the sample container was beryllium. The data collection was carried out at pressures of 0.001, 0.5, 1 and 2kbar.

## RESULTS AND DISCUSSION

The measured intensities were corrected to obtain the corrected intensity  $I_{\text{corr}}(S)$ . The applied corrections were background, absorption for both sample and container together with the empty container<sup>6</sup>, and polarization correction.

To calculate the measured intensity per unit of composition,  $I(S)/n$ , i.e., per molecule, the corrected intensity  $I_{\text{corr}}(S)$  was scaled to one structural unit according to the relation:

$$I(S)/n = [\alpha I_{\text{corr}}(S) - \sum_i I_c(S)],$$

where  $n$  is the number of molecules in the sample and  $\alpha$  is a scale factor which puts the data on an absolute scale of electrons per molecule. The method of Krogh-Moe<sup>7</sup> was used to calculate  $\alpha$ .  $\sum_i I_c(S)$  represents the Compton scattering correction, where the sum is over all the atoms in the unit of composition.

The reduced intensity  $i(S)$ , then computed from  $I(S)/n$  using the equation:

$$i(S) = [I(S)/n - \sum_i f_i(S)] M(S),$$

where  $f_i(S)$  is the atomic scattering factor of atom  $i$  and the sum extends over the unit of composition.  $M(S)$  is a modification function and is equal to  $[\sum_i f_i(S)]^{-2}$ .

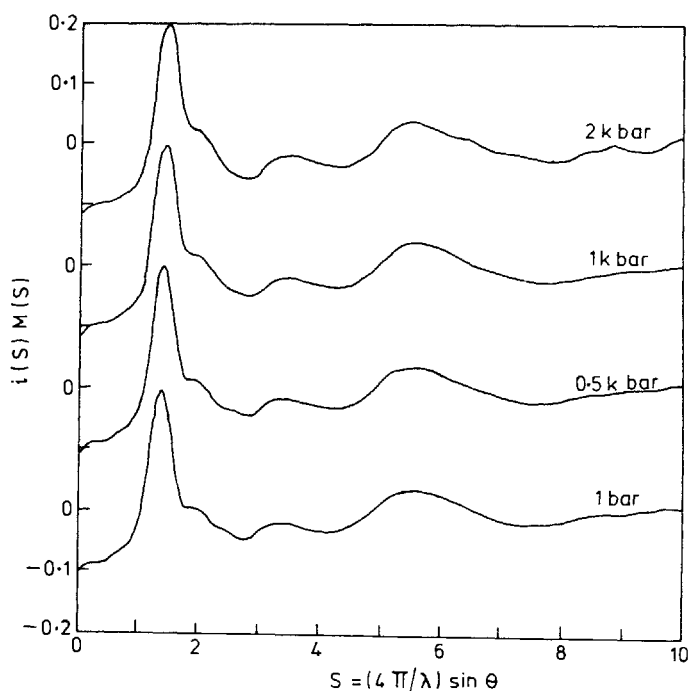


FIG 1 The reduced intensity functions of liquid benzene at pressures of 0.001, 0.5, 1 and 2 kbar

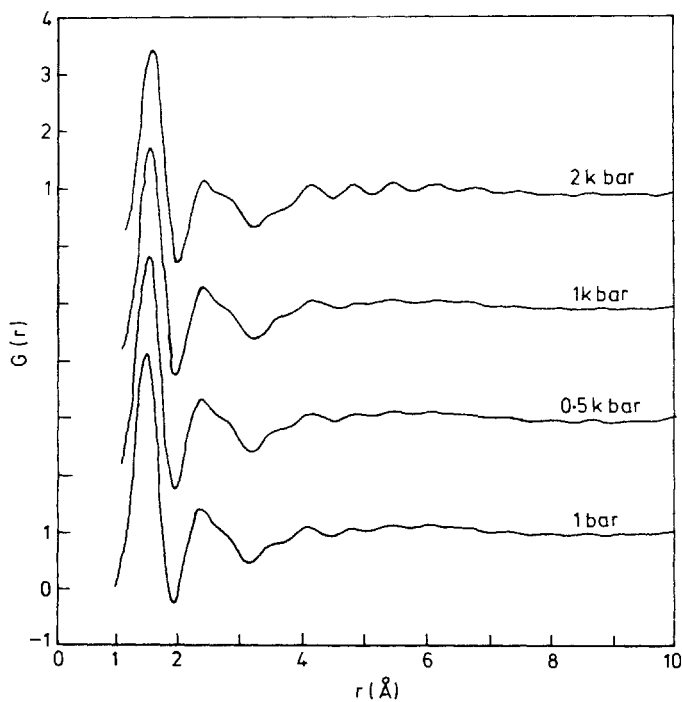


FIG 2 The corresponding radial distribution functions  $G(r)$  to distances of  $10 \text{\AA}$

The radial distribution function  $G(r)$  was obtained by Fourier transformation of  $i(S)$  according to the following equation:

$$G(r) = 1 + 1/2\pi^2 \rho r \int_0^\infty Si(S) \sin Sr \, dS,$$

where  $\rho$  is the average density of molecules. The function  $G(r)$  approaches unity for large values of  $r$ .

The reduced intensity functions of liquid benzene at pressures of 0.001, 0.5, 1 and 2 kbar are shown in Fig 1. Fig 2 shows the corresponding radial distribution function  $G(r)$  to distances of 10 Å. The peak at 1.39 Å corresponds to intramolecular  $C_{-1}-C_{-2}$  interaction and the broad double peak around 2.5 Å correspond to  $C_1-C_3$  and  $C_1-C_4$  interactions whose maxima lie at 2.41 Å and 2.78 Å respectively. These results agree with the known intramolecular structure of benzene molecule.<sup>3,8</sup>

The peaks in the radial distribution functions were analysed in terms of specific pair corrections  $G_{ij}(r)$  using a model first proposed by Bol.<sup>9</sup> This involved a three parameters Gaussian fit to a peak of the form:

$$4\pi r^2 G_{ij}(r) = n_0 (r/r_0) (2\pi/\beta)^{1/2} \exp [-(r-r_0)^2 \cdot (2\pi^2/\beta)],$$

where  $n_0$  is the coordination number  $r_0$  is the mean distance between atom  $j$  and  $i$ .  $\beta$  is the temperature factor  $= 4\pi^2 \bar{t}^2$  where  $\bar{t}^2$  is the mean square deviation of distance between neighbouring atoms. The function  $4\pi r^2 G_{ij}(r)$  is normalized, so that:

$$\int_{r_{\min}}^{r_{\max}} 4\pi r^2 G_{ij}(r) \, dr = n_0,$$

where  $r_{\min}$  and  $r_{\max}$  are the chosen interval. Then a reduced intensity  $i_{\text{calc}}(S)$  is calculated according to the following equation:

$$i_{\text{calc}}(S) M(S) = \sum_i \sum_j f_i(S) f_j(S) \int 4\pi r^2 G_{ij}(r) \frac{\sin Sr}{Sr} \, dr$$

and by Fourier transformation  $i_{\text{calc}}(S)$  we get the calculated radial distribution function that can be compared directly with the experimental ones. By changing the value of the three parameters  $n_0$ ,  $r_0$  and  $\beta$  one can get the best fit between the calculated and experimental distribution functions.

The parameters  $n_0$ ,  $r_0$  and  $\beta$  for the intramolecular interactions which give the fit to the experimental  $G(r)$  peaks are listed in Table I. It can be seen from this table that the coordination numbers and the bond lengths of the intramolecular  $C_1-C_2$ ,  $C_1-C_3$  and  $C_1-C_4$  are pressure independent. The temperature factor  $\beta$ , which is a measurable quantity for the linewidth is affected by pressure. It decreases with increase in pressure, in a way similar to that found for O-H peak in light water.<sup>10</sup> The

TABLE I

*Benzene, intramolecular C-C distances,  $r$ , coordination numbers,  $n_o$  and the associated temperature factors,  $\beta$ , as a function of pressures*

Pressure in kbar	$C_1 - C_2$			$C_1 - C_3$			$C_1 - C_4$		
	$r$	$n_o$	$\beta$	$r$	$n_o$	$\beta$	$r$	$n_o$	$\beta$
0.001	1.39(2)	2	0.124(2)	2.41(2)	2	0.193(3)	2.78(2)	1	0.253(2)
0.5	1.40(2)	2	0.121(2)	2.40(2)	2	0.188(2)	2.77(2)	1	0.243(3)
1	1.39(1)	2	0.116(3)	2.40(2)	2	0.184(3)	2.77(2)	1	0.239(3)
2	1.41(2)	2	0.112(3)	2.41(2)	2	0.178(3)	2.78(3)	1	0.232(3)

structural range beyond  $3\text{ \AA}$  does not show well-resolved correlations and it is not possible to draw any conclusions about the change in intermolecular structure with pressure in benzene.

### CONCLUSION

The work described here was performed to determine the extent to which the structure of benzene depends on pressure. The results showed that the intramolecular bond lengths and coordination numbers are pressure independent in the range of pressure used in this work. However, the linewidths of the radial distribution peaks change with pressure. It decreases with increase in pressure.

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