

Structural transitions in liquid benzene

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The integrated intensity of a scattered depolarized light in benzene is studied experimentally in the temperature range in which this liquid exists. The temperature dependence is found to vary nonmonotonically. From a comparison of molecular dynamics with the calculation results, which show that there are dimers with various optical anisotropies in liquid benzene, it can be concluded that there are transitions between local structures of liquid benzene.

In studying the depolarized scattering of light in liquid benzene we have found that the integrated intensity of the depolarized component of scattered light exhibits a nonmonotonic temperature dependence. The integrated intensity of the depolarized component of scattered light in liquids is determined by that part of the dielectric

tensor, $\Delta\epsilon'_{ik}$, which stems from fluctuations of the optical anisotropy of the medium¹ (fluctuations in the orientation of anisotropy molecules, deformation of electronic shells due to the intermolecular interaction in the condensed phase). The corresponding scattering coefficient for the vertical polarization of incident light is related to the effective optical anisotropy of the molecules in a liquid, γ_{eff}^2 , by

$$R_{\text{dep}}^z = \frac{16\pi^4}{\lambda^4} \cdot \frac{7}{45} N_0 \left(\frac{n^2 + 2}{3} \right)^2 \gamma_{\text{eff}}^2 F(n), \quad (1)$$

where $F(n)$ is the correction for the refractive index which takes into account the change in the aperture angle, $[(n^2 + 2)/3]^2$ is the internal-field factor, N_0 is the number of molecules per unit volume, and $\gamma_{\text{eff}}^2 = \gamma_{\text{gas}}^2 g_2$ (g_2 is the orientational-pairing-correlation factor). For axially symmetric molecules we have

$$g_2 = 1 + \left\langle \sum_{k \neq l} \frac{1}{2} (3\cos^2 \theta_{kl} - 1) \right\rangle, \quad (2)$$

where θ_{kl} is the angle between the axes of a pair of neighboring molecules. The value $g_2 = 1$ corresponds to an absence of angular correlations in the orientation of anisotropic molecules. In turn, $g_2 > 1$ and $g_2 < 1$ correspond to preferential parallel or perpendicular orientation of the adjacent molecules.² For a liquid benzene we have $\gamma_{\text{eff}}^2 = 24 \text{ \AA}^2$ (Ref. 6) and for gaseous benzene $\gamma_{\text{gas}}^2 = 33 \text{ \AA}^2$ (Refs. 3 and 6); i.e., $g_2^{20^\circ\text{C}} < 1$.

Upon heating, the ratio

$$R_{\text{dep}}^z / \left(\frac{n^2 + 2}{3} \right)^2 N_0$$

increases linearly with increasing temperature, a consequence of a gradual disordering and the tendency of γ_{eff}^2 to approach γ_{gas}^2 as the boiling point is approached.

The temperature dependence was studied with use of a photometer built in our laboratory. As the light source we used an "Amazon" 40-mW He-Ne laser with $\lambda = 632.8 \text{ nm}$. The cell holding the scattering fluid was designed in such a way that the stray light could be eliminated. In the detecting system the scattered light enters the FÉU-79 photocathode (photomultiplier), cooled down to -20°C , which operates in the photon-counting mode. The signal from the FÉU-79 is fed to the PI-4 ratemeter. This ratemeter discriminates the pulses with respect to amplitude, amplifies them, and converts the pulses to an analog signal which is detected by a KSP-4 chart recorder which simultaneously receives a reference signal from the FÉU-15A. The results of measurements are shown in Fig. 1, in which the ratio $R_{i\rho_{20}}^z (n_{20}^2 + 2) / R_{20}^z \rho_i (n_i^2 + 2)$ is plotted along the ordinate. The measurements were carried out in the temperature interval $5.5^\circ\text{--}65^\circ\text{C}$. Chromatography-grade benzene was rendered dust-free and outgassed through a fourfold vacuum distillation into a cell. Each temperature was maintained to within 0.3°C for at least 4 hours. The curve in Fig. 1 has four straight sections with different slopes corresponding to different temperature intervals. The linear approximation of these sections and the mean-square errors are given by

8 – 27°C	$(0.841 + 8.0 \times 10^{-3});$	$\pm 1.7 \times 10^{-3}$
27 – 30°C	$(1.063 + 0.6 \times 10^{-3});$	$\pm 0.7 \times 10^{-3}$
30 – 42°C	$(0.908 + 7.1 \times 10^{-3});$	$\pm 2.6 \times 10^{-3}$
48.5 – 58°C	$(0.719 + 10.6 \times 10^{-3});$	$\pm 2.2 \times 10^{-3}$

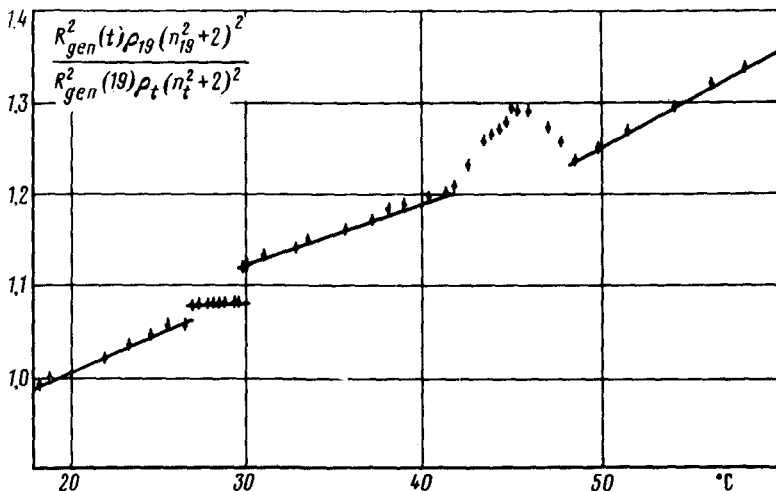


FIG. 1.

The integrated intensity of the depolarized component of scattered light peaks in the temperature range 42°–48.5° C.

Comparison of the calculated results obtained by the molecular-dynamics method with the results of many experiments on neutron and x-ray scattering⁴ showed that liquid benzene may have aggregates of three types of molecules: (a) an *L*-configuration is a configuration in which at least one hydrogen atom in the molecule situated at the coordinate origin comes in contact with a hydrogen atom and a carbon atom of the neighboring molecule and a pair of molecules resembles skewed toothed wheels whose C_6 axes are at right angles to each other; (b) a “stack configuration” is one in which one molecule is situated above another, with the ring centers slightly displaced; (c) a *T*-configuration is one in which the carbon atom of one molecule is situated near the center of another molecule and the C_6 axes of the neighboring molecules form an angle of nearly 90°.

At a temperature close to the melting point, the structure of liquid benzene seems to repeat short-range order, which is similar to the structure of a crystal with typically a *T*-configuration.⁵ Stack- and *L*-configurations may appear as the temperature is raised. Jandak and Cetall⁶ showed that benzene pairs have dimers with a dipole moment, suggesting that an *L*-configuration may be formed.

Calculations based on the molecular-dynamics method show that $g_2 > 1$ for benzene, whereas a scattering experiment always gives $g_2 < 1$. Steinhauser⁴ suggested that this result is a consequence of the superimposition of the peaks of the angular-correlation functions corresponding to the *T*-configuration and the peaks of the displaced parallel configuration; i.e., the factor g_2 in benzene is approximately equal to unity because of the coexistence of the *T*-configuration and the stack-configuration.

Figure 2 shows the temperature dependence of the heat capacity of benzene. At temperatures $> 30^\circ$ C, the slope of the curve begins to rise, which suggests that the

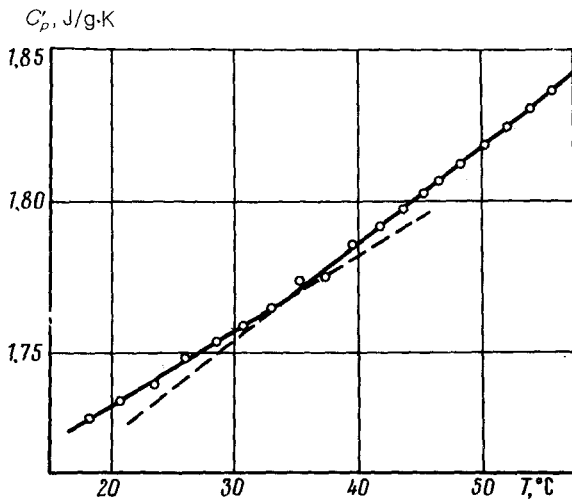


FIG. 2.

order in the system rises. The highest order in the structure of liquid benzene apparently exists in the temperature range 42°–48.5° C.

Here it seems pertinent to draw the following analogy: If we follow the curve from the high temperature to the peak at 45° C, we see that the shape of the curve resembles the $R_{\text{dep}}^z(t)$ curve for the isotrope phase of nematic liquid crystals upon approaching the transition to the mesophase.⁷

The possible manifestation of structural transitions in the liquid phase at the macroscopic level was recently investigated by Patashinskii *et al.*⁸

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