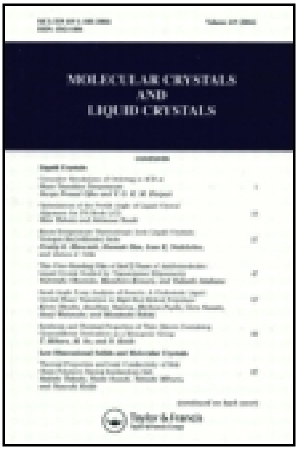

Molecular Crystals and Liquid Crystals

NMR Study of Benzene/Thiophene Solid Solutions

J. E. Anderson [a]

[a] Ford Motor Company Scientific Research Staff, Dearborn, Michigan, 48121

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NMR Study of Benzene/Thiophene Solid Solutions

J. E. ANDERSON

Ford Motor Company
Scientific Research Staff
Dearborn, Michigan 48121

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Abstract—NMR methods have been used to study molecular motion in solid benzene, solid thiophene, and their solid solutions. NMR second moment studies show that both benzene and thiophene reorient about axes perpendicular to their molecular planes in these solids. Molecular motion persists in solid thiophene well below its lowest-temperature phase transition. T_1 studies of C_4H_4S/C_6D_6 and C_6H_6/C_4D_4S samples show that thiophene and benzene reorient at about equal rates in thiophene-rich solutions. Interestingly enough, as the benzene concentration increases, the motion of C_6H_6 slows down, while that of C_4H_4S speeds up. The benzene molecules reorient ten times slower than those of thiophene in a 0.75 mole fraction benzene solution.

1. Introduction

Molecular motion has been observed in many organic solids, some of which form binary solid solutions. One might ask how the mobilities of the individual components change upon dilution in one another. This is a very intriguing question, for it is related to the presence, or absence, of cooperative mechanisms for molecular reorientation in organic solids. The reorientation frequencies of both components can be nearly identical if (A) all molecules move independently (no strong cooperative mechanism is involved), or (B) a strongly cooperative mechanism occurs; i.e., the reorientation process involves the concerted motions of many neighboring molecules. Conversely, when the reorientation frequencies of the two components are widely different, this can only be explained in terms of case (A)—by a reorientation mechanism that is weakly cooperative at best.

The present work deals with molecular motion in the benzene/

thiophene system. This appeared to be a logical starting point for such studies, as benzene and thiophene are known to form a continuous series of ideal solid solutions.(1,2)

Several previous NMR studies of solid benzene have been reported.(3–5) Jaffrain(6) has published dielectric relaxation measurements on solid thiophene. Oliver, Eaton, and Huffman(7) studied the heat capacity of solid benzene between 13 °K and the melting point. No solid-solid phase transformations were detected. In contrast, Waddington *et al.*(8) observed three phase transitions in solid thiophene: lambda transitions at 112 and 138 °K and an isothermal transition at 172 °K. Heat capacity measurements have not been made on the solid benzene/thiophene system. Upon freezing, benzene and thiophene(9,10) adopt orthorhombic unit cells with approximately the same dimensions. The crystal structures of the three low temperature modifications of thiophene are not known. There is some evidence for a tetragonal unit cell in the phase stable at lowest temperatures.(11) Very few studies of benzene/thiophene solid solutions have been published. The phase diagram for solid benzene/thiophene has not been reported; it is not known whether the components segregate as the temperature is lowered. We saw no evidence of phase separation in our NMR measurements.

2. Experimental

Isotopically pure (99%) C_6D_6 and spectroquality C_6H_6 were obtained from commercial sources. They were used without subsequent purification. Reagent grade thiophene was purified by distillation, b.p. 81.5–82.0 (748 mm). Deuterated thiophene was synthesized from C_4H_4S by prolonged treatment with 69% D_2SO_4 at 23 °C.(12) The product was twice distilled, b.p. 82.5–82.6 °C (750 mm); no impurities were detected in its high resolution PMR spectrum. The integrated intensity of the PMR spectrum of the final product was compared with that of C_4H_4S. It was estimated that some 7% thiophene protons remained in the final product. In spite of this residual proton content, this material will be called C_4D_4S throughout this article.

Benzene/thiophene solutions containing 0.25, 0.50, and 0.75 mole fraction benzene were prepared. Two samples of each concentration were made. The first contained C_6D_6 and C_4H_4S; the second, C_6H_6 and C_4D_4S.

The NMR spin-lattice relaxation of each sample was examined over the temperature interval between − 190 and − 50 °C. T_1, the spin-lattice relaxation time, was determined by the 180–90 pulse technique on a Bruker pulsed spectrometer operating at 36 mHz. The null method was used.(13) Pulse lengths ranged between 2 and 4 μsec. Steady-state NMR measurements were made on a Varian DA60 spectrometer operating under wideline conditions.

3. Results

The PMR linewidths of solid benzene, solid thiophene, and their solid solutions are independent of temperature between − 150 °C and the melting point of each sample. Line-broadening was evident in several samples below − 150 °C. NMR second moments were determined from data obtained above − 140 °C; corrections for the modulation field were employed.(14) The experimental second moments, ranging between 0.8 and 1.7 G^2, are consistent with the reorientation of benzene and thiophene molecules about axes perpendicular to their molecular planes.(15)

The experimental second moment of C_4H_4S is 2.85 gauss^2 at − 180 °C. This is considerably smaller than the second moment calculated for immobile C_4H_4S molecules (6.8 gauss^2), and indicates that rotational freedom persists in solid thiophene well below its lowest phase transition at − 161 °C.(8) Furthermore, it is noteworthy that no linewidth changes were observed at any of the three solid-solid phase transitions of thiophene.(8)

The spin-lattice relaxation is C_4H_4S/C_6D_6 solutions is shown in Fig. 1. Fluctuations in nuclear dipole-dipole interactions among thiophene protons provide the dominant relaxation mechanism in these samples; consequently, these data reflect the motions of the thiophene molecules alone. Note that the T_1 minima shift to lower temperatures as the C_6D_6 concentration is increased. This demonstrates that additional benzene enhances the reorientational freedom of thiophene. In contrast, the mobility of benzene *decreases* in going from thiophene-rich solid solutions to pure C_6H_6! This is shown by the T_1 data on C_6H_6/C_4D_4S solutions (Figure 2). In 0.75

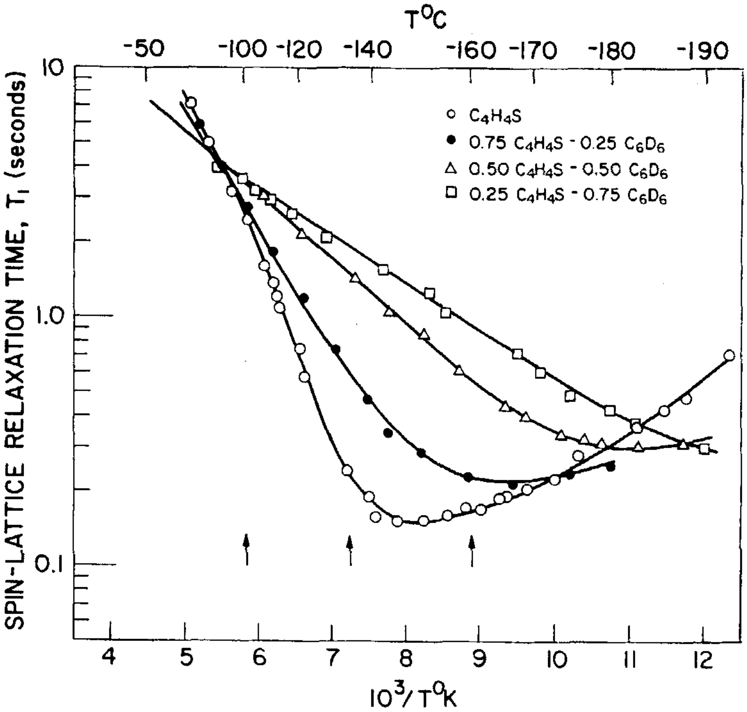

Figure 1. Proton spin-lattice relaxation in C_4H_4S/C_6D_6 solid solutions. These curves characterize the motions of thiophene molecules alone. The arrows indicate the three solid-solid phase transformations of thiophene (Ref. 8).

mole fraction thiophene solutions, the benzene and thiophene T_1 minima occur at roughly the same temperature, implying that both compounds reorient at about the same rate. In 0.25 mole fraction thiophene, the reorientational correlation times appear to differ by a factor of ten.

It is difficult to account for these findings. Explanations based on changes in local friction coefficients, or on variations in local free volume, can probably be ruled out. Either of these explanations would require the mobility of both components to increase or decrease concurrently with changes in composition. It is tempting to postulate a cooperative reorientation mechanism in the thiophene-rich solutions. This would be consistent with the near equality of the correlation times in 0.75 mole fraction thiophene. It would not ex-

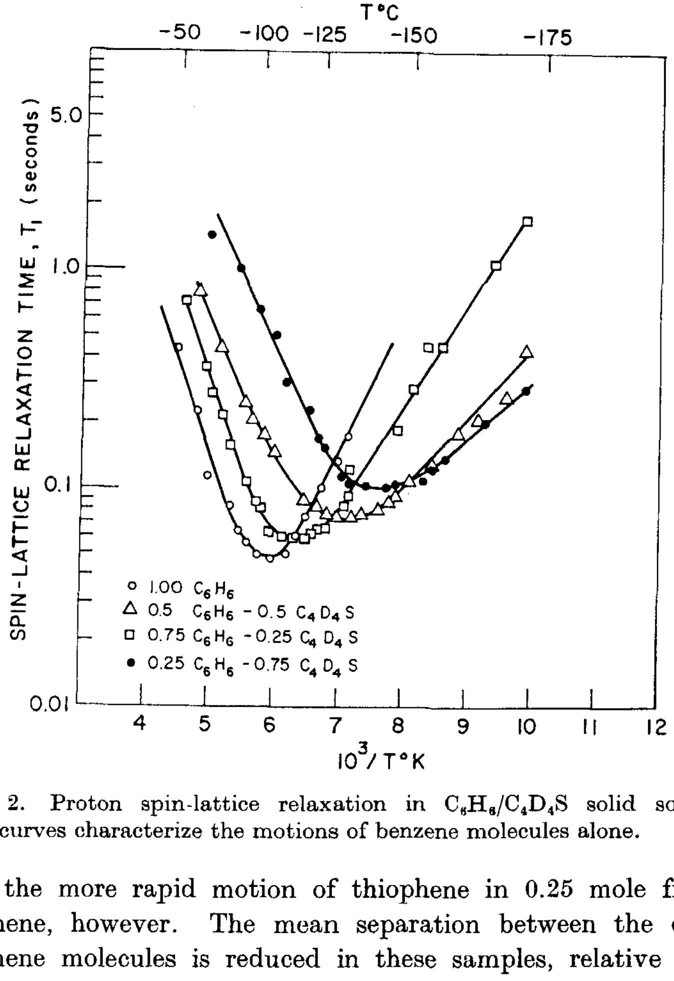

Figure 2. Proton spin-lattice relaxation in C_6H_6/C_4D_4S solid solutions. These curves characterize the motions of benzene molecules alone.

plain the more rapid motion of thiophene in 0.25 mole fraction thiophene, however. The mean separation between the dipolar thiophene molecules is reduced in these samples, relative to the thiophene-rich solutions, and the weaker electric dipole-dipole interactions may allow more rapid motion. Of course, these latter observations are speculative and should be viewed as such.

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