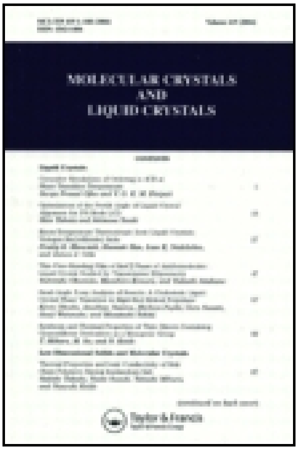

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Dielectric Study on Some Solid Complexes: Molecular Motion in the Isomorphous High-temperature Forms

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DIELECTRIC STUDY ON SOME SOLID COMPLEXES: MOLECULAR MOTION IN THE ISOMORPHOUS HIGH-TEMPERATURE FORMS

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The relative permittivity of pyrene-2,4-dinitrofluorobenzene, -2,4-dinitrochlorobenzene, -2,4-dinitrotoluene, -2,4-dinitrophenol complexes, and fluoranthene-2,4-dinitrophenol complex increases abruptly upon the polymorphic transition. The molar polarization measured below the transition temperature agrees with the molar refraction except for the second complex which shows a marked positive deviation. The dipole moment of the acceptor molecules in the high-temperature form was calculated on the assumption that the rotational freedom around the axis perpendicular to the ring plane gives rise to the orientation in an externally applied electric field and was found in good accordance with the literature or estimated value.

Keywords: relative permittivity; polymorphic transition; molecular rotation; isomorphism

INTRODUCTION

Crystalline complexes composed of pyrene **1** and 2,4-dinitrofluorobenzene **3**(X = F),2,4-dinitrochlorobenzene **3** (X = Cl), 2,4-dinitrotoluene **3**(X = CH_3), 2,4-dinitrophenol **3**(X = OH), and 2,4,6-trinitrochlorobenzene, respectively, were reported to become isomorphous upon the polymorphic transition with rather large entropies [1]. The isomorphism in these complexes was demonstrated by essentially identical and very simple X-ray diffraction patterns and/or by the formation of continuous solid solutions between pairs of these forms. The onset of a large degree of molecular motion, possibly the rotation around the axis perpendicular to the ring plane, at the transition temperature was suggested to account for the absence of the specific interaction between the polycyclic aromatic

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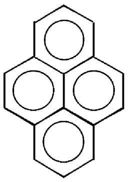
hydrocarbon molecule and the substituents on the acceptor molecule in the high-temperature forms. This proposition was firmly supported by a broad-line ^{1}H NMR study at 40 MHz which revealed a marked reduction in the second moment at the transition temperature to as small as 1 G^2(1 G = 10^{-4} T) [2]. Not only the above-mentioned complexes, but many pyrene, fluoranthene **2**, and phenanthrene complexes were shown to behave similarly [3]. A trigonal lattice was proposed as the probable structure of these high-temperature forms. As the molecular motion demonstrated by ^{1}H NMR study concerned essentially with the hydrocarbon molecules. we planned to examine particularly the motion of the polar acceptor molecules by comparing the dielectric polarizations below and above the transition temperature. The pyrene complexes with the above-mentioned substituted dinitrobenzenes and fluoranthrene-2,4-dinitrophenol complex were selected for the present study because of large dipole moments of the acceptor molecules and wide separations between the transition temperature and the melting point.



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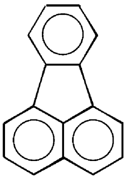

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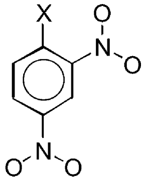

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EXPERIMENTAL

The thermal behavior of the molecular complexes prepared for the present work agreed well with that of the previously reported ones [1,3]. The relative permittivity was measured at frequencies from 110 to 10^6 Hz with a Rigaku temperature-controlled capacitance bridge, SER.2532N. The specimens were pressed pellets of a diameter of 20 mm and of a thickness of about 1.5 mm. They were annealed above the transition temperature before the measurements. The permittivity was independent of frequency at room temperature but some rise below 100 kHz was noted at higher temperatures, especially above the transition point.

RESULTS AND DISCUSSION

The molecular weight, density, and relative permittivity measured at a temperature within several degrees below the transition point at 300 kHz

TABLE 1 Relative Permittivities (ε_{r1}) and Molar Polarizations (P_1) Below the Transition Temperature and Molar Refractions (R)

Complex	$M/g\,mol^{-1}$	$d/g\,cm^{-3}$	ε_{r1}	$P_1/cm^3\,mol^{-1}$	$R_1/cm^3\,mol^{-1}$
Py-DNF	388.4	1.37	2.8	106	113
Py-DNC	404.8	1.41	5.4	171	118
Py-DNT	384.4	1.36	3.1	116	118
Py-DNP	386.4	1.41	3.1	113	115
Fl-DNP	386.4	1.36	3.2	120	113

(ε_{rl}), molar polarization (P_1), and estimated molar refraction for the sodium D line (R) of the five solid complexes are listed in Table 1. Here, DNF, DNC, DNT, and DNP denote 2,4-dinitrofluorobenzene, 2,4-dinitrochlorobenzene, 2,4-dinitrotoluene, and 2,4-dinitrophenol, respectively. The observed relative permittivities are normal for nonrotating molecules, but that for pyrene-DNC complex is unusually large. The density given in the table is of the pressed disk employed for the permittivity experiment and is measured at room temperature. The values of pyrene-DNC and -DNT complexes agree with those reported by Inabe et al. [3], namely $1.414\,g\,cm^{-3}$ and $1.350\,g\,cm^{-3}$. The molar polarization was calculated by the Clausius-Mosotti equation.

The molar refractions of the hydrocarbons, $74.0\,cm^3\,mol^{-1}$ for pyrene and $71.5\,cm^3\,mol^{-1}$ for fluoranthene, were taken from the work by Schuyer et al. [4]. The molar polarization of the former hydrocarbon reported by Kronberger and Weiss is $67.5\,cm^3\,mol^{-1}$[5]. The molar refractions of the acceptors were calculated by extending the relation $R_d = R_{m1} + R_{m2} - R_b$ proposed for disubstituted benzene by Curran and Palermetti [6], where R is the molar refraction and the subscripts d, m, and b refer to the disubstituted and monosubstituted benzenes and to benzene [6]. For example, R_{DNF} was calculated by $2R_N + R_F - 2R_b$, where R_N and R_F denote the molar refraction of nitrobenzene and fluorobenzene, respectively. For the calculation of the molar refractions of the acceptors we used the following values in $cm^3\,mol^{-1}$: benzene, 26.26; nitrobenzene, 32.88; fluorobenzene, 26.15; chlorobenzene, 31.15; toluene, 31.06; and phenol, 28.03. The results are 39.4 $cm^3\,mol^{-1}$ for DNF, 44.4 $cm^3\,mol^{-1}$ for DNC, 44.3 $cm^3\,mol^{-1}$ for DNT, and 41.3−$cm^3\,mol^{-1}$: for DNP. We add that the experimental values of polysubstituted benzenes reported by Thomson [7] can be well reproduced by the same procedure; for example, the observed value for trichlorotrinitrobenzene is $59.5\,cm^3\,mol^{-1}$ and the calculated one is $60.8\,cm^3\,mol^{-1}$ [7].

The distortion polarization, the sum of atom and electron polarizations, of the complex was assumed to be approximated by the molar refraction of the complex, which is given by the sum of those of donor and acceptor compounds. It may be noted that, within the limit of rather large experimental errors in the permittivity measurements, the observed molar polarizations are in agreement with the molar refraction, indicating that the acceptor molecules in the room-temperature form cannot be oriented by an externally applied electric field. The only exception is pyrene-DNC complex, for which the molar polarization (P_1) is distinctly larger than the molar refraction (R).

The transition temperature, permittivity measured at a temperature within several degrees above the transition point at 300 kHz (ε_{r2}), molar polarization (P_2), and estimated molar orientation polarization (P_0) are presented in Table 2. The relative permittivity increases abruptly upon the polymorphic transition by a factor of 1.6 in the pyrene-DNC complex to 4.3 in the pyrene-DNT complex and then decreases gradually by further increase of the temperature. The density was assumed to be not changed by the transition in the calculation of molar polarization. The error arising from this assumption may be 1 to 4%. For example, Inabe et al. reported 1.396 g cm^{-3} for pyrene-DNC complex exhibiting the smallest permittivity changes and 1.305 g cm^{-3} for pyrene-DNT complex exhibiting the largest permittivity change on the polymorphic transition. If we employ these reported values, the molar polarization becomes a little larger; 208 cm^3 mol^{-1} for pyrene-DNC comples and 237 cm^3 mol^{-1} for pyrene-DNP complex. The molar orientation polarization was estimated by the difference between P_2 and R. The appearance of the orientation polarization upon the transition clearly indicates the onset of a large degree of molecular motion, possibly rotation around the axis perpendicular to the ring plane.

When the Debye equation is applied to the molar orientation polarization in Table 2, the apparent dipole moment (m_{app}/D) (1D=3.3336 × 10^{-30} Cm) in Table 3 is obtained for the acceptor molecule. The temperature in the Debye equation was approximated by the transition point. In the present molecular complexes, the molecule is allowed to rotate only around the

TABLE 2 Transition Temperatures (T), Relative Permittivities (ε_{r2}), Molar Polarizations (P_2) Above the Transition Temperature, and Orientation Polarizations (P_0)

Complex	T/K	(ε_{r2})	P_2/cm^3 mol^{-1}	P_0/cm^3 mol^{-1}
Py-DNF	349.5	7.0	189	73
Py-DNC	314	8.7	206	88
Py-DNT	326.5	13.4	228	110
Py-DNP	326	6.3	175	60
Fl-DNP	330	7.1	190	77

TABLE 3 Comparison Between Estimated and Experimental Dipole Moments of the Acceptor Molecules

Complex	m_{app}/D	m_{eff}/D	m/D[a]
Py-DNF	2.05	3.22	(3.25)
Py-DNC	2.13	3.35	3.15, 3.20
Py-DNT	2.43	3.81	(3.88)
Py-DNP	1.79	2.81	2.95, 3.20, 3.55, 3.65
Fl-DNP	2.04	3.20	2.95, 3.20, 3.55, 3.65

[a] Taken from McClellam [8].

The estimated values are in parentheses.

axis perpendicular to the ring plane; therefore, the angle between the directions of the moment and the applied electric field in the Debye equation is not enough to specify the spatial relation between the given molecule and the electric field. The ring planes of a number of molecules may be distributed with the same probability around the moment. Only when the ring is in the plane defined by the directions of the moment and the field is the molecule allowed to orient following the expression given by Debye. If the ring is perpendicular to the latter plane, the molecular motion is not affected by the field at all. When the angle between the two planes is ϕ, the dipole moment (m) may have a component $m\cos\phi$ to be influenced by the electric field.

Then, the average component effective to the molecular orientation would be $2\,m/\pi$. In Table 3, m_{app} divided by $2/\pi$ is represented by m_{eff}. The experimental dipole moment is available only for DNC and DNP [8]. For DNF and DNT the moments for comparison were estimated based on those of m-dinitrobenzene (3.72 D), fluorobenzene (1.40 D), and toluene (0.30 D) [8]. Although the experimental values for DNP are rather scattered, the general agreement between m_{eff} and m implies that the acceptor molecule can be freely oriented by the applied electric field, supporting the existence of a large degree of the molecular motion in the high-temperature form. The apparent dipole moment of DNC in the low-temperature form is 1.65 D and the effective one is 2.60 D, showing the occurrence of molecular motion but with some restriction. This conclusion is consistent with the rather small second moments of broad-line ^{1}H NMR spectra of pyrene-DNC complex recorded below the transition temperature.

Attempts to calculate the apparent dipole moments by analyzing the temperature dependence of molar polarization above the transition point were not successful because the available temperature range is narrow and the complexes tend to decompose by prolonged heating at high temperatures.

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