

# The Validity of an Aggregation-Assisted Induced Electric Order in a Metalloorganic Complex

A. Th. Ionescu,<sup>†</sup> N. Scaramuzza,\* and C. Versace

Dipartimento di Fisica dell'Università degli Studi della Calabria and Istituto Nazionale per la Fisica della Materia, I-87036 Arcavacata di Rende, Cosenza, Italy

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The aggregation of metalloorganic nematogenic molecules of 4,4'-bis(hexyloxy)azobenzene–palladium complex (AZPAC) is analyzed by using recent measurements of volume polarization of AZPAC. The dipolar electric moment of the AZPAC molecule has been measured. The average aggregation number and also the energy required for this aggregation have been estimated. The superparaelectric behavior of AZPAC has been thus explained.

## Introduction

Nematics are usually formed by rodlike organic molecules.<sup>1</sup> For symmetry reasons, nematic phases are not ferroelectric. Most of them behave like good insulators. Liquid crystals containing transition metals were synthesized by different groups several years ago.<sup>2,3</sup> Some of those organometallic liquid crystals show interesting electric properties and have been studied intensively because they might improve the electrical performances of useful devices.

4,4'-Bis(hexyloxy)azoxybenzene–palladium complex (AZPAC) is a palladium-containing metalloorganic liquid crystal<sup>4</sup> whose formula is given in Figure 1. Some electric properties of AZPAC have been reported,<sup>5–9</sup> concerning both general liquid crystal properties and specific electrical ones.

In a recent paper,<sup>10</sup> we discussed the aggregation-assisted induced electric order in the nematic phase of AZPAC by comparing records of depolarization currents to measurements of clearing point transition temperatures under different applied electric fields on different widths of the cells. In that paper, we interpreted the somewhat contradictory measurements on AZPAC, i.e., the fact that the maxima of the depolarization curves depend strongly on the applied electric field whereas the transition temperatures do not, in terms of an electric order set in liquid crystal which is, geometrically, orthogonal to the nematic order and, in many respects, independent of it. We suggested that this was due to two main facts, i.e., AZPAC is not entirely rodlike as usual nematics but rather semidiscotic, which prevents a free rotation about the long molecular axis, and also there is a possibility of Pd–O(N) bonding, considered as being responsible for a transitory ferroelectric order in a direction orthogonal to the nematic director. The suggestion of aggregation-assisted induced electric order<sup>10</sup> was inferred only by analyzing the depolarization currents and the clearing point transition temperatures. Later, we obtained new evidence for this suggestion by measuring directly the polarization of AZPAC and its dependence on the temperature.

As one can see in Figure 1, AZPAC is a large, semidiscotic, polar molecule, resembling more of a brick or a fish than a rod. We expect several kinds of intermolecular interactions; in particular, owing to the presence of the azoxy group, nearby AZPAC molecules could interact through the palladium center

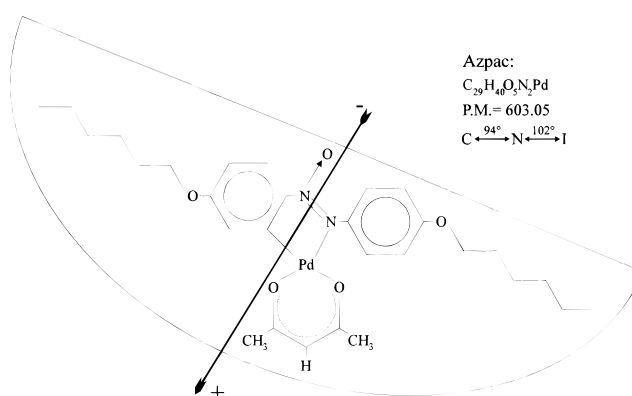


Figure 1. The molecule of AZPAC.

and the nitrogen-bonded oxygen atom. The molecules in this array, with parallel symmetry planes, can have nonzero electric dipoles oriented in several ways, from parallel to antiparallel, giving birth to multimers of various degrees of dipole moments, ranging from zero for random orientation to several times the molecular dipole moment for ordered orientation. These orientations cannot have the same probability of occurrence, but, in the case of free molecules, these probabilities are not quite different. On the other hand, in the condensed phase, be it solid, nematic, or isotropic liquid, only two orientations of the dipole moments are most likely, namely those compatible to a closer packing: the parallel orientation and the antiparallel one. When one applies an electric field, individual molecules tend to orient with the dipole moments along the field, but the thermal motion prevents it. The net result is a macroscopic polarization of the sample which, for not too large field strengths, is proportional to the applied field. The proportionality factor depends on the square of the molecular electric dipole and is inversely proportional to the temperature, as is well-known. On the other hand, when multimers can be formed, the polarization of the sample may increase.

Let us consider a molecular dipole moment which makes an angle  $\theta$  to the electric field  $\mathbf{E}$ , the direction of which is taken as the  $z$ -axis. The supplementary potential energy in this case may be expressed as

$$W = -\mathbf{E} \cdot \mathbf{p} = -Ep \cos \theta \quad (1)$$

The average value of the  $z$ -component of  $\mathbf{p}$  is

<sup>†</sup> On leave from Faculty of Physics, University of Bucharest, Romania.

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$$\bar{p}_z \equiv \bar{p} = \frac{\int_0^\pi p \cos \theta \exp(Ep \cos \theta/kT) \sin \theta d\theta}{\int_0^\pi \exp(Ep \cos \theta/kT) \sin \theta d\theta} \quad (2)$$

For  $Ep \leq kT$ , the expression of  $\bar{p}$  is  $p^2E/3kT$ , whereas for  $Ep > kT$ , the value of  $\bar{p}$  is just  $p$ ; that is, we have complete alignment. Let  $N$  be the number of molecular dipoles, i.e., of molecules, per unit volume, then the latter condition gives the macroscopic polarization

$$P = N\bar{p} = Np \equiv P_{\text{sat}} \quad (3)$$

where  $P_{\text{sat}}$  is the maximum value of  $P$ . But in the first case,

$$P = N\bar{p} = \frac{Np^2}{3kT}E = \epsilon_0\chi_r E \quad (4)$$

where

$$\chi_r = \frac{Np^2}{3\epsilon_0 kT}$$

is the relative dielectric susceptibility.

Let us now consider that we have aggregations of  $n$  parallel molecular dipoles, so that one may consider entities of a greater electric dipole,  $p' = np$ . In the limit of weak fields, the average value of  $p'$  is

$$\bar{p}' = \frac{n^2 p^2}{3kT}E$$

and multiplying this value by  $N/n$ , the number of aggregates, one gets

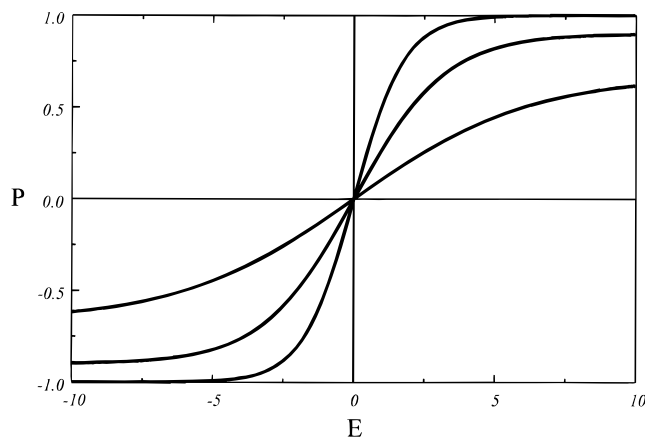
$$P_n = \frac{N}{n} \frac{n^2 p^2}{3kT}E = n \frac{Np^2}{3kT}E = nP \quad (4')$$

that is  $n$  times stronger than the case when there are no such aggregations.

Of course, in the limit of high fields, one has to get the same saturation value:

$$\bar{p}' = np \quad \text{and} \quad P_n = \frac{N}{n} np = Np = P_{\text{sat}} \quad (5)$$

In Figure 2, we represented a plot of  $P(E)$  as a function of  $E$  for three different values of  $n$ : for  $n = 1$ , one gets the true paraelectric case; for  $n \rightarrow N$ , one gets the ferroelectric case; and for an intermediate value  $1 \leq n \leq N$ , the behavior may be called "super-paraelectric". This state may be considered as a superposition of a paraelectric state resulting from averaging small ferroelectric particles. Actually, there are well-known magnetic powders of very tiny particles of several nanometers in diameter which are each monodomain ferromagnets and which, by thermal motion, give birth to a paramagnetic state characterized by a stronger magnetic susceptibility. These powders are called superparamagnets. One can see that the aggregation process may increase the electrical response of the system up to values very close to the ferroelectric state, depending on how many molecules aggregate in each "particle". Measuring the dielectric susceptibility in the weak field region, knowing or measuring the value of individual molecular dipole moment, and comparing eqs 4 and 4', one may get the value of  $n$ , the aggregation number. Of course, this number must be an average over a broader distribution of monomers, dimers, trimers, and so on. This distribution, in turn, must depend on temperature and also on the free energy involved in forming dimers, trimers, etc. We have to stress here that these multimers



**Figure 2.** Polarization versus electric field plots showing para-, superpara-, and ferroelectric behavior.

are not stable or permanent aggregations but labile entities, and their number is also an average value on the statistical ensemble. By studying the temperature dependence of the polarization of AZPAC, one may determine not only the average number of multimers but also the free energy involved in multimer bonding.

## Experimental Section

The transition temperatures of AZPAC are  $T_{\text{KN}} = 94^\circ\text{C}$  and  $T_{\text{NI}} = 102^\circ\text{C}$ . This substance has been obtained by complexing the liquid crystal 4,4'-bis(hexyloxy)azoxybenzene, i.e., its ligand, which shows a nematic phase between 80 and  $126^\circ\text{C}$ .

To measure the polarization of AZPAC, we used a pulse technique that involves analyzing the current response to a square-wave voltage.<sup>11-13</sup> The sample was prepared by introducing AZPAC between two glass plates covered with ITO electrodes and separated by Mylar spacers of known widths. This sample actually is a plane condenser which can be represented schematically by a parallel combination of a resistor ( $R$ ) and a capacitor ( $C$ ), as in Figure 3. In series to the cell, there is a load resistor used to monitor the series current by measuring the voltage drop on it. The square-wave voltage is provided by a function generator in series to a voltage amplifier of very fast response time (up to several megahertz). Actually, the applied voltage is not entirely "square" but has an exponential risetime,  $\tau$ , which is the same for the decreasing end. The time dependence of the applied voltage is

$$U(t) = U(1 - e^{-t/\tau}) \quad \text{for } t \in [0, t_1] \quad (6)$$

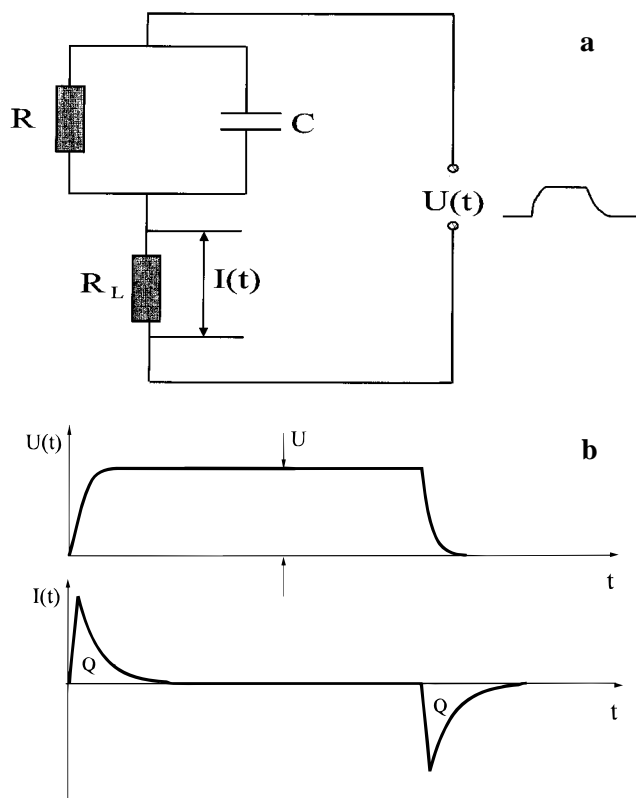
where  $t_1$  is the period of the wave and is much greater than  $\tau$ . We are not concerned about the decreasing part of the wave because the current response is similar to what happens at the beginning of the wave. The current through the sample is

$$I(t) = \frac{U(t)}{R} + C \frac{dU(t)}{dt} = \frac{U}{R}(1 - e^{-t/\tau}) + \frac{CU}{\tau}e^{-t/\tau} \equiv I_R + I_C \quad (7)$$

Integrating over an interval greater than the characteristic time  $\tau$  one gets

$$\int_0^T I(t) dt \equiv Q = \frac{U}{R}(T + \tau(e^{-T/\tau}) - CU(1 - e^{-T/\tau})) = \frac{U}{R}(T - \tau) + \frac{U}{R}\tau e^{-T/\tau} + CU(1 - e^{-T/\tau}) \quad (8)$$

For  $T \approx 10\tau$ ,  $Q \approx (9\tau/R)U + CU$ , because  $e^{-10} < 5 \times 10^{-5}$ . In our case,  $9\tau/R$  was 5 orders of magnitude less than  $C$ , and we may conclude that  $Q = CU$ . Measuring  $Q$  and knowing  $U$ ,



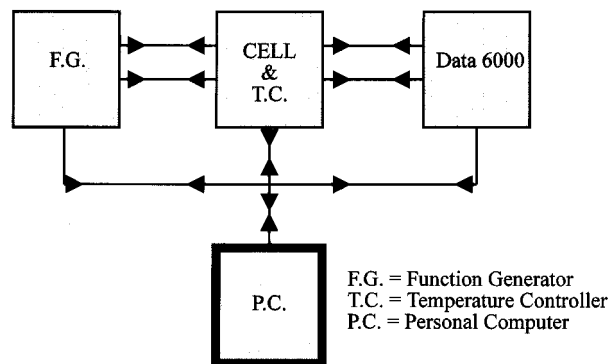
**Figure 3.** (a) Electric scheme. (b) Plots of voltage and current versus time.

we get the value of  $C$ , which gives us information about the dielectric constant and, consequently, information on the electric susceptibility. As a matter of fact, one may separate the capacity  $C$  in two parallel parts: one which is the real capacity of AZPAC and a parasite one which includes the contribution of the spacers, contacts, and glue, as well as  $9\tau/R$  discussed above. Considering the whole capacity as an equivalent capacity, we can write

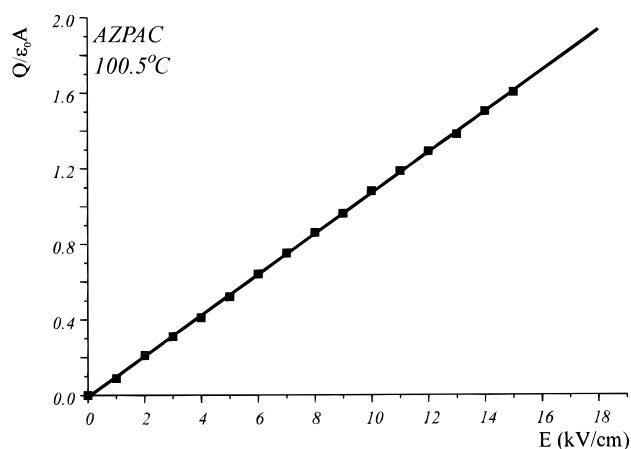
$$Q = C_e U = \frac{\epsilon_0 \epsilon_e A}{d} U = \epsilon_0 \epsilon_e A E \quad (9)$$

where  $A$  is the area of AZPAC sample and  $d$  the width of the condenser, i.e., the width of the spacer.  $\epsilon_e$  is an equivalent dielectric constant. If one plots  $Q/\epsilon_0 A$  as a function of  $E$ , the slope of the linear fit gives the value  $\epsilon_e$ . The equivalent dielectric constant  $\epsilon_e$  is actually composed of the dielectric constant  $\epsilon$  of the substance which fills the space of the cell and a term  $k$  which takes into account all the parasitic terms, including  $9\tau/R$ . This term  $k$  stays practically constant during the experiments and can be subtracted. First, measuring the void cell, one gets a value  $\epsilon_e(\text{void}) = 1 + k$ , whereas measuring the same cell filled with substance, one gets  $\epsilon_e(\text{substance}) = 1 + \chi_r + k$ . Subtracting the two values gives us the value of the susceptibility,  $\chi_r$ .

Our measurements consisted of two steps. We first measured the temperature dependence of AZPAC susceptibility by using a commercial cell of  $2 \mu\text{m}$  width and  $0.2 \text{ cm}^2$  area. Second, we used a homemade cell to measure the actual value of the AZPAC molecule's dipole moment. To do this, we mixed a nonpolar solvent, tetrachloroethylene, whose dielectric constant is known, with AZPAC, obtaining dilute solutions of known concentrations. In these dilute solutions, the probability of encountering two interacting AZPAC molecules is very small, so AZPAC contribution to the total susceptibility of the solution is purely paraelectric. Because, in the case of the homemade cell, we did not know with great accuracy the area of the cell,



**Figure 4.** General experimental setup.



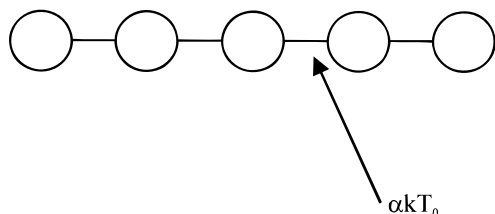
**Figure 5.** Plot of  $Q/\epsilon_0 A$  versus  $E$  for AZPAC at  $100.5^\circ\text{C}$ .

we used the standard value of tetrachloroethylene dielectric constant at  $20^\circ\text{C}$  to find the area.

In Figure 4, the general experimental setup is presented. To integrate the charge, we used a voltage spectrum analyzer, Data 6000, from Data Precision. The square-wave voltage was provided by a function generator, HP 8904A Multifunction Synthesizer, in series with a fast response amplifier, KROHN-HITE Model 7500. We used a frequency of  $7 \text{ Hz}$ , which is sufficiently small to obtain a good response to the applied voltage. The spectrum analyzer accumulated hundreds of current versus time plots before computing the charge  $Q$ . All the data were stored and processed on a PC, including graphs and fits.

## Results and Interpretation

In Figure 5, we present a plot of  $Q/\epsilon_0 A$  versus  $E$  for AZPAC at  $100.5^\circ\text{C}$ . From the plot, one can immediately find out the value  $\epsilon_e$ . As was mentioned in the previous section, by subtracting the value of  $\epsilon_e(\text{void})$  obtained with the empty cell from  $\epsilon_e(\text{AZPAC})$  one can find the dielectric susceptibility of AZPAC,  $\chi_r$ . Actually,  $\chi_r$  consists of two parts: the electronic part and the dipolar part. We are interested in the dipolar part of the susceptibility, which has been defined in eq 4. To get this, we must take into account the fact that polarizing a material comes both from orienting the permanent electric dipoles (if there are any, and which is a statistic process) and from the electronic polarizability of each molecule. The latter process is always present, and its contribution is practically the same for a very large frequency spectrum from dc state to visible frequencies. It is well-known that, in this spectral region, the dielectric constant is equal to the square of the refractive index, i.e.,  $\epsilon_{\text{vis}} = 1 + \chi_{\text{electronic}} = n^2$ , where  $n$  stands for the refractive index of the visible light. In the visible region of the spectrum, the permanent dipole of the AZPAC molecule cannot follow



**Figure 6.** Linear aggregate of AZPAC molecules.  $\alpha kT_0$  is the energy per bond.

the change of the electric field. The dielectric absorption frequencies have been found in regions of much lower frequencies.<sup>7</sup> Taking out the electronic part of the susceptibility, only the dipolar contribution remain, and so one can determine the value of the average electric dipole moment,  $p'$ , of the aggregates, either monomers, dimers, trimers, and so on:

$$p' = \sqrt{\frac{3kT\epsilon_0\chi_{\text{pol}}}{N}} \quad (10)$$

where  $\chi_{\text{pol}}$  is just the polar part of the susceptibility we have discussed above.  $N$  stands for the number of AZPAC molecules per cubic meter, a value which can be calculated knowing the molecular mass of AZPAC, 603.5 g/mol, and its density, 1.60 g/cm<sup>3</sup>. Dividing this value,  $p'$ , by the true value of the AZPAC molecule's electric moment, we get the average number,  $\langle n \rangle$ , of aggregation. This number must be analyzed in terms of a statistic theory.<sup>14</sup> In Figure 6, we considered a linear aggregate of  $n$  molecules. Let  $\alpha kT_0$  be the bond energy between two adjacent molecules, i.e.,  $\alpha$  is the numerical value of bond energy in units of  $kT_0$ . The total interaction free energy of an aggregate of  $n$  monomers is

$$n\mu_n^0 = -(n-1)\alpha kT_0 \quad (11)$$

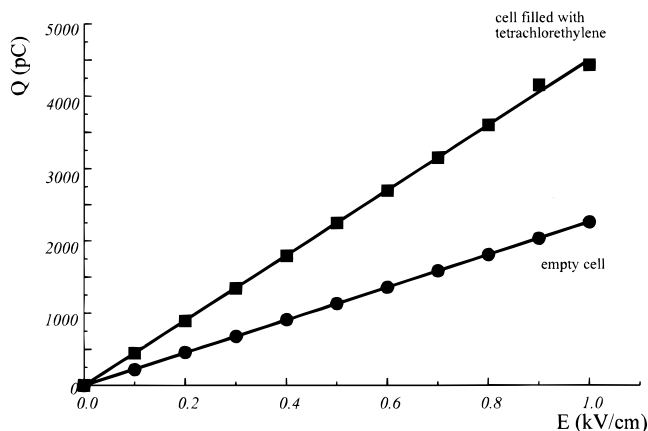
where we took into account the fact that the terminal monomers are nonbonded. The free energy per particle in an aggregate of  $n$  particles is, therefore,

$$\mu_n^0 = -(n-1)\alpha kT_0 = \mu_\infty^0 + \alpha kT_0/n \quad (12)$$

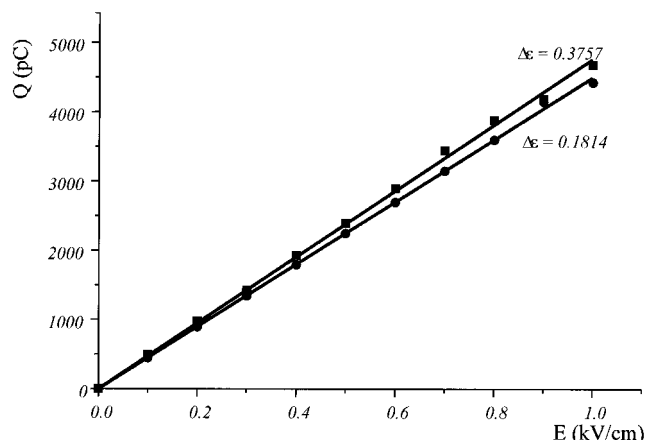
Thus, as  $n$  increases, the mean free energy decreases asymptotically toward  $\mu_\infty^0$ , the "bulk" energy of a molecule in an infinite aggregate. Let us denote by  $X_n$  the concentration of molecules in aggregates of  $n$  molecules. *This is not to be confused with the concentration of aggregates of  $n$  molecules, which actually is  $X_n/n$ .* The concentration  $X_n$  can be expressed in terms of  $X_1$ , the concentration of monomers:<sup>14</sup>

$$X_n = n\{X_1 \exp[(\mu_1^0 - \mu_n^0)/kT]\}^n = n\left\{X_1 \exp\left[\frac{T_0}{\alpha}(1 - 1/n)\right]\right\}^n = n[X_1 e^\beta]^n e^{-\beta} \quad (13)$$

where  $\beta$  stands for  $\alpha T_0/T$ . Summing the values of  $X_n$  over all the values of  $n$  from 1 to  $\infty$ , one gets the total concentration, which is not 1 as one could imagine because, from all the AZPAC molecules, we must separate those which could give aggregates with parallel dipole moments. Assuming a Boltzmann distribution and taking into account that the configuration with parallel dipoles is less favored energetically than the antiparallel one, the number of molecules which aggregate in particles with nonzero dipole moment is only a fraction of the total number of molecules. Let this fraction be  $C$ , expressed as a subunit number. Now we can write



**Figure 7.**  $Q$  (pC) versus  $E$  (kV/m) for the empty cell and for the cell filled with tetrachloroethylene.



**Figure 8.**  $Q$  versus  $E$  for two solutions of AZPAC in tetrachloroethylene.

$$C = \int_{n=1}^{\infty} X_n = \int_{n=1}^{\infty} n [X_1 e^\beta]^n e^{-\beta} = e^{-\beta} [X_1 e^\beta + 2(X_1 e^\beta)^2 + 3(X_1 e^\beta)^3 + \dots] = X_1 / (1 - X_1 e^\beta)^2 \quad (14)$$

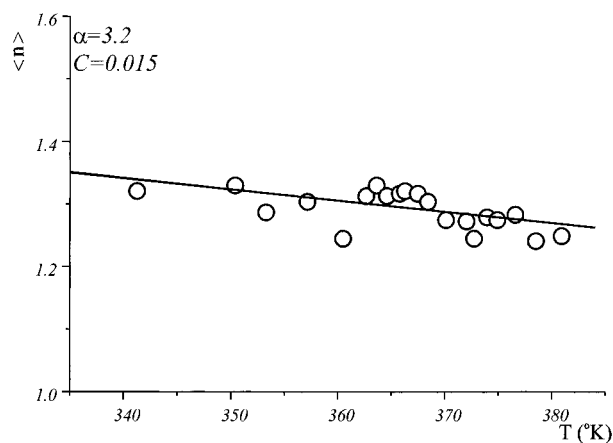
where we have made use of the identity  $\sum_{n=1}^{\infty} nx_n = x/(1-x)^2$ . Thus,

$$X_1 = \frac{(1+2C e^\beta) - \sqrt{1+4C e^\beta}}{2C e^{2\beta}} \quad (15)$$

The expectation value of  $n$ , defined by  $\langle n \rangle = \sum n X_n / \sum X_n = n X_n / c$ , is given by

$$\langle n \rangle = \sqrt{1 + 4C e^\beta} = \sqrt{1 + 4C \exp\left(\frac{T_0}{\alpha T}\right)} \quad (16)$$

The only thing we have to do now is to measure the value of the AZPAC molecule's electric dipole. To do this, we used two dilute solutions of AZPAC in tetrachloroethylene (C<sub>2</sub>Cl<sub>4</sub>), which is a nonpolar solvent because of the symmetry of its molecule, D<sub>2h</sub>. Tetrachloroethylene is liquid between -22 and 121 °C, and has a molecular mass of 165.83 g/mol, a density of 1.62 g/cm<sup>3</sup>, a refractive index of 1.5053, and a dielectric constant at 20 °C of 2.4. It is a very good solvent for AZPAC. Actually, we tried other nonpolar solvents as well, but they were either too volatile or not very good solvents for AZPAC. In Figure 7, we show two plots ( $Q$  versus  $E$ ), one for the empty cell and the other for the cell filled with tetrachloroethylene. In Figure 8, another two plots are shown, this time for two different concentrations of AZPAC in tetrachloroethylene, namely



**Figure 9.** Average  $\langle n \rangle$  versus temperature  $T$ . The fit uses the function  $\langle n \rangle = [1 + 4C \exp(\alpha T_0/T)]^{1/2}$ .

0.000 736 298 g of AZPAC in 0.016 145 g of solution for the first one, and double the value for the second. Defining  $\Delta\epsilon$  as the difference between the dielectric constant of the solution and the dielectric constant of pure tetrachloroethylene, for the two concentrations mentioned above, we got  $\Delta\epsilon = 0.1814$  in the first case and  $\Delta\epsilon = 0.3757$  in the second case. Their ratio is 2.07, in good concordance with the fact that the concentration doubles. This increase in the dielectric constant is practically due to the replacement of some nonpolar solvent molecules with polar molecules of AZPAC. Of course, there is not a one-to-one correspondence between the replaced solvent molecule and the replacing AZPAC molecule. Actually, the ratio of the two numbers of molecules must be the same as the ratio of their molecular masses, which is practically the same as that of their molecular volumes. But electronic polarizabilities are also proportional to molecular volume, so, although the replacing AZPAC molecules are less than the replaced solvent molecules, the total electronic polarizability varies very little. We may say that, within the experimental errors, the increase  $\Delta\epsilon$  in the dielectric constant is due to the polar part of AZPAC's susceptibility,  $\chi_{\text{pol}}$ . Knowing the number of AZPAC molecules per unit volume of the solution, we can easily calculate the electric dipole moment of the AZPAC molecule. From our experiments, we determined the following value:  $p_{\text{azpac}} = (3.54 \pm 0.09) \text{ D} = (3.54 \pm 0.09) \times (3.336 \times 10^{-30}) \text{ C}\cdot\text{m}$ .

We have measured the equivalent dielectric constant of pure AZPAC for 20 different temperatures, ranging from the isotropic to the glassy state, the largest number of records being in the nematic temperature range. (When cooling, AZPAC first presents a metastable glassy state and then crystalizes.) In Figure 5, we present the measurements for a temperature of 100.5 °C. For all other temperatures, the plots look practically the same, of course giving different values for  $\epsilon_e$ , for  $\chi_{\text{pol}}$ , and  $p'$ . Now dividing  $p'(T)$  by the value of the AZPAC molecule's dipole moment just measured above, we obtain the average values  $\langle n \rangle$  of the aggregation number as a function of temperature.

In Figure 9, we have shown the average aggregation number  $\langle n \rangle$  as function of the absolute temperature  $T$ . Experimental data are represented by large squares to stress the experimental errors. On the same plot, by a solid curve, is shown the best fit obtained with the following expression (eq 16):

$$\langle n \rangle = [1 + 4C \exp(\alpha T_0/T)]^{1/2}$$

The fit returned the best values for  $\alpha$  and  $C$ . These values are  $\alpha = 3.2$  and  $C = 0.015$ . Because of the experimental errors, the confidence in these values is not very large; we must accept

for both  $\alpha$  and  $C$  an error of 25%. The value of  $\alpha$  gives the aggregation energy of  $3.2 kT_0 = 3.77 \times 10^{-21} \text{ J} = 0.024 \text{ eV} = 2.27 \text{ kJ/mol}$ . The value of  $C$  looks rather small, but if one takes into account that  $C$  really means the concentration of molecular aggregates which *might* give birth to greater dipoles, the value of  $C$  is not unnatural. As we have mentioned before, in condensed phases, we expect only two relative orientations of the molecular dipoles in dimers, namely parallel and antiparallel. The energetic difference of these two orientations is  $\epsilon = 4p_{\text{AZPAC}}^2/4\pi\epsilon_0 r^3$  where  $r$  is the distance between the two molecules. Considering a Boltzmann distribution, the concentration  $C$  must be  $C = \exp(-\epsilon/kT)$ .

Knowing  $p_{\text{AZPAC}}$  and  $C$ , one may determine the value of  $r$ , which is  $r = 5.46 \times 10^{-10} \text{ m}$  between the centers of two AZPAC molecules, a value which is quite reasonable.

## Conclusion

In this paper, we have carried out our investigations on the polar organometallic nematogen molecule AZPAC. By measuring the AZPAC molecule's dipole moment, and also the average dipole moment which gave rise to the observed paraelectric behavior of the substance, we have brought about new evidence in support of our assumption that, apart from the nematic order and orthogonal to it, there is an electric order due, in part, to a process of aggregation. We have analyzed this fact in terms of a statistical theory and have obtained an estimation of the energy which is involved in this aggregation process. It turned out that the aggregation of AZPAC molecules is not very strong, because there is no special interaction which could favor the parallel orientation of molecular dipoles. If there were such an interaction or, at least, if the probabilities of parallel and antiparallel orientations had been the same, we would expect, then, a very strong superparaelectric behavior. If such a molecule had been synthesized, one would most likely see very interesting and useful electrical properties.

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