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EFFECT OF PAA MOLECULAR STRUCTURE ON THE NEMATIC LIQUID CRYSTAL PHASE

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Abstract The dipole moment and the valence electron density of p-azoxyanizole (PAA) molecule were calculated using the theoretical semiempirical method CNDO/2. On the basis of these results a model of the nematic liquid crystal phase ordering was proposed.

Valence electron density and dipole moment of PAA with quantum mechanical semiempirical method CNDO/2 were calculated, using the original programmes of Pople and Beverige[1] and the X-ray structure data of Krigbaum, Chatani, Barber[2]. The results are given on Fig.1.

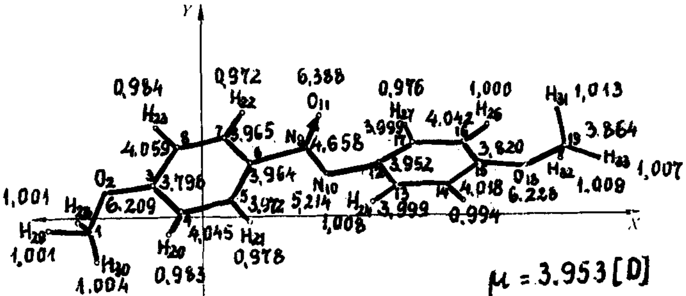

FIGURE 1

The conclusions that could be drawn from these results are:

1. The atom O_{11} will be effective nucleophylic agent. It will join willingly the next molecule CH_3-O group, forming a C-H...O_{11} intermolecular bond (verified by X-ray structure data[2])

2. From the valence electron densities of O_{11}, H_{22}, H_{27} follows that intramolecular bonds C-H...O take place between the central oxygen atom and the para-C-H bonds of both benzene rings. The distances $R(O_{11}...H_{22})$=2.27 Å and $R(O_{11}...H_{27})$ =2.3 Å are typical of a C-H...O bond also.[3] (The distance C-H...O[4] measured is 3.35 Å, theoretically determined is 2.9 - 3.3 Å). Hence the molecule is stick at the center by these C-H...O bonds. At the same time this bond is the weakest of all hydrogen bonds - its energy is 2.3 - 2.7 kcal/mole. Hence, above certain temperature the angle between both benzene rings may be expected to be temperature sensitive. To the clearing temperature 135°C (temperature of the transition isotropic-nematic phase) an energy of 2.9 kcal/mole corresponds. That means that at temperature less than 135°C a temperature depending angle may be expected. It was confirmed using deuteron fast Fourier transform spectra of the ring deuterated PAA that in the temperature region 124° - 135°C the angle between orientations of both benzene rings is temperature dependent[6].

3. The dipole moment of PAA was calculated to be

$$\mu_{PAA}=3.953\ [D]$$

The value $\mu^{solv.}_{PAA}$=2.48 [D] measured by Tzvetkov and Marinin[7] in benzene solution cannot be taken as dipole moment of a single molecule, because as was shown by Otterbein[8] the dipole moments measured in gas phase and in solution may differ significally.

By the same way it will not be less wrong to insist that $\mu_{PAA}=\mu^1$ (measured in nematic liquid crystal phase(μ^1=2.22 [D]) as alleged de Jeu and Lathouwers[9], since we can hardly pretend that molecules are independent or quaziindependent in nematic liquid crystal phase. All the more that it was established by X-ray data[10] that the nematic phase PAA incorporates cybotactic groups with smectic order. To be able to describe this complicated nematic phase with complicated dielectric properties[11] the dipole-dipole interaction was supposed[11] to be very important (the dipole-dipole interaction will be more important for the smectic than for the nematic phase) and a new theoretical model proposed. (Because such interactions are not accounted for in the usual Onsager approach which has been used by Maier and Maier[12] to describe the dielectric properties of nematic liquid crystals). In this model the dipole moments were taken into consideration, but calculations of the dipole-dipole interaction terms were not attempted because of their complexity. The discrepancy theory-experiment was explained by the neglecting of these terms. The importace of both the dipole moment and the dipole-dipole interactions may be explained by the value $\mu = 3.95$ [D] .

The dipole moment of a single molecule PAA is the dipole moment of the central N-O group[11] ($\mu_{N-O}=4.16$ [D])[13]. In order to have the real value $\mu_{PAA} \approx 4$ [D] measurements in gas phase should be made. Since that is impossible (the molecule distructes before being evaporated) measurements at very low concentrations, less than 1 % PAA in nonpolar solvent have to be made[14].

Starting from the structure of the molecule PAA we can say:two types of molecular ordering are possible i/ the dipole moments are in opposite directions (the polar N-O groups oriented outside) ii/ the dipole moments are in one direction (the polar groups oriented in one direction) (The polar N-O groups cannot be oriented tower each other.Because of the large negative charges on the oxygen atoms a repultion will take place) If so, we might expect groups with these two typ types of ordering in liquid phase. The dipole moment of the first groups (with opposite)will be zero;the dipole moment of the second groups will be $\mu = \sum \mu_i$. The existance of these two groups is a possible explanation of the great difference

$\bar{\mu}^1$, μ_{PAA}. On Fig.2 a smectic-A ordering is given, as well(the last group).

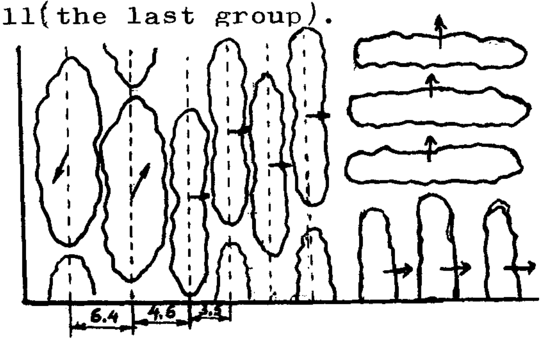

FIGURE 2

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