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THEORETICAL CONFORMATIONAL STUDY OF DIMETHYL
AZOXY BENZENE MOLECULE

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Abstract A conformational analysis of dimethyl azoxybenzene has been performed using a quantic semi-empirical method: PCIO. The results allow us to deduce the low energy zones and the most stable conformations. A comparison between these results and those for the aromatic core of PAA is made.

INTRODUCTION

Many experimental studies have emphasized the role of internal rotations in mesogen molecules like TBBA¹⁻⁴ and PAA⁵⁻⁸. In precedent studies, we performed a theoretical conformational analysis on these isolated molecules⁹⁻¹⁰ to roughly estimate the intramolecular contribution of these motions from an energetic point of view. Now we are interested by

the motions in nematic polyesters and especially for the mesogen moiety of these polymers, the dimethyl azoxy benzene. As it was noted before for the PAA and TBBA molecules, the conformational changes of the core have no influence on the conformational changes of the chains and vice versa. We will compare the possibilities of motion in this molecule to those in the azoxy benzene, aromatic core of PAA.

METHOD AND GEOMETRY

The calculations were carried out using a quantum semi-empirical method, the PCILO one: this is a perturbational method in which the wavefunction is built from orbitals localized on the chemical bonds. It was shown that this method leads to satisfying results when it is employed for conjugated molecules of similar structure¹¹.

The precise geometry of the dimethyl azoxy benzene is unknown so we used standard geometry for the benzene rings and the methyl groups i.e. the benzene groups are hexagonal with C-C bonds of 1.39 Å and C-H bonds of 1.08 Å, and the methyl groups are tetrahedral with C-C bonds of 1.54 Å and C-H bonds of 1.09 Å. The geometry of the central azoxy group was assumed to be the same as that of the PAA determined by RX¹²:

$$r_{\phi-N} = 1.496 \text{ Å}, r_{N=N} = 1.218 \text{ Å}, r_{N-O} = 1.279 \text{ Å}$$

$$\phi-C-N = 123^\circ, C-N=N = 112^\circ, N=N-C = 115^\circ, N-C-\phi = 131^\circ,$$

$$C-N-O = 118^\circ.$$

We considered the rotations around the two C-N bonds and those of the methyl groups around the C-C bonds. (On the figure 1 all the torsional angles are at 0°.)

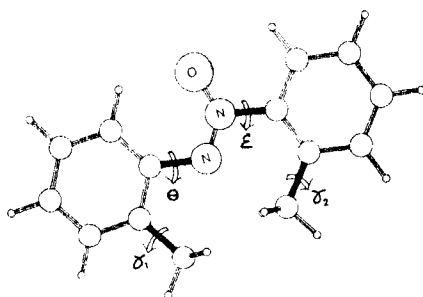
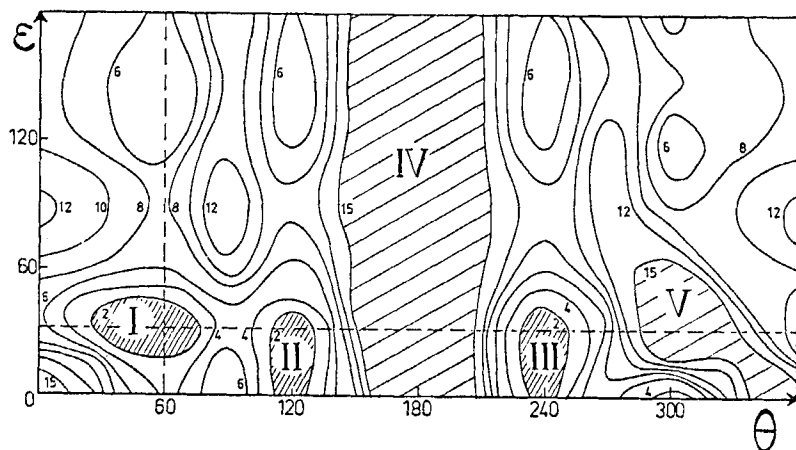


FIGURE 1. The dimethyl azoxy benzene molecule.

RESULTS OF THE CALCULATIONS

The energy map $E=f(\theta, \epsilon)$ is presented in figure 2 for the positions of the methyl groups which lead to lowest energy. We will discuss about these positions later.

FIGURE 2. Energy map $E=f(\theta, \epsilon)$ for dimethyl azoxy benzene.

A very important result is that the rotations around the C-N bonds are no more independent. This fact is in opposition to the conclusions of the precedent study on the PAA¹⁰.

We can see on this figure three low energy zones (corresponding to energy less than 2 KJ/mole, the thermal agitation energy kT) and two high energy zones (above 15 KJ/mole):

- the first one (I) spreads around the minimum energy (at $\theta=60^\circ$ and $\epsilon=30^\circ$) from 30° to 75° for θ and from 15° to 45° for ϵ .
- the two other low energy zones (II and III) are similar each other, extended from 110° to 130° for θ (respectively from 230° to 250°) and from 0° to 40° for ϵ .
- the largest high energy zone (IV) is for all the ϵ values and for θ values between 160° and 210° : a close position of the oxygen atom and a methyl group is forbidden.
- the other one (V) spreads around the highest energy position ($\epsilon=30^\circ, \theta=300^\circ, E=20$ KJ/mole) i.e from 15° to 60° for ϵ , and from 285° to 310° for θ . In this zone the interaction between the methyl groups remains always strong whatever be their positions.

It is interesting to compare these results with those obtained for the azoxy benzene so we show in figures 3 and 4 the energy curves $E=f(\theta)$ for ϵ_{\min} and $E=f(\epsilon)$ for θ_{\min} for the two molecules.

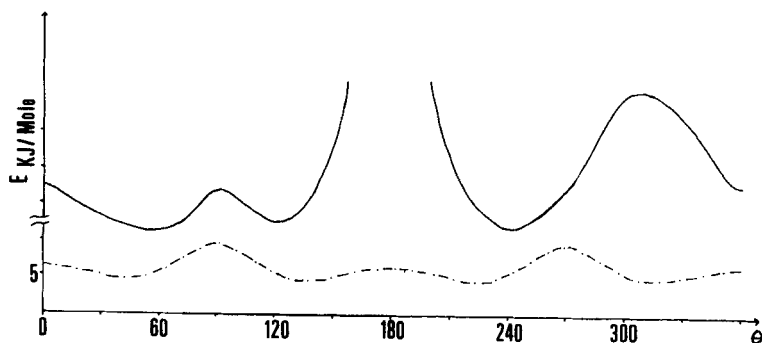


FIGURE 3. Energy curve $E=f(\theta)$ for $\epsilon_{\min}=30^\circ$.

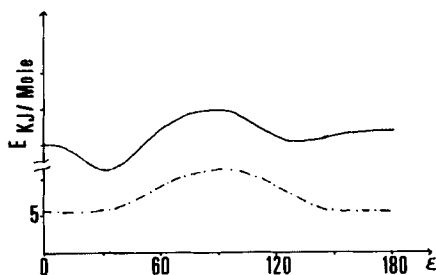


FIGURE 4. Energy curve $E=f(\epsilon)$ for $\theta_{\min} = 60^\circ$.

(—) dimethyl azoxy benzene; (-.-) azoxy benzene

We can note two points:

-the energy curves $E=f(\epsilon)$, ϵ varying between 90° and 180° are quite the same but the energy minimum in this zone, for the dimethyl azoxy benzene, is about 4 KJ/mole above the absolute minimum energy.

-the energy curves $E=f(\theta)$ and $E=f(\epsilon)$ (ϵ between 0° and 90°) present several differences, at first, the low energy zones are thinner and the minima are lightly shifted; in another part, the coplanar positions ($\theta=0^\circ$ or $\epsilon=0^\circ$) are less favoured than for the azoxy benzene and the barrier heights are near those of the perpendicular conformations (about 4-8 KJ).

This last fact is more evident if we consider all the positions of the methyl groups and not only the preferred ones. We calculated all energies $E=f(\gamma_1, \gamma_2)$ for each θ, ϵ and we observed important variations in the energy differences between the more and less favoured positions of the methyl groups. For example, the energy difference is about 120 KJ for $\theta=\epsilon=0^\circ$, it reduces to 40 KJ/mole when $\theta=60^\circ$ and $\epsilon=0^\circ$, it becomes 20 KJ/mole when $\epsilon=30^\circ$ and $\theta=0^\circ$ and is only 6.5 KJ for the minimum position. Thus the rotations of the methyl groups become much easier when the molecule is distorted.

CONCLUSION

If we summarize these results we can say that the presence of the methyl groups in ortho-positions to the azoxy group hinders the possibilities of motions around the C-N bonds. Some conformations become forbidden, or have a higher energy than in the azoxy benzene unsubstituted, principally when the methyl groups are too much near the oxygen atom; the interactions between the methyl groups contribute to increase the distorted character of the molecule. These two main conclusions are in agreement with the model used to fit the experimental results obtained in RMN¹³. Nevertheless this agreement is only qualitative because the temperature chosen for the fitting is near the transition one, between the solid and nematic phases, where the intermolecular forces are still strong, whereas the calculations consider only the intramolecular energy.

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