SEMI-EMPIRICAL CONFORMATIONAL ANALYSIS OF A LIQUID CRYSTAL MOLECULE: p-AZOXY-ANISOLE

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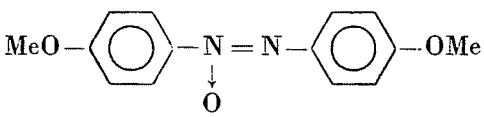
In order to study the rotational barriers in the molecule of *p*-azoxy-anisole, a compound readily occuring in the liquid crystal state, quantum chemical calculations were performed. Two different semi-empirical methods were used. PCILO [1, 2] is based on perturbation theory and the energy is evaluated up to third order terms. Thus correlation effects are considered, also. The method has been adapted successfully to conformational problems concerning large molecules [3]. The other method used was CNDO/2 [4], which does not take correlation effects into consideration.

The investigated compound *p*-azoxy-anisole, PAA



is nematic in the temperature range 116° to 136°.

Rotation of the methyl and methoxy groups

To save computer time the PAA molecule was modelled as shown in Fig. 1. The adequacy of this model is proved in [5].

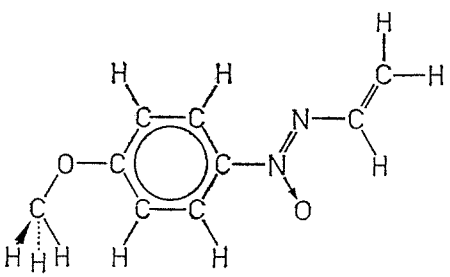


Fig. 1.

A rigid model of rotation of the methyl group was considered first. The author used the experimental molecular geometry obtained by X-ray diffraction in the solid phase [6]. Nothing but the torsional angle was altered. The rigid model combined with the PCILO method, yields 2.8 kcal mol^{-1} for the barrier height of the methyl group. Using CNDO/2 in a similar way 3.0 kcal mol^{-1} is obtained. Using the PCILO nonrigid model, where the COC angle was optimized for each value of the torsional angle, a torsional potential curve for the rotation of the methyl group was calculated. Seven points in the 0° to 60° range in intervals of 10° were calculated using the PCILO method. This curve obtained numerically was found to be very close to the usually applied threefold expression

$$V(\gamma) = \frac{V_3}{2}(1 - \cos 3\gamma)$$

with $V_3 = 3.83$ kcal mol^{-1}. γ is the torsional angle. The maximum deviation between both curves does not exceed 2 per cent. The barrier calculated in the CNDO/2 rigid model with experimental bond lengths and bond angles, except for the optimal COC angle taken from the PCILO, is 4.2 kcal mol^{-1}. The equilibrium conformation applying both methods was found to be a staggered one. The barrier measured by NMR method [5] and by neutron scattering [7] in the solid phase is 3.7 kcal mol^{-1} and 3.51 kcal mol^{-1}, respectively. There is a good agreement between the calculated and the experimental results.

To determine the rotational barrier around the OC (aromatic) axis the OCC (aromatic) angle was put equal to 120° and COC angle was varied within the 100° to 120° range. Using the PCILO method 4.5 kcal mol^{-1} was obtained for the barrier height of the methoxy group. In equilibrium the C—O—C plane was perpendicular to the plane of the benzene ring. According to Krigbaum's results [6] the two planes coincide in the solid phase although recent measurements [8] seem to confirm our result.

There was a great discrepancy (1 kcal $mole^{-1}$) at some points of the torsional potential curve when using different Kekule structures for the benzene π system in the PCILO input data. The reason of it lies in the method of calculation which uses localized double bonds.

Rotations around C—N bonds

Having limited computer capacity the author examined unsubstituted azoxy-benzene to determine the rotational barriers around C—N bonds. We had considerable difficulties in calculating the rotation barriers around C—N bonds by the PCILO method. The difference due to the use of the two Kekule structures was 2.5 to 3.0 kcal mol^{-1} in all conformations.

The CNDO/2 method was not used because it does not seem to be suitable for calculating rotational barriers around delocalized single bonds [9].

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Summary

The rotational barriers of p-azoxy-anisole nematic liquid crystal molecule were calculated by the PCILO and CNDO/2 methods.

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