

# Density Functional Study of a Helical Organic Cation

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**Abstract:** We report on the first stage of our theoretical study of the quino[2,3,4-kl]acridinium,1,13-dimethoxy-5,9-dipropyl-cation. This molecule, involved in the synthesis of novel triazaangulenium dyes of high chemical stability, is a chiral [4]-helicenium. The structure and the IR spectrum of the quino[2,3,4-kl]acridinium,1,13-dimethoxy-5,9-dimethyl-cation derived from theoretical calculations which use various density functional theory methods, are compared with the geometry derived from X-ray diffraction measurements and the experimental IR spectrum. Our study shows that the chosen variant of DFT methods (Becke88 for exchange, P86 for correlation, 3-21G\*\* basis set) reproduces the experimental geometry within 0.004 Å and the IR frequencies within 15 cm<sup>-1</sup>.

**Keywords:** Basis set · Computational chemistry · Density functional theory · Exchange-correlation functional · Helical cation

## 1. Introduction

Carbocations are a subject of interest due to their involvement in many key organic reactions.

The quino[2,3,4-kl]acridinium,1,13-dimethoxy-5,9-dipropyl (dipropyl DMQA<sup>+</sup>) cation is a chiral [4]-helicenium [1] involved in the synthesis of novel triazaangulenium dyes of high chemical stability.

In our group, we have started an extensive theoretical study of this molecule aimed at assisting/complementing experimental investigations by providing supplementary data concerning conformation, conformational equilibria, IR and VCD spectra.

In this work, we report the results of the first stage of this project, in which we compare the structure and the IR spectrum

derived from theoretical calculations which use various density functional theory methods, with the geometry derived from X-ray diffraction measurements [2] and the experimental IR spectrum. The aim of these comparisons is the selection among possible theoretical methods differing in their computational costs the one that is accurate enough to be used in further studies and not too expensive as the computational costs are concerned.

To this end, we considered a slightly smaller molecule, the quino[2,3,4-kl]acridinium,1,13-dimethoxy-5,9-dimethyl cation (Fig.), as the object of our studies.

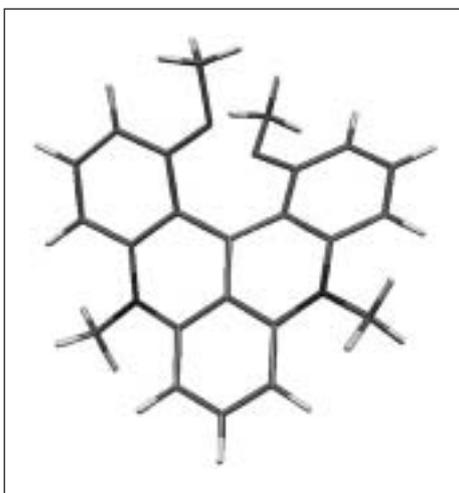


Fig. M enantiomer BP86 optimized geometry

## 2. Methods

Density functional theory (DFT) closed-shell calculations were performed using the Gaussian98 program [3]. All geometries were fully optimized. The vibrational frequencies were calculated at the optimized geometry.

The first series of calculations was carried out at the local density approximation (LDA) level with several basis sets ranging from the minimal one (STO-3G) to 6-31G\*\*.

The second series of calculations was carried out applying two different exchange-correlation functionals of the Generalized Gradient Approximation (GGA) type: BP86 [4][5] and BLYP [4][6] and one hybrid functional B3LYP [6][7]. In this series, the 3-21G and 3-21G\*\* basis sets were considered.

## 3. Results

To study the effects of the choice of the exchange-correlation functional and the basis set on the geometry we consider the O...O distance which characterizes the global shape of the cation.

At the LDA level, we note that the O...O distance is too short due to the overestimation of the strength of the O...O interaction. We note also that the O...O distance increases upon augmentation of the

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basis set ( $d_{\text{LDA/STO-3G}} = 2.48 \text{ \AA} \Rightarrow d_{\text{LDA/6-31G**}} = 2.59 \text{ \AA}$ ). Nevertheless, the comparison with the crystallographic data shows that, even with the largest basis set, the calculated distance is too short (theoretical value  $d_{\text{O...O(LDA/6-31G**)}} = 2.59 \text{ \AA}$  versus experiment  $d_{\text{O...O(X-ray)}} = 2.68 \text{ \AA}$ ).

Density functional theory offers two ways to improve LDA: by taking into account the gradient of the electron density (GGA) or by including the Hartree-Fock exchange (hybrid methods) in the exchange-correlation functional.

For the GGA and hybrid methods, the optimized geometry is very similar to the crystallographic one as measured by the root mean square deviation between the crystallographic and calculated bond lengths ( $\text{RMS}_{\text{B3LYP}} = 0.002 \text{ \AA}$ ;  $\text{RMS}_{\text{BLYP}} = 0.005 \text{ \AA}$ ;  $\text{RMS}_{\text{BP86}} = 0.004 \text{ \AA}$ ). Both GGA and hybrid functionals reproduce the experimental dihedral angle  $\alpha$ , which is a good measure to characterize the helicity of the cation ( $d_{\text{O...O(BP86/3-21G**)}} = 2.679 \text{ \AA}$  versus  $d_{\text{O...O(X-ray)}} = 2.680 \text{ \AA}$  and  $\alpha_{\text{(BP86/3-21G**)}} = -27 \text{ deg}$  versus  $\alpha = -28 \text{ deg}$ ).

As far as the IR spectrum is concerned, the comparison between the theoretical and the experimental result reveals a very good performance of GGA. In particular, the characteristic low and high frequencies derived from DFT (GGA) calculations agree very well with the experimental spectrum (agreement within  $2\text{--}3 \text{ cm}^{-1}$  (see Table)).

The maximum deviation observed between the theoretical and experimental frequencies is  $15 \text{ cm}^{-1}$ .

For the GGA functional, the analysis of the basis set effect on the frequencies reveals a significant modification of the theoretical spectrum upon increasing the basis set from 3-21G to 3-21G\*\* which occurs without any significant modification of the geometry. Interestingly, the use of the small basis sets leads to an artifact: the group of absorption bands close to  $1500 \text{ cm}^{-1}$ , which is not present in the experimental spectrum, disappears if the 3-21G\*\* basis set is used.

#### 4. Conclusions

Based on our results, we have chosen the BP86 exchange-correlation functional and the 3-21G\*\* basis set for the next stages of our project. The comparison between the three different methods LDA, GGA, B3LYP allows us to conclude that the most important effect of the introduction of the gradient of the density appears on the non-bonded interaction that becomes more repulsive.

This study shows that the theoretical calculations can reproduce the distance

Table. Calculated and experimental data for the geometry and vibrational parameters

Method	Basis set	O...O distance [Å]	Dihedral angle [degrees]	Characteristic low frequency <sup>a</sup> [cm <sup>-1</sup> ]	Characteristic high frequency <sup>b</sup> [cm <sup>-1</sup> ]
BLYP	3-21G	2.69	-28.7	763	2970
	3-21G**	2.69	-28.7	770	3018
BP86	3-21G	2.67	-28.6	759	2970
	3-21G**	2.67	-28.6	765	3011
B3LYP	3-21G	2.65	-28.5	800	3049
	3-21G**	2.65	-28.4	804	3095
X-ray		2.68	-26.9		
EXP				768	3009

<sup>a</sup>The most intense adsorption band below  $1000 \text{ cm}^{-1}$   
<sup>b</sup>The most intense adsorption band around  $3000 \text{ cm}^{-1}$

$\pm 0.004 \text{ \AA}$  and the frequency within  $15 \text{ cm}^{-1}$ , which is quite satisfactory for the next steps in our project.

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