Absorption spectra of the dibenzofluorene derivative belonging to the KuQuinones family

Igor Levkov, Serhiy Shilin, Tetyana Yegorova*

Department of Chemistry, Taras Shevchenko National University of Kyiv, Volodymyrska Street, 64/13, Kyiv 01601, Ukraine

tve2008@ukr.net

Keywords: *KuQuinones, dibenzofluorene derivative, UV-Vis spectra*, *keto–enol tautomerization, pH.*

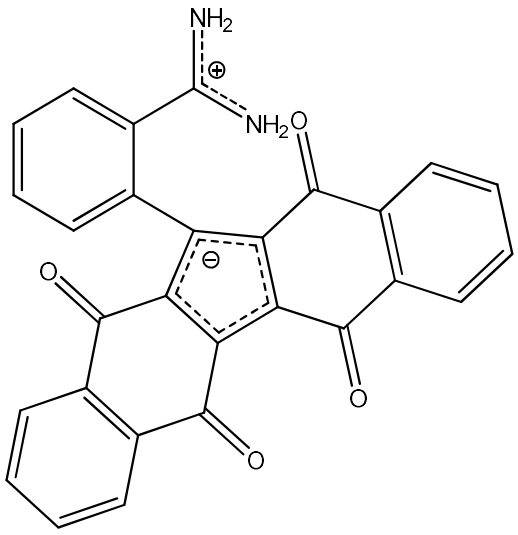
A detailed study of the UV-Vis spectra of the dibenzofluorene derivative belonging to the KuQuinones family was carried out in polar aprotic (CH_3CN), polar protic (CH_3OH), and slightly polar ($CHCl_3$) solvents. The spectral properties of this compound underscore its similarity to other KuQuinones on the one hand, while on the other hand they confirm that it is not a planar but a three-dimensional (3D) structure with separated charges. The existence of keto–enol tautomerization and acid-base equilibrium under different pH conditions has also been investigated.

Introduction

KuQuinones were first described by Galloni et al. in 2012 [1]. Since then, KuQuinone chemistry has been developing rapidly, because the broad and intense UV-Vis spectrum and the low first reduction potential of these compounds make them attractive for photoelectrochemical applications, while their oxidative properties open up prospects for photochemical applications [2–5]. Their use in medicinal chemistry is also promising [2].

We succeeded in synthesizing the only currently known member of the KuQuinones family, compound **1**, which exists in a zwitterionic form, unlike other KuQuinones [6] (**Figure 1**). We have examined its structural, morphological, and optical properties [5].

The present work provides a more detailed investigation of the spectral properties of compound **1** in solutions.



1

Figure 1. The KuQuinone family member we synthesized, which exists in a zwitterionic form.

Metods

The UV-Vis spectra were obtained with a Varian Cary 50 spectrophotometer in CH_3CN, .CH_3OH, $CHCl_3$.

Results and discussion

Other KuQuinones are known to undergo keto–enol tautomerization, which has been studied in detail by spectroscopic methods in various solvents [2, 4]. On the one hand, compound **1** belongs to the KuQuinones class, so it could be expected to exhibit typical KuQuinone properties. On the other hand, compound **1** differs from other KuQuinones in that it is not planar, but instead adopts a three-dimensional (3D) structure with charge separation and a large dipole moment (16.671 D) [5]. To determine how the polarity of the solvent affects keto–enol tautomerization of compound **1**, we conducted a detailed study of its UV-Vis spectra in polar aprotic (CH_3CN), polar protic (CH_3OH), and slightly polar ($CHCl_3$) solvents (**Figure 2**).

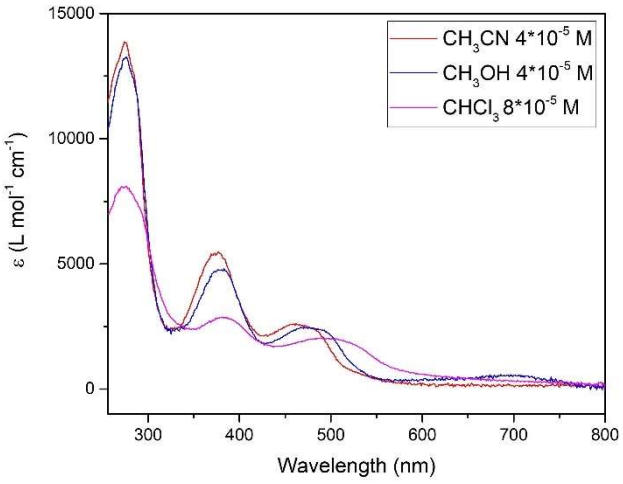


Figure 2. Absorption spectra of compound **1** in different solvents.

The absorption spectra in CH_3CN and CH_3OH are similar to each other and exhibit a characteristic enolate band at around 380 nm, correlating with literature data for other KuQuinones [2, 4]. Unlike other KuQuinones, these spectra contain a strong band at 275 nm. The charge-transfer band can serve as confirmation that compound **1** adopts a charge-separated structural form. The absorption spectrum in $CHCl_3$ differs from the others and indicates the presence of additional forms. A notable feature is the sharp decrease in intensity of the band at 275 nm.

The acid–base equilibrium of compound **1** was investigated via its spectral characteristics at different pH values (**Figure 3**).

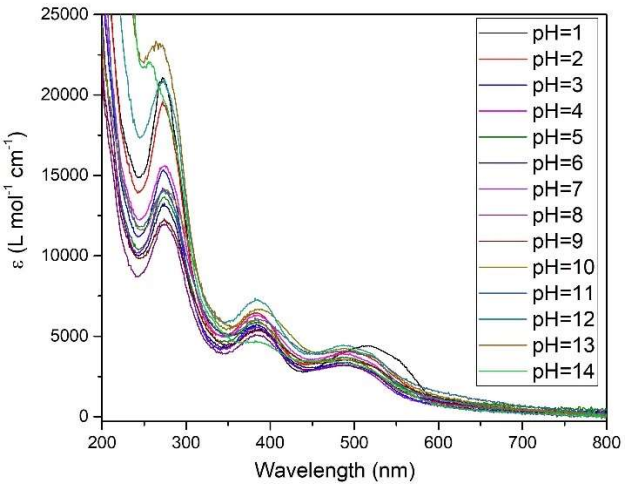


Figure 3. Absorption spectra of compound **1** at various pH values.

The acidity of the medium primarily affects the band at 275 nm. The highest intensity of this band occurs at pH = 13, 14, 12, 1, and 2, while the lowest intensity is observed at pH = 8 and 9. The intensity of the band around 380 nm is highest at pH = 12 and 10, and lowest at pH =

14 and 8. Notably, the spectra at pH = 14 and pH = 1 differ from all others. In the latter case, additional forms are observed (with maxima around 530 and 570 nm).

Conclusions

A detailed investigation of the UV-Vis spectra of the dibenzofluorene derivative belonging to the KuQuinones family was performed in polar aprotic (CH_3CN), polar protic (CH_3OH), and slightly polar ($CHCl_3$) solvents. On one hand, the spectral properties of this compound emphasize its similarity to other KuQuinones. On the other hand, they confirm that it is not planar but rather a three-dimensional (3D) structure with separated charges. The existence of keto–enol tautomerization and acid–base equilibrium at various pH values has also been investigated.

Acknowledgements

The authors thank Dr. Illia Guralskyi for helpful discussions.

References

[1] Coletti A, Lentini S, Conte V, Floris B, Bortolini O, Sforza F, Grepioni F, Galloni P. Unexpected One-Pot Synthesis of Highly Conjugated Pentacyclic Diquinoid Compounds. The Journal of Organic Chemistry 2012;77(16):6873-6879.

[2] Valentini F, Sabuzi F, Forchetta M, Conte V, Galloni P. KuQuinones: a ten years tale of the new pentacyclic quinoid compound. RSC Advances 2023;13(13):9065-9077.

[3] Onuki M, Ota M, Otokozawa S, Kamo S, Tomoshige S, Tsubaki K, Kuramochi K. Dimerizations of 2-bromo-3-methyl-1,4-naphthoquinone and 2-methyl-1,4-naphthoquinone in tetra-n-butylammonium bromide. Tetrahedron 2020;76(6):130899.

[4] Sabuzi F, Lentini S, Sforza F, Pezzola S, Fratelli S, Bortolini O, Floris B, Conte V, Galloni P. KuQuinones Equilibria Assessment for Biomedical Applications. The Journal of Organic Chemistry 2017;82(19):10129-10138.

[5] Haimeur A, Levkov I, Yegorova T, Kysil A, Bugera O, Konovalova I, Shishkina S, Bakkali H, Blanco E, Voitenko Z. Dibenzofluorene derivative for nonlinear optics and solar cells applications. Molecular Crystals and Liquid Crystals 2021;716(1):94-102.

[6] Levkov I, Yegorova T, Kysil A, Vedrenne M, Voitenko Z. Reaction of 1-aminoisoindole with 1,4-naphthoquinone and study of the product by spectroscopic methods. French-Ukrainian Journal of Chemistry 2018;6(2):27-31.