

P29 A Theoretical Study of the Nature of 3-Amidino-2-bromobenzanthrone Abnormally High Stokes Shift

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Modern fluorescent technology has a large practical significance in solving many problems of science, medicine and industry. In this regard, intensive investigations have been developed for obtaining new fluorescent materials. Long-wave shift of the fluorescence spectra maximum, relative to the absorption spectra maximum (Stokes shift), is typical in the range of 50–70 nm [1]. 3-Amidino-2-bromobenzanthrone has an abnormally high Stokes shift, which is 214 nm (solvent – ethanol).

The aim of this work is a theoretical study of the nature of this phenomenon using a quantum-chemical PM6 method [2]. The calculations of the geometric and electronic structure of this compound were carried out considering the presence of a solvent.

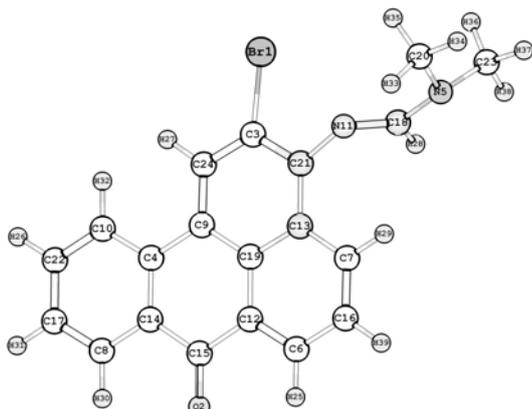


Figure 1. Optimized PM6 S_0 ground state structure and atom labelling of 3-Amidino-2-bromobenzanthrone

A theoretical model based on the Jablonski diagram was used for the absorption and fluorescence spectra maximum calculations. This model consists of 4 stages of calculations:

1. CISD calculation of the equilibrium geometry of the S_0 electronic state with full geometry relaxation.
2. Single point CISD calculation of the S_1 energy at the S_0 geometry to compute the corresponding $S_0 \rightarrow S_1$ absorption transition energy.
3. CISD calculation of the equilibrium geometry of the S_1 electronic state, with full geometry relaxation.
4. Single point CISD calculation of the S_0 energy at the S_1 geometry to compute the energy of the corresponding vertical $S_0 \rightarrow S_1$ emission transition [3].

To account for the solvent effect, Conductor-like Solvent Model (COSMO) was used. All the calculations were carried out by the PM6 method using the MOPAC2009 program. Calculations of the molecular geometry at the S_1 excited states

were carried out including configuration interaction (C.I.) using the microstate formalism. As can be seen from Table 1, the number of C.I., which reproduces the experimental data with the best accuracy, is 6. The obtained value of the Stokes shift of the fluorescence spectra maximum corresponds to experimental data.

TABLE 1
ABSORPTION AND FLUORESCENCE MAXIMA

	Absorption max., nm	Fluorescence max., nm
Experimental	445	659
C.I.=2	365	573
C.I.=5	417	577
C.I.=6	437	679
C.I.=7	466	720

It was found that in the S_1 excited state, there is a significant redistribution of the electron density, accompanied by an increase of the dipole moment by approximately 2 times: from 9.2 to 18.5 D.

This is accompanied by a flattening of the geometric structure of the molecule. Torsion angle C(13)-C(21)-N(11)-C(18) decreases from 69.74° to 13.17°.

In the excited S_1 state the bond orders, around which the rotation of the substituent occurs, are changed. C(21)-N(11) bond order changes from 1.118 to 1.394, N(11)-C(18) from 1.587 to 1.252 and C(18)-N(5) from 1.231 to 1.563.

All of these changes are associated with the process of relaxation in the excited state S_1 , the energy of which determines the Stokes shift and is equal to 14.52 kcal/mol.

The study of geometric and electronic properties of the molecule of the compound in the ground and excited states, as well as consideration of the relaxation mechanisms, allowed explaining the abnormally high Stokes shift of the fluorescence maximum.

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