

Theoretical Studies on Cycloaddition Reactions OF 1,4-Benzoquinones

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Abstract - Quinones constitute an important class of organic compounds that are involved in many biological processes and have considerable synthetic and industrial applications. A series of heteroacyl- and aroyl-1,4-benzoquinones have been synthesized by employing a facile three step synthetic procedure from readily available precursors. The new quinones have been characterized spectroscopically. The feasibility and mechanism of [2+2] and [4+2]-photochemical cycloaddition reactions of synthesized quinones would be explored in detail by quantum chemical calculations. The calculations were performed utilizing the AM1, PM3 hamiltonians in Gaussian 03 suite of quantum chemical programs. The regioselectivity of the cycloadducts and the transition states for the feasible cycloadditions would be explored.

Keywords: Quinones; semiempirical calculations; AM1 and PM3 hamiltonians.

I. INTRODUCTION

The chemistry of quinones and quinonoid-compounds has attracted enormous interest owing to their unique structure; properties and wide range of applications.¹ 1,4-benzoquinones are a class of quinones found in nature as subunits in many natural products.² In addition, benzoquinones are useful in organic synthesis as oxidizing and dehydrogenation agents³⁻⁴ and as reactive dienophiles in various cycloaddition reactions.⁵⁻⁶ The electron carrying potential is another fascinating aspect of benzoquinones. The photochemical cycloaddition reactions of benzoquinones yield interesting adducts which can act as precursors to potential antitumor drugs.⁷⁻⁸ Various aspects of [2+2] and [4+2]-photochemical cycloaddition reactions of these quinones have been explored using AM1 and PM3 level quantum chemical calculations.⁹⁻¹⁰

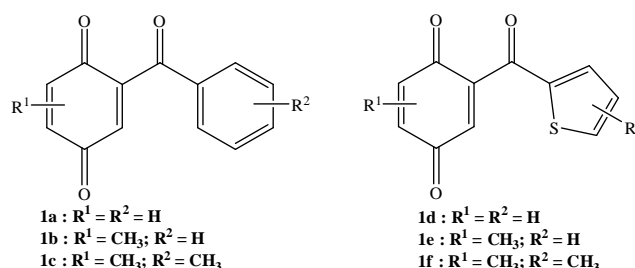
II. COMPUTATIONAL DETAILS

All the calculations were carried out using Gaussian 03 suite of quantum chemical programs. The geometry of all the reactants, products and intermediates will be optimized at AM1 level. The single point energy of the minimized geometry will be estimated using PM3 hamiltonian.

[2+2]- & [4+2]-Photochemical Cycloaddition Reactions : A semi-empirical study

Photochemical [2+2]- and [4+2]-cycloaddition reactions of quinones present very useful synthetic methods for

preparing four membered and six membered rings respectively. A series of heteroacyl- and aroyl-1,4-benzoquinones have been selected for the present study (Figure 1).

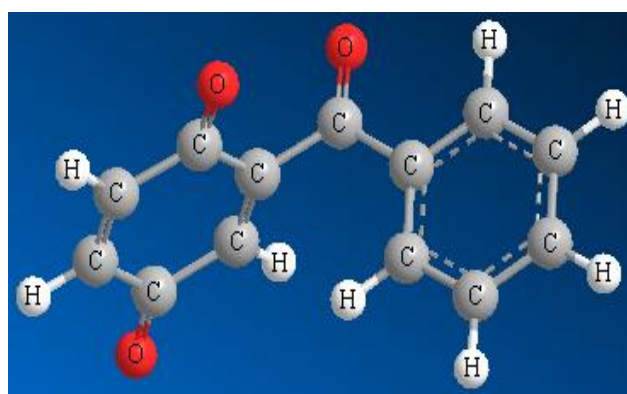


The energy and geometry of all the six quinone derivatives have been calculated at AM1 level. The results are presented in Table 1 below.

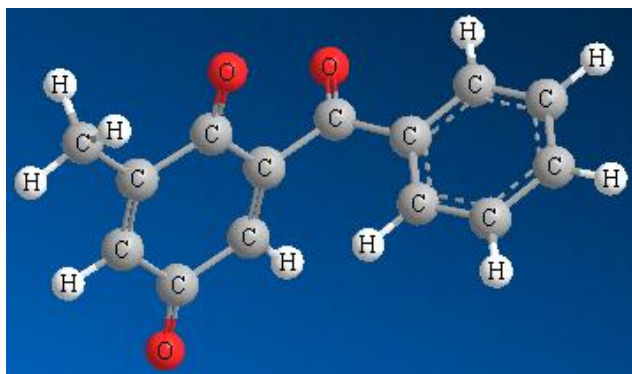
Table 1 : Energy of Quinones calculated at AM1 level

Quinone	Energy in Kcal/mol
1a	-23.08
1b	-30.84
1c	-38.75
1d	-16.93
1e	-26.26
1f	-34.16

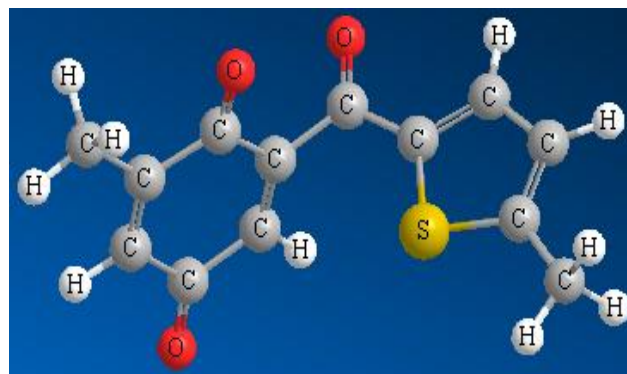
The optimized geometries of all the quinones are shown below.



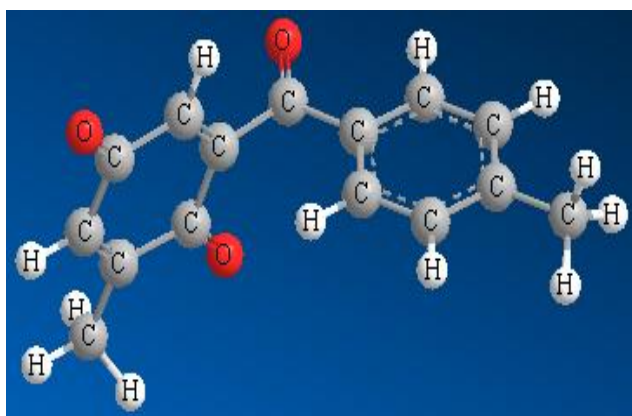
1a



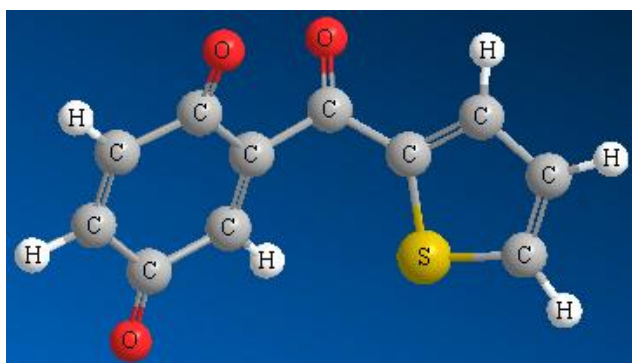
1b



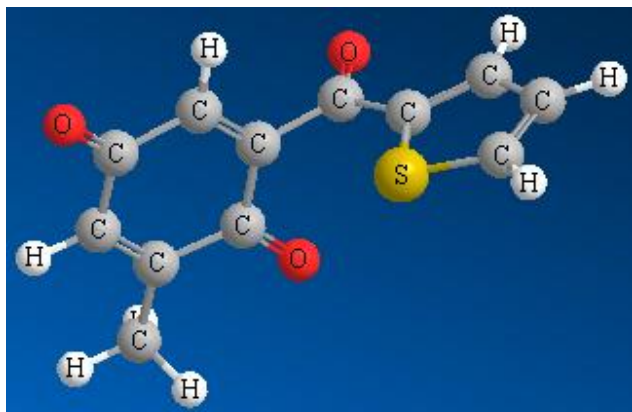
1f



1c



1d



1e

The [2+2]-/ [4+2]-photocycloaddition reactions of quinones **1a-f** were explored in detail. A range of dienes and dipolarophiles were utilized to perform the theoretical investigations on the above photocycloaddition reactions. The most stable cycloadduct was ascertained based on the heat of formation values. The cycloaddition route to the most stable cycloadduct is explored by transition state studies.

III. CONCLUSIONS

The geometry and energy of a series of quinones were estimated by AM1 level in Gaussian03 suite of quantum chemical program. The results of these calculations will be utilized to estimate the relatively stable cycloadduct and to further explore the transition state of the most feasible cycloaddition.

IV. ACKNOWLEDGEMENTS

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