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Use of Norbornadiene in Solar Energy Storage: Theoretical Study of a Copper(I) Photosensitizer for the Norbornadiene−Quadricyclane Transformation

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Density functional calculations with the hybrid B3LYP functional have been used to study the ground state of norbornadiene bound to the photosensitizer [Cu(8-oxoquinolinato)]. The main bonding interaction between the ligand and the metal is π back-donation, metal to ligand, which reduces the $\pi-\pi^*$ band gap in norbornadiene. CIS calculations performed on free norbornadiene and on the system where norbornadiene interacts with the photosensitizer have shown that the photosensitizer reduces the excitation energy to promote the system to the first excited singlet state. In terms of wavelength, this difference implies that light with λ almost 100 nm longer can be used to photoactivate the norbornadiene with respect to free norbornadiene.

Introduction

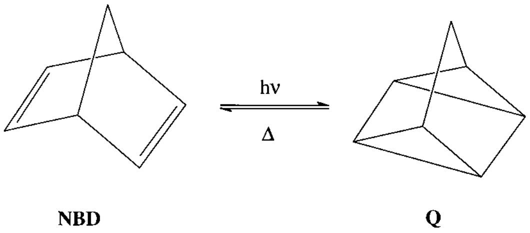
The photochemical conversion of norbornadiene (NBD) to quadricyclane (Q) is an extensively studied reaction for its potential in the context of light-energy storage.[1]

As it is shown in Scheme 1, NBD can be photochemically converted to Q, which can release thermal energy in the reverse catalyzed process. The conversion between the two species is accompanied by the formation and cleavage of two C−C bonds: π bonds in NBD and σ bonds in Q, which, however, is less stable than NBD being a strained molecule.

A challenge presented by the reaction shown in Scheme 1 is that NBD does not absorb above 250 nm:[2] a suitable sensitizer[3] is therefore necessary in order to obtain the isomerization of NBD to Q using visible light. Recently, several copper(I) photosensitizer have been proved to be active in assisting the NBD → Q conversion, the best results being provided by [Cu(2-methyl-8-oxoquinolinato)].[4]

To understand the role played by the photosensitizer in assisting the isomerization of NBD to Q, we performed ab initio calculations on the system [Cu(8-oxoquinolinato)(NBD)], considered as a model of the experimental system [Cu_2(2-methyl-8-oxoquinolinato)$_2$(μ-NBD)],[4] as well as on the free NBD molecule. The photochemical conversion of NBD to Q, as well as the reverse reaction, has been theoretically investigated by several authors,[5] while to our knowledge no theoretical investigations have been reported on the system studied in this work.

Scheme 1



Computational Details

Density functional theory (DFT), which has been found to be a very cost-effective method to study transition metal systems,[6] has been used for the determination of equilibrium geometries of the ground state of the investigated systems. The B3LYP hybrid exchange-correlation functional was used for all the calculations. This is based on Becke's three-parameter functional[7] including a Hartree−Fock exchange contribution with a nonlocal correction for the exchange potential proposed by Becke in 1988[8] together with the local correction for the correlation energy according to Lee et al.[9]

It has been demonstrated that the B3LYP functional gives accurate optimized geometries for a wide range of molecules.[10]

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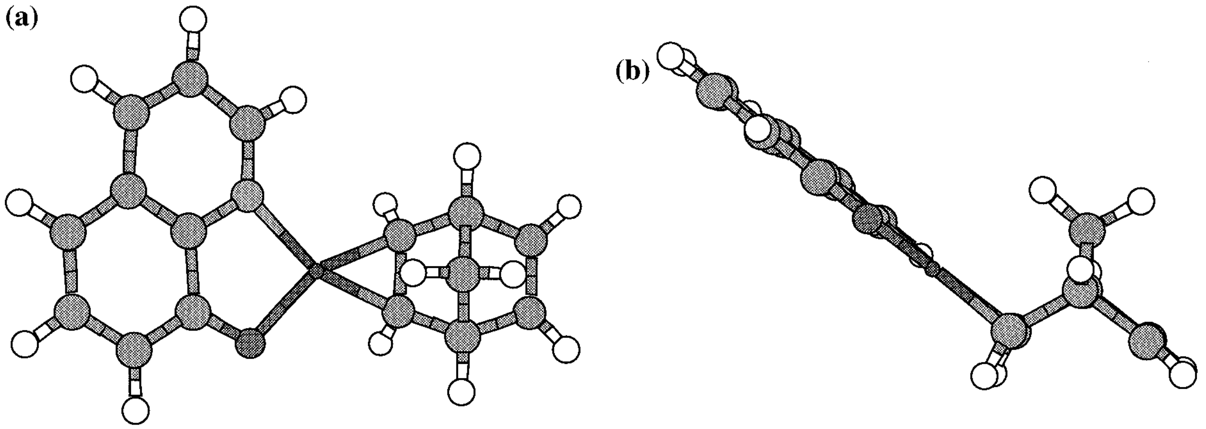


Figure 1. Optimized structure of [Cu(8-oxoquinolinato)(NBD)]: (a) top view; (b) side view.

The system [Cu(8-oxoquinolinato)(NBD)] has been considered as a model of the experimental system [Cu_2(2-methyl-8-oxoquinolinato)$_2$-(μ-NBD)].[4]

In the model system we have replaced the methyl group with a hydrogen and we have considered only one molecule of sensitizer interacting with NBD, this choice being suggested by the experimental synthesis[4] of the photoactive monomeric species [Cu(2-methyl-8-oxoquinolinato)(NBN)] [NBN ≡ norbornene].

The excited states of free norbornadiene and norbornadiene interacting with the copper(I) photosensitizer have been computed with the single-excitation configuration interaction (CIS) method.[11]

It is well-known that CIS suffers from several deficiencies,[12] in particular the neglect of dynamic correlation which implies transition energies often in error by more than 1 eV. This has been confirmed by the study of the electronic spectrum of norbornadiene.[13]

However, this problem should not be relevant in a comparative study of NBD and [Cu(8-oxoquinolinato)(NBD)].

The basis set employed for the calculations performed on the ground state of the investigated species is based on the Wachters−Hay set[14] for the copper and on the 6-31G* set[15] for all the other atoms. For the CIS calculations, diffuse functions[16] have been added to the basis set in order to treat in an adequate way the Rydberg states, while polarization functions have been removed. Only the spherical harmonic components of the basis sets are used.

All the calculations have been performed using the Gaussian 94[17] program package and were done on a cluster of IBM RISC/6000 workstations and on an SGI Origin2000 computer.

Results and Discussion

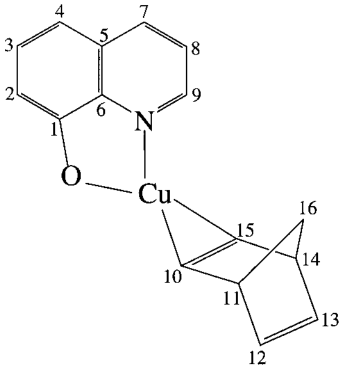
The optimized structure of [Cu(8-oxoquinolinato)(NBD)] is shown in Figure 1 and the main geometric parameters are reported in Table 1. The numbering of the atoms is shown in Chart 1.

Table 1. Pertinent Geometrical Parameters of the Optimized Structure of [Cu(8-oxoquinolinato)(NBD)], Compared with the Experimental Geometry of [Cu_2(2-methyl-8-oxoquinolinato)$_2$(μ-NBD)][a]

parameter	optimized	experimental
r(Cu−O)	1.926	1.941
r(Cu−N)	1.989	1.992
r(Cu−C_{10})	1.956	1.993
r(Cu−C_{15})	1.954	2.015
r(O−C_1)	1.301	1.328
r(N−C_6)	1.368	1.376
r(N−C_9)	1.327	1.325
r(C_{10}−C_{15})	1.409	1.396
$\angle C_{10}CuC_{15}$	42.2	40.8
$\angle NCuC_{15}$	117.0	124.1
$\angle NCuC_{10}$	159.2	164.8
$\angle OCuC_{15}$	156.7	150.2
$\angle OCuC_{10}$	114.5	109.5
$\angle OCuN$	86.3	85.8
$\angle CuOC_1$	110.7	111.1
$\angle CuNC_9$	132.1	132.1
$\angle CuNC_6$	108.3	108.2
$\angle C_6NC_9$	119.6	119.6
$\angle CuC_{10}C_{11}$	115.8	114.0
$\angle CuC_{10}C_{15}$	68.8	70.5
$\angle CuC_{15}C_{10}$	69.0	68.8
$\angle CuC_{15}C_{14}$	115.9	115.7

[a] For the numbering of the atoms, see Chart 1. Bond Lengths in Å, angles in deg.

Chart 1



From Table 1, where we have also reported the geometrical parameters of the experimental system [Cu_2(2-methyl-8-oxoquinolinato)$_2$(μ-NBD)],[4] we can see that the choice of the model system is correct, in light of the satisfactory agreement between optimized and experimental parameters. Among the geometrical

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Table 2. Atomic Charges (Electronic Units) Obtained by Accumulating the Mulliken Populations for the Complex and the Free Fragments[a]

atom	[Cu(8-oxoquinolinato)(NBD)]	[Cu(8-oxoquinolinato)]	norbornadiene
Cu	+0.96	+0.70	
O	−0.72	−0.70	
N	−0.63	−0.72	
C_1	+0.39	+0.30	
C_2	−0.22	−0.16	
C_3	−0.12	−0.12	
C_4	−0.23	−0.19	
C_5	+0.18	+0.12	
C_6	+0.16	+0.20	
C_7	−0.15	−0.13	
C_8	−0.16	−0.14	
C_9	+0.03	+0.06	
C_{10}	−0.30		−0.17
C_{11}	−0.13		−0.27
C_{12}	−0.10		−0.17
C_{13}	−0.10		−0.17
C_{14}	−0.13		−0.27
C_{15}	−0.35		−0.17
C_{16}	−0.30		−0.27

[a] For the numbering of the atoms, see Chart 1.

Table 3. Total Energies (hartree) of the Ground State, Orbital Energies (eV) of the HOMO and LUMO, and Relative Energies (eV) of the First Three Excited Singlet States for [Cu(8-oxoquinolinato)(NBD)] and NBD[a]

	[Cu(8-oxoquinolinato)(NBD)]	NBD
E_{GS}[b]	−2388.561082	−271.477282
ϵ_{HOMO}	−4.76	−5.90
ϵ_{LUMO}	−1.40	0.01
$\Delta E_{HOMO-LUMO}$	3.36	5.91
S_1	4.15 (299)	5.84 (212)
S_2	4.97 (249)	6.59 (188)
S_3	5.28 (235)	6.90 (180)

[a] Values in parentheses are in nm. [b] The total energy of [Cu(8-oxoquinolinato)] is −2116.982244 hartree.

parameters one notices that $r(C_{10}-C_{15})$ is equal to 1.409 Å. This value should be compared with the corresponding value optimized for free NBD which is 1.343 Å. We can say, therefore, that the C=C bond which interacts with the copper sensitizer is strongly elongated with respect to the C=C bond of the free molecule. The analysis of the electronic structure of the investigated system suggests that the main interaction between NBD and the copper sensitizer is π back-donation from copper to the π* antibonding orbital of NBD in a Dewar−Chatt−Duncanson manner.[18]

This is confirmed also by the atomic charges obtained by accumulating the Mulliken populations reported in Table 2 for the whole complex and the separated NBD and [Cu(8-oxoquinolinato] fragments. We can observe from Table 2 that upon coordination the electron density on copper decreases by 0.26 electrons, while those on C_{10} and C_{15} increase by 0.13 and 0.18 electrons. The only other significant changes are on the densities of C_{11} and C_{14} which both decrease by 0.14 electrons. The predominant effect of π back-donation from metal to ligand is also confirmed by the total charge of NBD which is −0.29 electron in the complex.

The binding energy between NBD and [Cu(8-oxoquinolinato)] is computed to be 63.7 kcal mol^{-1} at B3LYP level, as seen from the total energies reported in Table 3. Table 3 shows also the energy of the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO, respectively) of NBD and [Cu(8-oxoquinolinato)(NBD)]. These orbitals, both in the complex and in free NBD, are C=C π bonding and π* antibonding orbitals, respectively, and they are clearly involved in the electronic transition from the S_0 ground state to the S_1 first excited singlet state. The gap between these orbitals, which is 5.91 eV in free NBD, is decreased to 3.36 eV in the complex, mainly due to the π back-donation metal to ligand. A photoexcitation of the complex should require, therefore, less energy with respect to NBD. This is supported by the CIS calculations, whose results relative to the first three excited singlet states are reported in Table 3, in which it is shown that the first excited singlet state is 5.84 eV above the ground state in NBD and 4.15 eV above the ground state in the complex. It has been demonstrated[13] that for free NBD this value is overestimated due to the known deficiencies of the CIS treatment.[12]

A comparable, or even larger, error is expected for the complex. We can say therefore that the first excited singlet state of the complex should be more than 300 nm above the ground state and the complex should absorb near the visible.

Conclusions

This study at ab initio level of NBD interacting with the photosensitizer [Cu(8-oxoquinolinato)] has shown that the photosensitizer reduces the HOMO−LUMO gap of NBD through the donation of electron density from the metal to π antibonding orbitals of the ligand. The decrease in the HOMO−LUMO gap implies a lowering of the energy of the first excited singlet state of NBD with respect to the ground state. This decrease suggests that in the presence of the photosensitizer NBD is able to absorb light of longer wavelengths and could be used to store visible light.

We are currently exploring other variations of the metal and the ligands coordinated to the metal in order to improve the system and to lower the excitation energy further. This will be the subject of future work.

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