Theoretical Modeling of Alkynes

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ABSTRACT: In this work we report a semiempirical investigation of the first excited states and of the spectroscopic properties of a series of substituted alkynes. The analysis of the calculated and experimental absorption spectra and theoretical emission spectra resulting from semiempirical/configuration interaction calculations gives us some insight as to how chemical modifications of these molecules could affect the nonlinear optical properties of alkynes. © 2003 Wiley Periodicals, Inc. Int J Quantum Chem 95: 137–143, 2003

Key words: alkyne; experimental absorption spectra; semiempirical/CI method (AM1/CI); theoretical absorption spectra (INDO/S-CI); theoretical emission spectra (DNdM-INDO/S-CI)

Introduction

The preparation of carbon-rich compounds containing extended π-systems has attracted considerable attention in many areas of knowledge, especially in materials science, as they have shown interesting photoluminescence, conductivity, and nonlinear optical properties [1–3]. Structural modifications of these compounds that involve altering, for example, the nature of the substituent(s), size of the π-conjugation, etc., are essential to induce the desired properties [highest occupied molecular orbital (HOMO) lowest unoccupied molecular orbital (LUMO) gap, solubility, etc.].

Alkynes are valuable synthetic feedstocks in organic and organometallic chemistry. Their syntheses have been the subject of intensive investigations, because of the interest in introducing an ethynyl group into organic structures, which leads to an increase in the organic chain size. Important classical methods for the synthesis of these compounds include the halogenation/dehydrogenation of ketone or olefin derivatives, displacement of halogens with cupric acetylides (Castro reaction), use of Vilsmeier reagent with acetophenones, Sonogashira–Heck coupling, etc. [4].

In this work we have examined the changes in the spectroscopic properties of different alkynes by
theoretical and experimental methods. The alkynes studied have been grouped according to the nature of the substituent on the benzene rings (see Fig. 1), as follows: alkynes containing acceptor groups (I, II, III), a donor group (IV), an extended conjugated chain (V) and an –OH-containing group that can interact via a hydrogen bond (VI) [5, 6].

**Methodology**

All reactions were carried out under dry Ar using standard Schlenk techniques. Solvents were dried and distilled prior to use. Ultraviolet (UV)-vis spectra were obtained from CH₂Cl₂ and hexane solutions, in a 1-cm-path–length quartz cuvette, on an HP8452 spectrometer. Compounds I–VI were prepared and characterized as previously described [7, 8].

The electronic structures of compounds I–VI, shown in Figure 1, were modeled. The geometries of their neutral ground and excited states were fully optimized using the well-known AM1 method/ (MOPAC package) [9, 10]. The convergence criterion for optimization was modified from standard to a maximum step size of 0.005 to ensure good-quality geometries. The simulated absorption spectra were obtained using the INDO-S/Ci (intermediate neglect of differential overlap–spectroscopy/configuration interaction) package [11–16] with geometries from AM1 calculations. The ZINDO calculations were carried out with parameters chosen to give the best description of the UV-visible optical transitions [17–22] and using on average 200 configurations including singlet and doublet states. This level of approximation was used within the restricted Hartree–Fock approaches to determine the ground state.

The emission (fluorescence and phosphorescence) spectra were obtained by using the Del Nero and de Melo modification of the ZINDO package [23] and considering the geometry of the first excited states (singlet and triplet) in the description of the emission process. (To this new approach we gave the name of DNdM-INDO/S-Ci calculation.) In this calculation, we have taken into account the first eight UMOs (unoccupied molecular orbitals) through the last eight OMOs (occupied molecular orbitals) and adopted the Mattaga–Nishimoto γ.

**Results and Discussion**

The UV-visible spectra of compounds I–VI in CH₂Cl₂ (Fig. 2) and hexane (Fig. 3) were very similar. In all cases a strong absorption ($ε \approx 25000$ L mol⁻¹ cm⁻¹) was observed in the 300–400-nm range. Taking alkyne IV as the reference, observed in all spectra was a red shift of this band that was associated with the increasing strength of the elec-
tron-withdrawing group (R) in the phenyl para position: IV (R = OCH₃, electron-donor group) < II (R = CN) < III (R = CHO) < I (R = NO₂), strongest electron-withdrawing group). An increase in the π-bridge length (alkyne V) led to an even larger red shift of this band in comparison with alkyne I.

To obtain the theoretical absorption spectra of these alkynes we first had to determine their corresponding optimized geometries under ground- and excited-state conditions. The molecules correspond to the linear conformation in all cases and the most stable structures were found to be essentially planar. In Figure 4 can be seen the atom index for alkynes calculated used in Table I and Table II for the corresponding bond length. The corresponding dipole moments for structures I, II, III, IV, V, and VI, calculated using the AM1 technique, were found to be 6.37, 3.92, 3.34, 1.31, 6.63, and 6.83 Debye, respectively. Table IV shows the calculated dipole moments for the ground and excited states of the alkynes shown in Figure 1.

To examine the differences in the experimental and theoretical optical properties of these molecules, the INDO/S-CI absorption spectra were calculated for the corresponding semiempirical geometry. For the simulation of the fluorescence and phosphorescence spectra (Figs. 6 and 7, respectively) we used the DNdM-INDO/S-CI methodology for the AM1/CI geometry, and the principal transitions for the optical spectra of these molecules are listed in Tables I and II. We described each of the principal transitions by a suitably weighted Gaussian function normalized to the values of the corresponding oscillator strengths. The resulting spectra are in good agreement with the experimental ones shown in Figures 2, 3, and 5. It can be observed that the experimental spectra of the different solutions are red-shifted relative to the corresponding theoretical estimates, probably because of the strong interaction of the alkynes with the solvents used.

Figure 5 (I) shows three main absorption bands centered at 330 nm, 260 nm, and 195 nm. The first band, whose estimated oscillator strength (o.s.) is 1.15, is essentially a HOMO-to-LUMO transition, the second band is a HOMO to LUMO +1 transition, and the last one is composed of two transitions involving lower occupied and unoccupied orbitals, as shown in Table I.

The calculated spectrum of compound II [Figure 5(II)] exhibits a band at ~300 nm with an o.s. equal...
to 1.58, which corresponds to a pure $|H\rightarrow L>$ transition, and bands between 205 nm and 170 nm, which are composed of a mixing of transitions from $|H\rightarrow 4>$ to $|L+6>$ orbitals (Table I).

The spectra of alkynes III and IV [Figure 5 (III) and (IV)] are similar, with four main bands, $|H\rightarrow L>$ [from the highest occupied (H) to the lowest unoccupied (L) molecular orbital], $|H\rightarrow L+1>$ and $|H\rightarrow 4\rightarrow L+1>$ being the most important transitions (Tables I and II).

The experimental and calculated spectra of alkynes V and VI shown in Figures 2, 3, and 5, respectively, show good agreement, except for the high energy region (over 6 eV), because the measurements in this region could not be carried out by this equipment. The results of the analyses of both spectra are also presented in Table III.

The dipole moments of the ground and excited states of alkynes I–VI are presented in Table IV. The
emission spectra. A reduction in the band gap is

explanations seem to be relevant for the absorption and

contributions, because a different number of tran-

sitions come from the analysis of the CI

Stokes shift for the alkynes family, and a possible

explanation comes from the analysis of the CI

resonance spectra.

larger number of LUMO levels than does the fluo-

rescence spectra. It can be

part of the low energy band (in the 180–200-nm

region). Other transitions also contribute to the flu-

phorescence spectrum (Fig. 7). For all molecules,

the UV-visible spectrum (Fig. 5) vanish in the phos-

rescence spectra. Only in the case of

alkyne I does the band centered at about 265 nm in

the respective absorption spectra. Only in the case of

alkyne I does the band centered at about 265 nm in

the UV-visible spectrum (Fig. 5) vanish in the phos-

phorescence spectrum (Fig. 7). For all molecules,

the |L→H> transition accounts for a significant

part of the low energy band (in the 180–200-nm

region). Other transitions also contribute to the flu-

orescence and phosphorescence spectra. It can be

said that the phosphorescence spectra involve a

larger number of LUMO levels than does the fluo-

rescence spectra.

In general terms, the results indicate a large

Stokes shift for the alkynes family, and a possible

explanation comes from the analysis of the CI

contributions, because a different number of trans-

itions seem to be relevant for the absorption and

emission spectra. A reduction in the band gap is

predicted on going from the absorption to the

values found for the ground and singlet-excited

states are very close, and those calculated for the

triplet-excited states are about twice as large, except

for the case of alkyne VI. The anomalous behavior

predicted for the singlet- and triplet-excited state
dipoles of alkyne VI can be interpreted in terms of

their different geometries.

Finally, in the fluorescence and phosphorescence

spectra of alkynes I–VI (Figs. 6 and 7, respectively)

the most important line, in the 320–400-nm region

corresponds essentially to the |L→H> transition

for fluorescence and phosphorescence, respectively.

These bands show a red shift compared with the

respective absorption spectra. Only in the case of

alkyne I does the band centered at about 265 nm in

the UV-visible spectrum (Fig. 5) vanish in the phos-

phorescence spectrum (Fig. 7). For all molecules,

the |L+2→H> transition accounts for a significant

part of the low energy band (in the 180–200-nm

region). Other transitions also contribute to the flu-

orescence and phosphorescence spectra. It can be

said that the phosphorescence spectra involve a

larger number of LUMO levels than does the fluo-

rescence spectra.

In general terms, the results indicate a large

Stokes shift for the alkynes family, and a possible

explanation comes from the analysis of the CI

contributions, because a different number of trans-

itions seem to be relevant for the absorption and

emission spectra. A reduction in the band gap is

predicted on going from the absorption to the
The analysis of the main transitions presented in the calculated spectra reveals that the $|\text{H} \rightarrow \text{L}>, |\text{H} \rightarrow \text{L}+1>,$ and $|\text{H} \rightarrow \text{L}+1>$ transitions are dominant for this class of alkynes.

**Summary**

Alkynes are strategically important molecules in the design of new materials, and therefore it is important to understand their physical and electronic properties. In this work we have used the AM1, INDO/S, and DNdM-INDO/S (including electronic-correlation CI) methodologies to investi-

gate the first singlet- and triplet-excited states of a series of alkynes that differ with respect to their substituents and extent of their unsaturation.

From the above results it seems possible to improve the nonlinear optical activity of alkynes by suitable chemical modifications that combine an increase in the unsaturation and a tuning of the donor/acceptor properties of the substituents, but further theoretical and experimental investigations are needed to test this hypothesis.

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**References**


**TABLE IV**

Dipole moment (in Debye) for neutral and excited (singlet and triplet) states of the alkynes presented in Figure 1.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>G.S.</th>
<th>S.E.S.</th>
<th>T.E.S.</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>6.37</td>
<td>6.78</td>
<td>15.83</td>
</tr>
<tr>
<td>II</td>
<td>3.92</td>
<td>3.77</td>
<td>8.88</td>
</tr>
<tr>
<td>III</td>
<td>3.34</td>
<td>3.54</td>
<td>9.06</td>
</tr>
<tr>
<td>IV</td>
<td>1.31</td>
<td>1.93</td>
<td>4.22</td>
</tr>
<tr>
<td>V</td>
<td>6.63</td>
<td>7.97</td>
<td>15.80</td>
</tr>
<tr>
<td>VI</td>
<td>8.83</td>
<td>12.18</td>
<td>11.27</td>
</tr>
</tbody>
</table>

Abbreviations: G.S., ground state; S.E.S., singlet-excited state; T.E.S., triplet-excited state.