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

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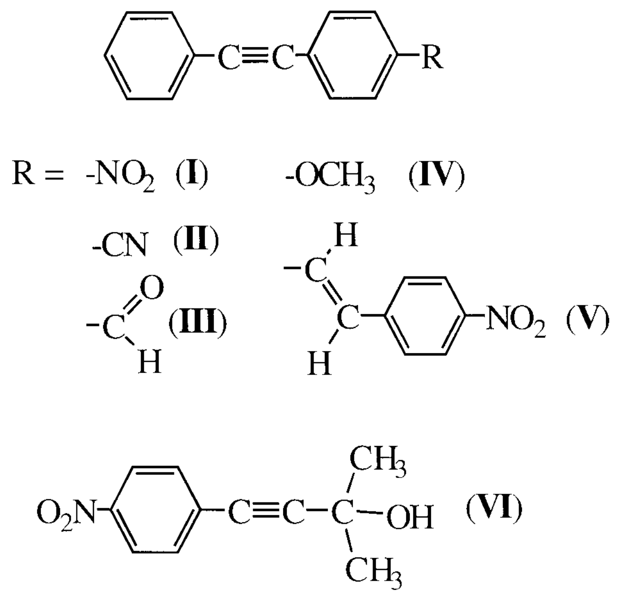

FIGURE 1. Schematic structures of the alkynes studied.

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 CH_2Cl_2 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 CH_2Cl_2 (Fig. 2) and hexane (Fig. 3) were very similar. In all cases a strong absorption ($\epsilon \cong 25000$ 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-

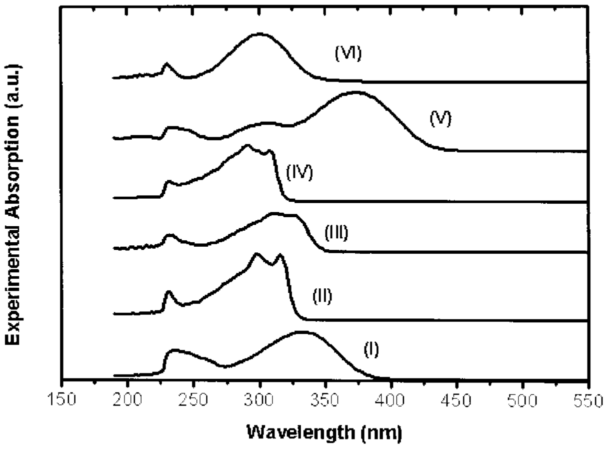

FIGURE 2. Experimental UV-vis absorption spectra of alkynes I–VI (Fig. 1) in CH_2Cl_2 (see methodology).

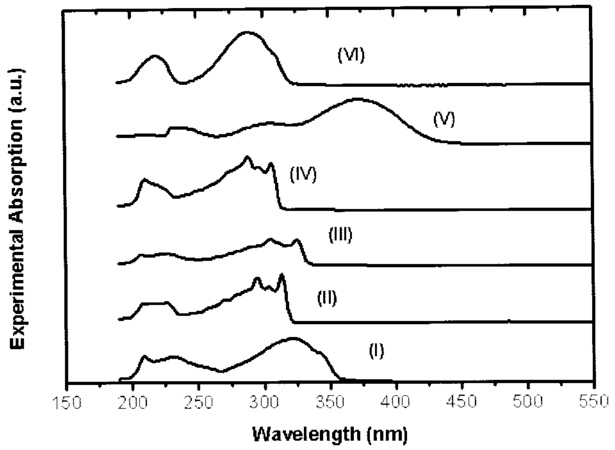

FIGURE 3. Experimental UV-vis absorption spectra of alkynes I–VI (Fig. 1) in hexane (see methodology).

tron-withdrawing group (R) in the phenyl *para* position: IV (R = OCH_3, electron-donor group) < II (R = CN) < III (R = CHO) < I (R = NO_2), 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- (first singlet and triplet configurations) 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

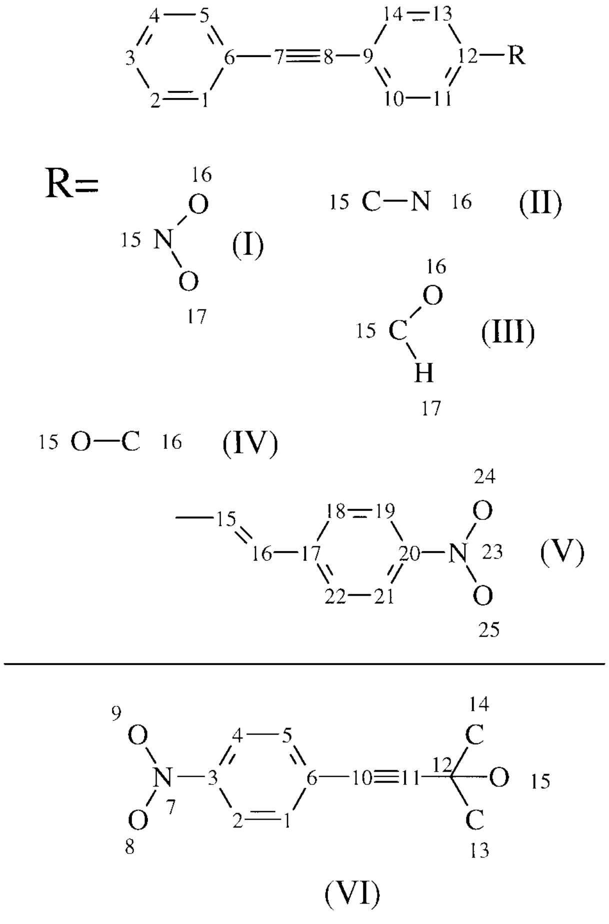

FIGURE 4. Atomic index of the alkynes calculated using semiempirical methodology.

TABLE I

Bond length (Å) of the alkyne molecules described in Figure 4.

Atom no.	Bond length (Å)				
	I	II	III	IV	V
2-1	1.392	1.392	1.392	1.392	1.392
3-2	1.395	1.395	1.395	1.394	1.395
4-3	1.395	1.395	1.395	1.394	1.395
5-4	1.392	1.392	1.392	1.392	1.392
6-1	1.405	1.405	1.405	1.405	1.405
7-6	1.406	1.406	1.406	1.405	1.405
8-7	1.200	1.200	1.200	1.200	1.200
9-8	1.404	1.405	1.405	1.404	1.404
10-9	1.406	1.405	1.405	1.407	1.405
11-10	1.390	1.391	1.391	1.387	1.389
12-11	1.404	1.402	1.400	1.408	1.406
13-12	1.404	1.402	1.400	1.400	1.402
14-13	1.390	1.391	1.390	1.392	1.391
15-12	1.485	1.421	1.471	1.380	1.451
—	—	—	—	—	—
16-15	1.202	1.163	1.233	1.423	1.344
17-15	1.202	—	1.114	—	—
—	—	—	—	—	—
17-16	—	—	—	—	1.452
18-17	—	—	—	—	1.403
19-18	—	—	—	—	1.391
20-19	—	—	—	—	1.403
21-20	—	—	—	—	1.405
22-21	—	—	—	—	1.389
23-20	—	—	—	—	1.484
24-23	—	—	—	—	1.202
25-23	—	—	—	—	1.202

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 $|H-4>$ 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 $|H-4\rightarrow L+1>$ 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

TABLE II

Bond length (Å) of the alkyne VI described in Figure 4.

Atom no. VI	Bond length (Å)
2-1	1.404
3-2	1.390
4-3	1.405
5-4	1.405
6-5	1.390
7-1	1.486
8-7	1.202
9-7	1.202
10-4	1.406
11-10	1.197
12-11	1.451
13-12	1.530
14-12	1.529
15-12	1.434

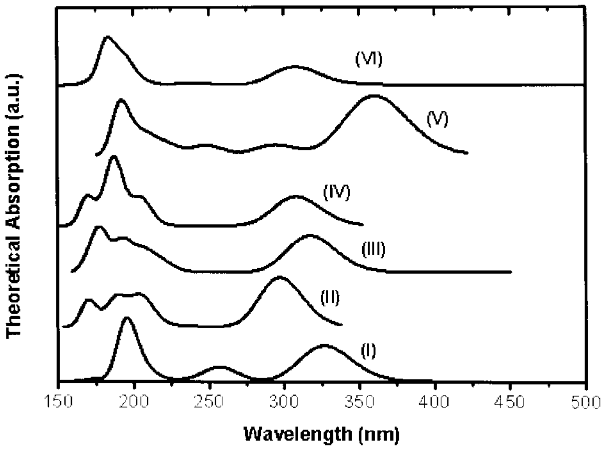

FIGURE 5. Theoretical UV-vis absorption spectra of alkynes I–VI (Fig. 1) calculated for optimized geometries by INDO/S-CI using the AM1 method.

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 phosphorescence 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 fluorescence and phosphorescence spectra. It can be said that the phosphorescence spectra involve a larger number of LUMO levels than does the fluorescence 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 transitions 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 emission spectrum, but further work is in progress to explore these results in the extended alkyne (polymer case).

TABLE III

Principal electronic UV-vis absorption transitions as determined from INDO/S-CI calculations based on optimized ground-state geometry by AM1 for molecules I, II, and III.

Molecule	λ/nm[a]	o.s.[b]	Absorption
I			
	330	1.15	0.93|H→L>
	260	0.44	−0.93|H→L+1>
	195	0.93	0.70|H−1→L+3> 0.57|H−3→L+2>
II			
	300	1.58	0.97|H→L>
	205	0.71	−0.64|H→L+3> 0.63|H−1→L>
	190	0.85	−0.80|H−4→L+1>
	170	0.60	−0.65|H−3→L+3> 0.48|H−2→L+6>
III			
	295	1.18	−0.92|H→L>
	205	0.55	0.64|H−1→L> −0.63|H→L+3>
	195	0.94	0.65|H−2→L+2> −0.64|H−1→L+3>
	177	1.01	0.47|H−6→L> 0.46|H−4→L+1> 0.43|H−1→L+3>
IV			
	310	0.93	−0.93|H→L>
	205	0.83	0.54|H−4→L> −0.50|H→L+1>
	188	2.03	−0.59|H−4→L+1> −0.47|H−2→L+2> 0.40|H→L+4>
	169	0.59	0.63|H−4→L+3> 0.41|H−2→L+3>
V			
	360	1.90	0.80|H→L>
	193	1.33	−0.59|H−5→L+3> 0.65|H−4→L+4> 0.33|H−2→L+5>
VI			
	310	0.57	−0.96|H→L>
	185	1.17	0.79|H−2→L+2> −0.38|H→L+4>

[a] Wavelength of transition.
[b] Oscillator strength of transition.

TABLE IV

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

Molecule	G.S.	S.E.S.	T.E.S.
I	6.37	6.78	15.83
II	3.92	3.77	8.88
III	3.34	3.54	9.06
IV	1.31	1.93	4.22
V	6.63	7.97	15.80
VI	6.83	12.18	11.27

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

The analysis of the main transitions presented in the calculated spectra reveals that the $|H \rightarrow L>$, $|H \rightarrow L+1>$, and $|H-4 \rightarrow L+1>$ 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 investigate 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.

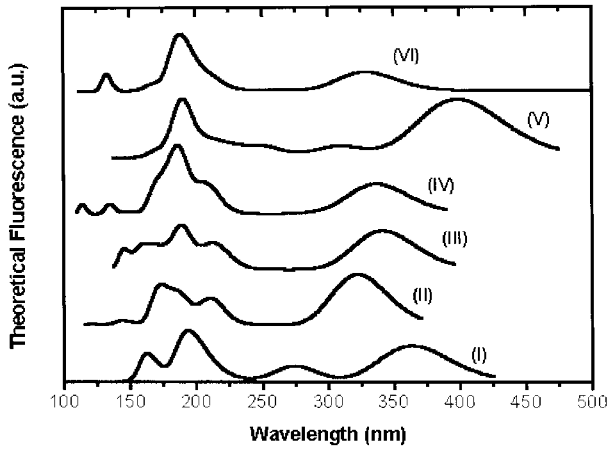

FIGURE 6. Theoretical UV-vis spectra of molecules I–VI calculated for optimized geometries by DNdM-INDO/S-CI (fluorescence spectra) using the AM1/CI method.

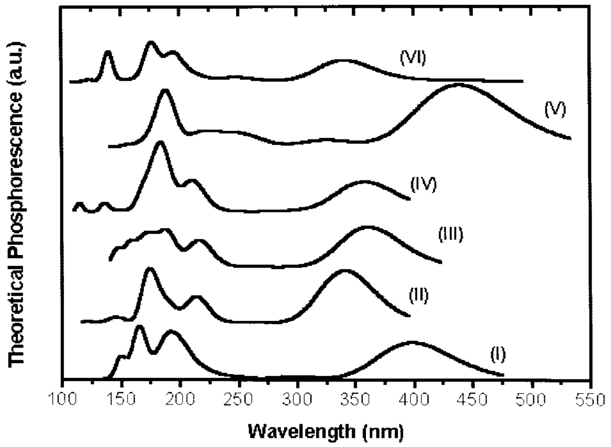

FIGURE 7. Theoretical UV-vis spectra of molecules I–VI calculated for optimized geometries by DNdM-INDO/S-CI (phosphorescence spectra) using the AM1/CI method.

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References

1. Davey, A. P.; Elliott, S.; O'Connor, O.; Blau, W. J Chem Soc Chem Commun 1995, 1433–1434.
2. Ofer, D.; Swager, T. M.; Wrighton, M. S. Chem Mater 1995, 7, 418–425.
3. Prasad, P. N.; Williams, D. J. Introduction to Nonlinear Optical Effects in Molecules and Polymers; John Wiley and Sons: New York, 1991; Chapter 7.
4. Patai, S. The Chemistry of Carbon–Carbon Triple Bond; John Wiley and Sons: New York, 1978.
5. Braga, D.; Grepioni, F.; Walther, D.; Heubach, K.; Schmidt,

A.; Imhof, W.; Görls, H.; Klettke, T. Organometallics 1997, 16, 4910–4919.

6. Brock, C. P.; Duncan, L. L. Chem Mater 1994, 6, 1307–1312.
7. Sonogashira, K.; Tohda, Y.; Hagihara, N. Tetrahedron Lett 1975, 50, 4467–4470.
8. Stephens, R. D.; Castro, C. E. J Org Chem 1963, 28, 3313–3322.
9. Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. P. J Am Chem Soc 1985, 107, 3902–3909.
10. Stewart, J. J. P. MOPAC 93, Fujitsu Limited 1993.
11. Ridley, J.; Zerner, M. C. Theoret Chim Acta 1976, 42, 223–236.
12. Bacon, A. D.; Zerner, M. C. Theoret Chim Acta 1979, 53, 21–54.
13. Head, J. D.; Zerner, M. C. Chem Phys Lett 1985, 122, 264–270.
14. Head, J. D.; Zerner, M. C. Chem Phys Lett 1986, 131, 359–366.
15. Anderson, W. D.; Edwards, W. D.; Zerner, M. C. Inorg Chem 1986, 25, 2728–2732.
16. Edwards, W. D.; Zerner, M. C. Theoret Chim Acta 1987, 72, 347–361.
17. Del Nero, J.; Laks, B. Synth Met 1997, 84, 423–424.
18. Del Nero, J.; Laks, B. Synth Met 1999, 101, 440–441.
19. Del Nero, J.; Laks, B. Synth Met 1999, 101, 379–380.
20. Doretto, R. L.; Del Nero, J.; Laks, B. Synth Met 1999, 101, 178–179.
21. Del Nero, J.; Melo, C. P. Synth Met 2001, 121, 1741–1742.
22. Del Nero, J.; Laks, B. J Mol Model 2001, 7, 354–359.
23. Del Nero, J.; Melo, C. P. (to appear).