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Semiempirical/CI of the Excited States Characterization of Retinal Molecules

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Semiempirical/CI of the Excited States Characterization of Retinal Molecules

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We report results from a semiempirical investigation of the charge distribution and dipole moments of the ground state and first excited states of the *all-trans* and 13-*cis* retinoic aldehydes. We also calculate the theoretical absorption spectra of these molecules at the INDO/S-CI level with geometries fully optimized by the PM3/CI method.

Keywords: Retinal and derivatives; excited states; semiempirical CI; theoretical absorption spectra.

INTRODUCTION

Due to their inherent large optical nonlinear properties, conjugated organic compounds represent a promising class of materials for use in photonics. Recently, for instance, measurements of the third-order optical susceptibilities of retinal molecules by the Z-scan and the optical Kerr gate techniques have been compared to values of the hyperpolarizabilities obtained by semiempirical calculations at the Hartree-Fock level[1].

As part of a more extensive investigation of the excited states of retinal derivatives and of their corresponding spectroscopic properties, in this work we report results for the liquid charge distributions and the dipole moments of the ground state and first singlet and triplet excited states of *all-trans* retinoic aldehyde (ATRA) and 13-*cis* retinoic aldehyde (CRA). The theoretical absorption spectra of these molecules

was also calculated and interpreted in terms of transitions between occupied and virtual levels.

METHODOLOGY

Semi-empirical calculations at the AM1[2] and PM3[3] levels were performed for the two retinal molecules examined (Figure 1), so that the corresponding fully optimized geometry could be determined. Standard MOPAC[2-5] parameters were used (except for the convergence criterion, for which a maximum step size of 0.05 was adopted). For both molecules, a planar configuration was assumed as the starting point for the geometry optimization calculations.

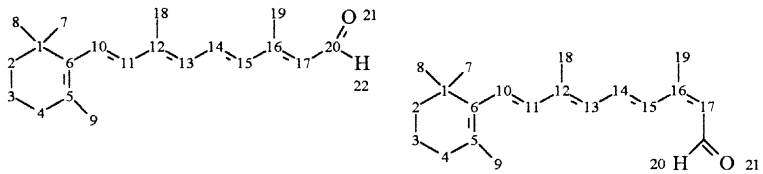

FIGURE 1: The structures of *all-trans* retinoic aldehyde (left) and 13-*cis* retinoic aldehyde (right).

Absorption spectrum calculations were made using the ZINDO package[6] with geometries fully optimized at the PM3 level. The absorption spectra were calculated at the INDO/CI (Intermediate Neglect of Differential Overlap/Configuration Interaction) level, with parameters chosen to give the best description of the UV-visible optical transitions[7]. This level of approximation was utilized within a restricted closed-shell Hartree-Fock approach to determine the ground state. Approximately 200 configurations were investigated for each molecule, including singlet and doublet states[8].

RESULTS AND DISCUSSIONS

A comparison between the liquid charge distributions for the ground state (a singlet) and the lowest singlet and triplet excited states of the CRA molecule is presented in Figure 2.

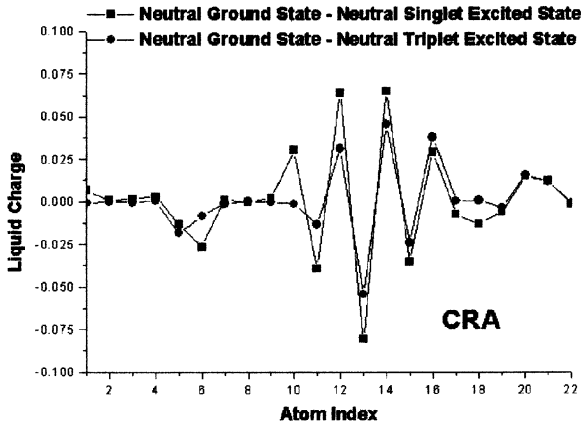

FIGURE 2: Differences in the liquid charges between the ground state and the first singlet excited state (■) and the first triplet excited state (●) for the CRA molecule.

The most noticeable differences in the liquid charge distributions of these molecules upon excitation are associated to Carbon atoms 11, 12, 13, 14, 15 and 16 of the polyenic chain: while in the excited states atoms 12, 14 and 16 loose charge, there is a net gain for atoms 11, 13 and 15. The liquid charge in Carbon atom number 10 (the first atom in the polyenic chain) exhibits a peculiar behavior: while it decreases upon excitation from the ground state to the lowest singlet excited state, it increases upon excitation to the lowest triplet state.

A similar analysis was performed for the ATRA molecule, and the corresponding results, which were essentially similar to the above, can be found in Figure 3.

The principal transitions contributing to the optical spectra of these two molecules were identified, and the corresponding theoretical absorption spectra (Figure 4) were obtained by broadening each of these principal transitions by a suitably weighted Gaussian function normalized to the calculated oscillator strengths[7].

Although all spectra are similar, with the largest band centered in the 340-350 nm region, there are a few differences in the nature of the transitions that give origin to such features. For the ATRA molecule the band at ≈ 345 nm has an oscillator strength (o.s.) equal to 1.64 and is essentially (coefficient 0.9) a pure |H→L> transition, i.e., a transition

from the highest occupied (H) to the lowest unoccupied (L) molecular orbital, while the band at ≈ 260 nm corresponds to a mixing of the transitions |H-2→L+1> and |H-1→L+4> (with equal coefficients of 0.5) with o.s.= 0.26.

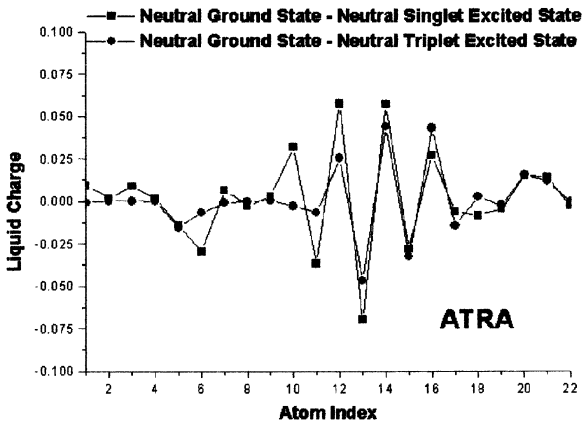

FIGURE 3: Differences in the liquid charges between the ground state and the first singlet excited state (■) and the first triplet excited state (●) for the ATRA molecule.

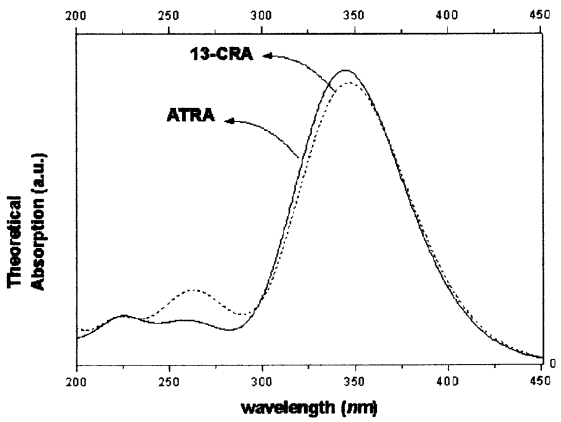

FIGURE 4: Calculated INDO/S-CI UV-visible absorption spectra of CRA and ATRA molecules.

Finally, for the CRA molecule the most important absorption line corresponds to the |H→L> transition (coefficient 0.9 and o.s.= 1.56), while the band at ≈ 260 nm has contributions from the |H-1→L> and |H→L+1> transitions (with coefficients of 0.5 and 0.7, respectively) and o.s.= 0.4.

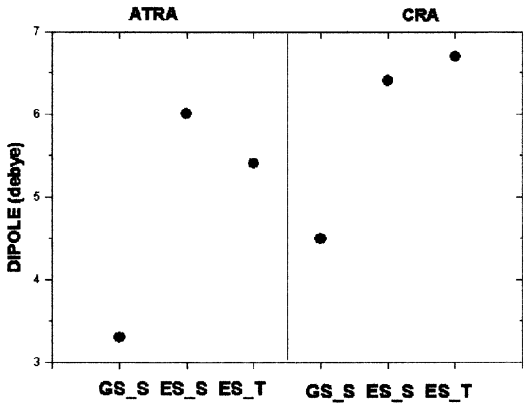

FIGURE 5: Dipole moment for the ATRA and CRA molecules in the ground state (GS_S), first singlet excited state (ES_S) and the first triplet excited state (ES_T).

Using the MOPAC PM3/CI[4-6], we have also calculated the dipole moments for the ground state and for the first singlet and triplet excited states of these retinal derivatives (Figure 5). In all cases the ground state has the lowest value of dipole moment, but while the largest of the three values is for first singlet excited state in the case of ATRA, for the CRA molecules the triplet excited state has a larger dipole moment than the first singlet excited state.

CONCLUSIONS

We reported theoretical results for the charge distribution and dipole moments for the ground state and first excited states of *all-trans* retinoic aldehyde and 13-*cis* retinoic aldehyde, and examined the corresponding absorption spectra. This work is part of a more complete

investigation of the excited states of retinal derivatives to be reported elsewhere[9].

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