Calculations of the electronic state TICT of the diphenyl polyenes P,P'- and O,O'-di-substituted using the functional density theory

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The polymers of type "pull-push" as diphenyl-polyenes, must present large optical nonlinearity, which can be incremented with increasing the size of the conjugation, (hence the delocalization of electrons), strength of donor groups and electron acceptors and the resultant flatness of the overlap of the orbital $2p_z$. The limiting factors can be affected by at least three points: (i) the types and positions of donor substituents and / or electron acceptors, (ii) the length of polyenic chain. (iii) the photophysical properties and dynamics of excited electronic states. Here were analyzed some diphenyl-disubstituted polyenes, for a series of polymers derived from D - Ph - (CH = CH) n - Ph - A, type P, P 'and O, O'-disubstituted 1,6-diphenyl-1,3,5-hexatrienos, (refered as D, A-DPH), where D and A are free internal rotation group (IRG) (OCH_3, CN) and groups with restricted internal rotation (RIR) [- N $(CH_3)_2$ and ($-NO_2$)], where P, P '(para-substituted) and O, O' (ortho-substituted), and (n) and (2, 3, or 4), with purpose of determining the low-lying electronic singlet state, S_1, a intramolecular charge-transfer state caracterized as resultant from a twisted molecular conformation (i. e., TICT state), the hyperpolarizability second order and β values and the dipole moment.

AM1 and Hartree-Fock methods were used with basis function 6-31 + G *, for the geometry optimization calculations and second-order hyperpolarizability β values. For the calculation of excitation energies were used the Functional Density Time dependent theory (TD-DFT), using the B3LYP functional and function base 6-31 + G *.

Two series of polymers were formed: series (a) p, p'sibstituintes; (1) [N $(CH_3)_2$], (NO_2); (2) (OCH_3), (OCH_3); (3) [N$(CH_3)_2$], (CN); (4) (NO_2), (NO_2); (5) (CN), (CN); (6) (OCH_3), (CN); (7) [N$(CH_3)_2$], [N$(CH_3)_2$]; (8) (CN), (NO_2); (9) [N$(CH_3)_2$], (OCH_3) and (10) (NO_2), (OCH_3); and the series (b), O, O'-substituents (1) [N$(CH_3)_2$], (NO_2); (2) (OCH_3), (OCH_3); (3) [N$(CH_3)_2$], (OCH_3); (4) (CN), (CN). Calculations of excitation energies showed that all molecules with twisted conformation has increased dipole moment and the presence of groups (RIR) D and A, both polymers produces the electronic state S_1, it is assigned as TICT (n, π *), involving a transition from the n orbital of D to the π * orbital of group A, for example, . the polymer (1), with n = 2,3 and 4, shows a state TICT with the following energies: 2.03 eV; 1.82 eV and 1.54 eV respectively. On the other hand, the polymer (2) where D and A are groups (NIR) with n = 2.3 and 4, does not produces the TICT state. The β values increase in the polymer (a) (1) where n = 2,3 and 4, respectively: (55, 48, 38) 48x10^{-30} seu, while for the polymer (DPH) without substituents the values are (0.032, 0.006 and 0.104) x10^{-30} esu. The theoretical methods used here are good tools for: (i) the determination of the non-linearity of these optical polymers; (Ii) detection of TICT origin and the most important factors for produçãio a strong TICT state in each polymer: the substituent (RIR) or (RIL); or molecular geometry, planar or non-planar or both.

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