THE MO-SCF QUANTUM APPROACH OF THE P-AZOXYANISOLE (PPA) MOLECULE I. QUANTUM ENERGETIC MOLECULAR CHARACTERISTICS

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abstract: For the first time in the literature of the liquid crystals (LC) a molecule LC type (p-azoxyanisole (PPA)) is approached by means of the nonrelativistic molecular quantum mechanics. The structural complexity of the quantum molecular system (33 nuclei, 196 electrons) imposes a MO-SCF-LCAO/CNDO quantum approach, having at its basis the Hartree-Fock-Roothaan equations with LCAO expansion of the molecular orbitals (MO) and with PPP parameters of the approximation used. The quantum computations have been performed in the CNDO-2 approximation, using a computing program of MO-SCF type. For the PAA molecule the following quantum energetic characteristics have been obtained: the orbital energies, the total electronic energy, the total molecular energy, the bonding energy, the ionization potential, the reduction potential (or the affinity of electrons) and the width of the forbidden interorbital zone. The quantum results related in this paper are interpreted and discussed for the PAA molecule of the nematic LC class.

Introduction

In spite of the decision [3] of settling down as early as 1979 a NATO Advanced Study Institute "devoted to the molecular physics of liquid crystals" [3], as far as we know, in the literature of the liquid crystals (LC) there is no quantum study on any quantum molecular system (QMS) of LC type and there are no LC molecular characteristics computed on the basis of the nonrelativistic quantum molecular mechanism for this type of molecules. We are greatly interested in the matter [13] as we dealt with the quantum study of some (QMS) of the nematic and smectic LC type as [4]: p-azoxyanisole (PAA), p-merhoxybenzylidene-p-n-butylaniline (MBBA), p-n-hexyl-p'cyanobifenil (HCB), p-n-octyloxybenzoic acid (OBA) and 4-butyloxybenzal-p'-ethylaniline (BBEA). The first three LC are of nematic class, the last two LC are of smectic class. In this paper we deal only with the PAA molecule [1÷3] with the rough chemical formula $C_{14}N_2O_3H_{14}$ and belonging to the nematic class. We have selected the PAA molecule because the PAA is the well-known and the most examined LC in the whole LC literature. Besides the quantum energetic characteristics which we shall relate, interpret and discuss in this paper, our quantum

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approach [13] of the PAA molecule still includes quantum results about some electrical characteristics too (the electronic charge density on the atom and net, the electric dipolmoment and its Cartesian distribution in the whole molecule) which we are going to present in a future paper.

Results and Discussion

1. The LCAO Roothaan equations in the approximation for the quantum study of the molecules of the LC type

As the LC type molecules represent (QMS) with relative great number of atoms (33 in PAA for example) the solving of their Schrödinger equation analytically accurate is impossible and it must be replaced by Hartree-Fock-Roothaan equations (HFR eqs.) from the MO-SCF (molecular orbital selfconsistent field) theory and method [5÷9]. For effective quantum computations using a computing program on the computer [9,13], the HRF eqs. [5]:

$$\hat{F}|\varphi_i\rangle = e_i|\varphi_i\rangle \text{ must be reduced to the LCAO form} \tag{1}$$

$$\sum \left(F_{pq} - e_i S_{pq}\right)\cdot c_{qii} = 0 \quad \left(p = \overline{1, n_{AO}}\right) \text{ or to matrix form} \tag{2}$$

$$\breve{F}\breve{C} = \breve{S}\breve{C}\breve{e} \tag{3}$$

with $\hat{F}\left(\text{or }\breve{F}\right)$ the Haartree-Fock operator (or matrix), $\breve{C}$ the eigenvectors (with the elements $\{c_I\}$) matrix, $\breve{S}$ the overlap matrix (with the elements $\{S_{pq}\}$), and $\breve{e}$ the eigenvectors matrix (with the elements – the orbital energies $\{e_i\}$), as far as the molecular orbitals (MO) $\{|\varphi_i\rangle\}$ have been LCAO (linear combination of atomic orbitals) expanded [5]:

$$|\varphi_i\rangle = \sum c_{qi}|\chi_q\rangle \tag{4}$$

through the basis of the atomic orbitals (AO) $\left\{|\chi_q\rangle; q = \overline{1, n_{AO}}\right\}$. The effective solvation of the equation (2) and (3) for a QMS with a relative great number of atoms as those of the LC type demands additional parameters for the computing of the molecular integrals which appear in the quantum approach. We have decided [13] for the Pariser-Parr-Pople (PPP) parameters [6÷8] with a CNDO (complete neglected of differential overlap) reduction of the computation quality in the CNDO-2 variant [9]. The MO-SCF-LCAO total wave function of the considered QMS of the LC type is a Slater determinant built from all the {MO} of the LC molecule.

2. The quantum energetic characteristics of the PAA molecule

2.1. Theoretical quantum consideration

Taking in (4) the atomic orbitals (AO) $\left\{ \left| \chi_q \right\rangle \right\}$ of Slater type [15], based on MO-SCF/CNDO-2 computing program [9,13] dealing MO-SCF-LCAO/CNDO-2 the molecules of LC type, we get the following quantum energetic characteristics of the PAA molecule [13]: (a) the orbital energies $\{e_i\}$ as solution of the LCAO Roothaan equation (2) and (3); (b) the total electronic energy (E_{el}); (c) the total molecular energy (E_t); (d) bonding energy (E_b); (e) the (first) ionization potential (IP) from e_i of the last occupied MO; (f) the reduction potential (or the affinity of electrons) (RP) from e_j of the first virtual (empty) MO and (q) the width of the forbidden interorbital zone (Δe).

In the SCF procedure of the MO-SCF-CLAO/CNDO-2 quantum approach of the PAA molecule, the SCF convergence criterion has been preestablished for the last two interactions at:

$$\varepsilon_{E\,el} \leq 10^{-3} \text{ Hartree} = 6.89716 \cdot 10^{-4} \text{ eV, for } \left| (\Delta E_{el}) \right| = \left| (E_{el})_j - (E_{el})_i \right| \qquad (5)$$

at a SCF cycle of 30 iterations maximum.

The total electronic energy (E_{el}) has been computed by the formula [5,9,13]:

$$E_{el} = \frac{1}{2} \sum_{p \prec q} P_{pq} \left(H_{pq} + F_{pq} \right) \qquad (6)$$

through the matrix elements: of the density (P_{pq}), of the core (H_{pq}), of Hartree-Fock (F_{pq}) respectively.

The total molecular energy (E_t) has been computed from the relation (6) by adding the energy of the internuclear interaction and the bonding energy (E_b) from the relation:

$$E_b = E_t - \sum_I E_I \qquad (7)$$

with E_I the energy of the component atom I.

The equilibrium geometry of the PAA molecule is given in figure 1 synthesizing data from literature [10÷13] on the bond lengths and on the angles between the bonds. The figure 1 shows the numbering of the atoms in the PAA molecule as well as the local system of Cartesian coordinates used in the MO-SCF-CLAO/CNDO-2 computations. Also, in the figure 1 in brackets (in the left part) 33 is the number of atomic nuclei and 136 is the total number of electrons, with the 99 valence electrons of the PAA molecule.
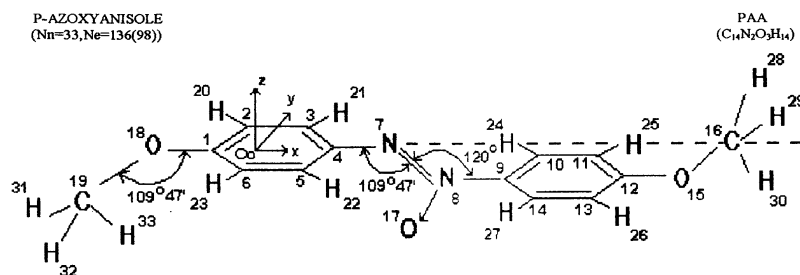
Fig. 1: *The coplanar structure of p-azoxyanisole (PAA) molecule and the local system of Cartesian coordinated used for the MO-SCF-CLAO/CNDO-2 quantum computations. The numbering of atoms in the molecule is necessary for the input data in the computing program used*

2.2. The SCF convergence from the MO-SCF-LCAO/CNDO-2 case of the PAA molecule.

The reach of SCF (selfconsistent field) convergence preestablished in the relation (5) for the MO-SCF-LCAO/CNDO-2 case of the PAA molecule can be notice in figure 2 and in the table 1, after 30 iterations obtaining:
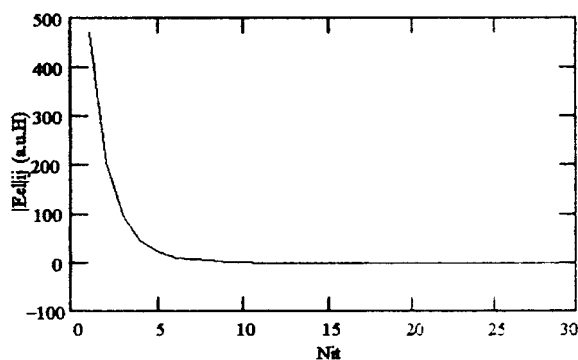
$$\left|\left(\Delta E_{el}\right)_{29-30}\right| \equiv \left|\left(E_{el}\right)_{30} - \left(E_{el}\right)_{29}\right| = 6.7 \cdot 10^{-4} \text{ Hartrees} \cong 0.0018 \text{ eV}$$

Fig. 2: *The SCF convergence from MO-SCF procedure of the quantum energetic computation in the case of the PAA molecule*

The figure 2 represent the dependence:

$$\left|\left(\Delta E_{el}\right)_{ij}\right| \equiv \left|\left(E_{el}\right)_{j} - \left(E_{el}\right)_{i}\right| = f\left(N_{it}\right) \tag{9}$$

with N_{it} the number of interactions from the SCF procedure [5] of the MO-SCF-LCAO/CNDO-2 program used [9,13] for the quantum computations. Also, the figure 2 and the table 1 in the confronting with the criterion (5) show a very good SCF convergence which assures the good quality for the quantum energetic characteristics computed for the PAA molecule.

The plotting of the graph from the figure 2 has been made with the help of the data $(\Delta E_{el})_{ij}$ presented in the table 1.

Table 1. $(\Delta E_{el})_{ij}$ in the case of PAA molecule and the SCF convergence obtained for N_{it} of 30 iterations maximum (in 1 a.u.H = 1 Hartree)

N_{it}	$(\Delta E_{el})_{ij}$ (Hartrees)	N_{it}	$(\Delta E_{el})_{ij}$ (Hartrees)	N_{it}	$(\Delta E_{el})_{ij}$ (Hartrees)
1	-471.15695	11	-1.26813	21	-0.02411
2	-205.56900	12	-0.85205	22	-0.01764
3	-94.77637	13	-0.57446	23	-0.01208
4	-45.24829	14	-0.38733	24	-0.00696
5	-22.72437	15	-0.26099	25	-0.00494
6	-12.21796	16	-0.17505	26	-0.00446
7	-7.19482	17	-0.12006	27	0.00323
8	-4.41473	18	-0.08148	28	-0.00140
9	-2.90424	19	-0.05444	29	-0.00098
10	-1.90198	20	-0.03674	30	-0.00067

2.3. The orbital energies $\{e_j\}$ of the PAA molecule. The MO-SCF-LCAO/CNDO-2 energetic spectrum

The MO-SCF-LCAO/CNDO-2 quantum results of the energetic type, obtained with the computing program described in reference 13 (as a CNDO[9] version adapted CNDO-2) contain the orbital energies $\{e_j\}$ for the 98 valence electrons (from the total of 136, the rest being core electrons) of the PAA molecule. The values of these orbital energies have been enlisted in the table 2 indicating 49 molecular orbitals completely (double) occupied with valence electrons. All these energies are eigenvalues of the Hartree-Fock operator $\hat{F}$ from

HFR eqs. (1) reduced to the LCAO form (2), with the operator $\hat{F}$ written for through the quantum approach of the structure from the figure 1 (with the input data for the 33 atoms in the computing program used).

The data from the table 2 represent the spectrum of the MO-SCF-LCAO/CNDO-2 orbital energies of the PAA molecule, which is illustrated in the figure 3. From the table 2 it is noticed that the orbital energies have two type of values. The negative values represent the energies of the orbital electronic levels double (completely) occupied by the 98 valence electrons and the positive values represent the energies of the virtual (empty) orbital electronic levels which can be occupied by electrons when the PAA molecule is excited. All these energetic levels are of the MO-SCF type.

The virtual (empty) orbital energetic levels will be occupied by electrons, when The PAA molecule is in an external electrical field, for example. In this case, he Hartree-Fock operator $\hat{F}$ will contain the term of external electrical interaction too.
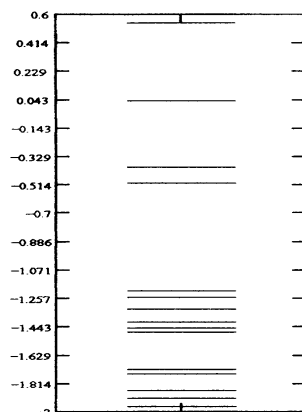
Fig. 3: *The MO-SCF-LCAO/CNDO-2 energetic spectrum of the orbital energies levels in the PAA molecule for its 98 valence electrons (in 1 u.a.H. = Hartree)*

Table 2. $(\Delta E_{el})_{ij}$ in the case of PAA molecule and the SCF convergence obtained for N_{it} of 30 iterations maximum [in 1 a.u.H = 1 Hartree (= 0.689 ±164 eV)]

No.[*]	$e_i \left(i = \overline{1, 90}\right)$	No.[*]	$e_i \left(i = \overline{1, 90}\right)$	No.[*]	$e_i \left(i = \overline{1, 90}\right)$
1	-1.9674	31	-0.6988	61	0.2900
2	-1.9139	32	-0.6943	62	0.1959
3	-1.8614	33	-0.6891	63	0.3013
4	-1.7556	34	0.6803	64	0.3018
5	-1.7207	35	-0.6498	65	0.3054
6	-1.4804	36	-0.6449	66	0.3083
7	-1.4511	37	-0.6006	67	0.3102
8	-1.4107	38	-0.5856	68	0.3104
9	-1.3289	39	-0.5744	69	0.3197
10	-1.2518	40	-0.5598	70	0.3216
11	-1.2082	41	-0.5313	71	0.3282
12	-1.1666	42	-0.5256	72	0.3325
13	-1.1467	43	-0.5053	73	0.3347
14	-1.1163	44	-0.4966	74	0.3460
15	-1.0956	45	-0.4956	75	0.3704
16	-1.0859	46	-0.4638	76	0.3817
17	-1.0720	47	-0.4486	77	0.4114
18	-0.09745	48	-0.4250	78	0.4260
19	-0.9599	49	-0.4002	79	0.4362
20	-0.9297	50	0.0367	80	0.4410
21	-0.8986	51	0.1253	81	0.4427
22	-0.8937	52	0.1322	82	0.4557
23	-0.8662	53	0.1389	83	0.4582
24	-0.8379	54	0.1621	84	0.4606
25	-0.7898	55	0.2560	85	0.4710
26	-0.7826	56	0.2645	86	0.4871
27	-0.7736	57	0.2677	87	0.5080
28	-0.7300	58	0.2686	88	0.5205
29	-0.7196	59	0.2761	89	0.5336
30	-0.7173	60	0.2798	90	0.5458

(*) the numbering of the eigenvectors $\{c_i\}$

2.4. The (first) ionization potential (IP), the reduction potential (RP) and the width of the forbidden interorbital zone (Δe)

The table 2 shows that the orbital energy of the last molecular orbital occupied with two valence electrons is:

$$e_{49} = -0.4002 \text{ Hartrees} = -0.2760 \text{ eV} \tag{10}$$

being in the absolute value just the MO-SCF-LCAO/CNDO-2 value of the first ionisation potential (IP) of the PAA molecule. It is also noticed that the first virtual (empty) molecular orbital has the energetic value:

$$e_{50} = +0.0367 \text{ Hartrees} = +0.0253 \text{ eV} \tag{11}$$

it is the negative value representing just MO-SCF-LCAO/CNDO-2 value of the reduction potential (or the affinity of electrons) of the PAA molecule.

Comparing the IP and RP values it is results that in the PAA molecule the electron acceptor character dominates over the electrons donor character, because:

$$IP \cong 10.9 \cdot |RP| \tag{12}$$

the big value of IP really maintaining the valence electrons in a deep potential pit in molecule. The fact described by the relation (12) is reinforced by the width of the forbidden interorbital zone as well:

$$\Delta e = IP + |RP| = |e_{49}| + e_{50} = 0.4396 \text{ Hartrees} = 0.3013 \text{ eV} \tag{13}$$

it can have implications in the interaction between the PAA molecule at micro and macromolecular levels, besides the possible implications of electrical nature through the dipole moment and the quadrupole moment.

2.4. The fundamental quantum energetic characteristics (E_{el}, E_t, E_b) of the PAA molecule

With the quantum formulas mentioned in 2.1. (explicitly presented in the reference 9 and 13), for the total electronic energy (E_{el}), the total molecular energy (E_t) and the bonding energy (E_b), from the MO-SCF computing program adapted and used [9,13], we have the following MO-SCF-LCAO/CNDO-2 energetic values [13]:

$$E_{el} = -871.997 \text{ Hartrees} = -601.4163 \text{ eV} \tag{14}$$
$$E_t = -188.755 \text{ Hartrees} = -130.1843 \text{ eV} \tag{15}$$
$$E_b = -17.103 \text{ Hartrees} = -12.1339 \text{ eV} \tag{16}$$

For the none of the three fundamental quantum energetic characteristics of the PAA molecule in literature (and above all in the LC literature) there are no values confronting with those we have obtained. The quality of the energetic values E_{el}, E_t and E_b from (14)-(16) is assured by the very good SCF convergence obtained, how we have shown in 2.2. For the bonding energy (E_b) we can still make a confrontation with the value $E_b^{'}$ which we have obtained [13] averaging Pauling values [14] of the energies of all direct chemical bonds between the 33 atoms of the PAA molecule, resulting the value:

$$E_b^{'} = -17.593 \text{ Hartrees} \tag{17}$$

In the relative error of 2.21% as compared to E_b from (16). The high value of the total molecular energy (E_t) as compared to the total electronic energy (E_{el}) is explained through the contributions of the positive energies of the interactions between the atomic nuclei, which are added to E_{el} for obtaining E_t.

Conclusion

➢ The nonexistence in the LC literature of a quantum study of any quantum molecular system (QMS) of the LC type has lead us to the MO-SCF-LCAO/CNDO-2 quantum study of {QMS} indicated in the introduction, from which we have presented here the quantum energetic results and there interpretations in the case of the PAA molecule belonging to the nematic LC class.

➢ The MO-SCF-LCAO/CNDO-2 quantum results of the energetic type have been obtained and reported on the basis of MO-SCF-LCAO/CNDO computing program [9] adapted CNDO-2 [13] for {QMS} of the LC type belonging to the nematic and smectic class.

➢ From the spectrum of the MO-SCF-LCAO/CNDO-2 orbital energies of the PAA molecule, with the help of the information about the ionization potential (IP), about the reduction potential (RP) (or the affinity electrons) it results a possible implication of the electrons acceptor character of the PAA molecule in the intermolecular interactions at the micro and macromolecular nematic levels, rather then of the electrons donor character, according to the relation (10)-(13) and to their interpretations for IP and RP.

➢ The energetic conclusion can be correlated to the electric aspect [13] through the MO-SCF-LCAO/CNDO-2 computation of the electronic charge of density on atom and net, of the electric dipolmoment and its Cartesian distribution in the whole PAA molecule.

➢ We have important information about inner interaction between the atoms of the PAA molecule through the bonding energy E_b for its value (16) a confrontation with a nonquantum value $E_b^{'}$ obtained through averaging the Pauling energies [14] of all direct chemical bonds among the 33 atoms of the molecule. Likewise, the good agreement between E_b (16) and $E_b^{'}$ can be correlated to the good values of the electronic charge of density on atom and net [13].

➢ For the fundamental quantum energetic characteristics E_b, E_t and $E_b^{'}$ of the PAA molecule not existing in the LC literature values for confrontation, the quality of the MO-SCF-LCAO/CNDO-2 values reported in our paper is assured by the very good SCF convergence obtained (according to the figure 2 and table 2).

➢ An extension of the present paper at the quantum energetic characteristics (E_{el}, E_t, E_b, IP, RP and Δe) computed MO-SCF-LCAO/CNDO-2 [13] for the rest of the molecules of the LC type enumerated in the introduction is possible in the future.

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