A theoretical study of 1,4-bis (3-carboxy-3-oxo-prop-1-enyl) benzene I

Estudo teórico do 1,4-bis (3-carboxi-oxo-prop-1-enil) benzene I

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Abstract

In the present paper we have a focus in a study the theoretical characterization of the 1,4-bis (3-carboxy-3-oxo-prop-1-enil) benzene acid, which is a recent target of experimental study with potentiality complexant of metal ions. Our study includes calculations of electric properties and optical linear properties and optical nonlinear (Polarizability and Hyperpolarizability). Because of being a relatively big molecule and with many atoms of carbon the calculations restricted the methods HF (Hartree-Fock), DFT (B3LYP, BPE) and MP2 (Möller-Plesset Perturbation Theory second order). Since it seems to these calculations to be the first one of the literature, we hope to contribute to the characterization in fact of this compound.

Key-words: 1,4-bis (3-carboxy-3-oxo-prop-1-enil) benzene acid. HF, DFT and MBPT. Electrical properties. Optical nonlinear properties.

Resumo

No presente trabalho, temos em foco um estudo de caracterização teórica do 1,4-bis (3-carbóxi-3-oxo-prop-1-enil) benzeno, que é um alvo recente de estudos experimentais com potencialidade complexante de íons metálicos. Nosso estudo inclui cálculos de propriedades elétricas e propriedades ópticas lineares e não lineares (polarizabilidade e hiperpolarizabilidade). Por ser uma molécula relativamente grande e com muitos átomos de carbono, os cálculos foram limitados aos métodos HF (Hartree-Fock), DFT (B3LYP, BPE) e MP2 (Teoria de Perturbação de Möller-Plesset em segunda ordem). Uma vez que esses cálculos são os primeiros da literatura, esperamos contribuir para a caracterização de fato deste composto.

Palavras-chave: Ácido 1,4-bis (3-carbóxi-3-oxo-prop-1-enil) benzeno. HF, DFT e MBPT. Propriedades elétricas. Propriedades ópticas não-lineares.

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Introduction

The environment is being degraded day-to-day track contamination by highly toxic metal species stemming from a variety of industries branches. So the study of materials chelating is a matter of fundamental interest. Knowing their properties can help control, reduce or even eliminate such ions. Thus, the study and characterization of chelating has had an increasing role in this direction (OLIVEIRA et al., 1993; MIYANO et al., 1993; SIQUEIRA et al., 1995; RASERA et al., 1995; PEREIRA et al., 1997; MARQUES et al., 1997). In recent article Bariccatti, Rosa e Oliveira (2004), summarizing the 1,4-bis (3-carboxy-3-oxo-prop-1-enyl)benzene (bis-bp) whose structure (figure1) indicates a possible application in the study of complexation of metal ions.

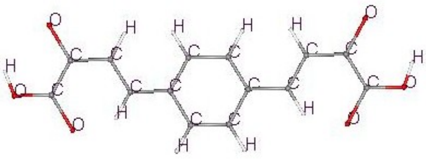

Figure 1. Structure of acid 1,4-bis (3-carboxy-3-oxo-prop-1-enyl)benzene

In this article the authors cite a possible analytical application of the compound. He could serve as a sensor chemical and spectroscopic, since the complexation of metals can change the spectroscopic properties of absorption and emission of light, causing variations in intensity and the position of maximum emission (MIYAZAKI et al., 1974) or absorption, respectively. Thus the calculation of non-linear optical properties (polarizabilities and hyperpolarizabilities) can help in confirmation of this study.

It is necessary a careful study of the properties of this new chelating compound, and therefore it is necessary characterization to its chemical, physical and spectroscopic. Thus the theoretical calculations made in this work can help particularly in this characterization.

Methodology

The study was conducted using the software Gaussian03 (FRISCH et al., 2004). To calculate the properties of polarizability and hyperpolarizability we use the electric fields; Ex = ± 0.001 a.u e $E_z = \pm 0.002$ a.u.. In all calculations the geometries were completely optimized. The optimization process was terminated when the sum of the energy gradients was lesser than 0.00045 kcal $Å^{-1}.mol^{-1}$.

The energy of interaction of a molecule subject to an external electric field can be expressed by an expansion of permanent and multipole moments of their coefficients are identified as moments of multipole and polarizabilities. According to Bishop (1998), when a molecule is placed in the presence and absence of an external electric field its energy is altered in accordance with the terms of the equation (1);

$$\Delta\varepsilon = -\mu_i E_i - \frac{1}{2}\alpha_{ii}E_i^2 - \frac{1}{2}\alpha_{ij}E_iE_j - \frac{1}{6}\beta_{ijk}E_iE_jE_k - \frac{1}{24}\gamma_{ijkl}E_iE_jE_kE_l - \dots \quad (1)$$

Where the indexes subscribed represent the components of the tensor and repetition represents the sum of all components cartesian. α, β and γ represent respectively the polarizabilities, the first and second hyperpolarizability molecular respectively; μ_i is the time to permanent dipole, in our case we α_{ii} as the components of the dipole polarizability; β_{ijk} and the components of the first independent polarizability of dipole. According as a method of finite field (DYKSTRA, 1988), and moments of multipole polarizabilities are obtained as numerical differentiation of energy calculated in the presence of different values of electric field applied. The average polarizability linear $<\alpha>$ and anisotropy, $\Delta\alpha$, are defined by the equations:

$$\langle\alpha\rangle = \left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right)/3 \quad (2)$$

$$\Delta\alpha = \left\{\frac{1}{2}\left[(\alpha_{XX}-\alpha_{YY})^2+(\alpha_{XX}-\alpha_{ZZ})^2+(\alpha_{YY}-\alpha_{ZZ})^2\right]\right\}^{1/2} \quad (3)$$

Components, β_{ikj} the first hyperpolarizability of dipole will compose the first molecular hyperpolarizability, β_{molec}, defined by equations:

$$\beta_i = \frac{1}{3}\sum_{i,k}(\beta_{ikk}+\beta_{kik}+\beta_{kki}),\; k = x, y, z;\; i = x, y, x \quad (4)$$

$$\beta_{molec} = \left(\beta_X^2+\beta_Y^2+\beta_Z^2\right)^{1/2} \quad (5)$$

In *ab initio* calculations of polarizability of small molecules, increasing the inclusion of electronic correlation (EC) is usually accompanied by the sequence of growth of more sophisticated methods. But for larger molecules (such as organic, eg) the treatment of electronic correlation is usually restricted to the MP2 level because of the large number of the basis functions. Whereas the MP2 method usually provides a large share of the total effect of the EC involving this type of molecule (NOTARIO et al., 1999; ELLEUCH; FEKI; ABID, 2007), Sim et.al. (1993) reported that the inclusion of the effect of EC affects so remarkable growth of the values of β for P-nitroaniline (PNA). More recently, Yang e Jiang (2001) showed that the longitudinal component of the second hyperpolarizability (γ) of squaraines symmetrical center is very sensitive to the effect of the EC.

In this work, the dipole moment of the HF level was calculated analytically. In other levels of approximation to the calculations of this property was obtained numerically, using the method of finite field (FF). The values of electric field used in this study provides the stability desired number in employment of the method FF because we know that the intensities of the fields have a crucial role in such molecules, as shown by Sim et.al. (1993).

A wide variety of items that expresses *ab initio* calculations on the number of base functions to be used is an important ingredient, as well as the inclusion of the correlation electronics. The set of functions used in basic organic molecules (with many carbon atoms) is normally the set 6-31G. Studies are showing that this basis set, supplemented with the addition of functions of the polarization type p and d gives the provisioning required for the proper estimate of the value of the second hyperpolarizability of small organic molecules. (YANG; JIANG, 2001; HEHRE; DITCHFIELD; POPLE, 1972; DILL; POPLE, 1975; HARIHARAM; POPLE, 1973; CLARK; CHANDRASEKHAR; SCHLEYER, 1983; KRISHNAN; FRISCH; PPOPLE, 1980; FRISCH; POPLE; BINKLEY, 1984)

Thus, we believe that this criterion justifies the use of the bases that were used in this work.

Results and discussion

Tables I and II show the comparison of properties between the methods HF, B3LYP, BPE and MP2. In all calculations the molecule was oriented in the x-axis and y and z axis taken perpendicular.

In Table I we see that the tensor, α_{xx}, is responsible for the greatest contribution both in the average polarizability and the anisotropy. In the case where the method is the HF/6-31G contribution represents 46 and 14% for the average polarizability and anisotropy respectively.

When a function of polarization is included contributions are 44 and 29% for $\langle\alpha\rangle$ and respectively, indicating an increase of more than 100% in the value of anisotropy.

If we observe the effect of inclusion of electron correlation increases the values found are 53 and 29% for $\langle\alpha\rangle$ and Δα respectively, when the method is B3LYP and 45 and 29% when we use MP2. When polarization is included the figures drop to 50 and 22% and remain at 45 and 29% for MP2.

The results show that the effect of electronic correlation is much lower when we include the function of polarization.

We can see also that the inclusion of electronic correlation does not affect significantly the average polarizability when the function of polarization is included.

We also observed that the dipole moment the value is more sensitive when comparing the results between the methods, with and without the addition of electronic correlation. Comparing HF/6-31G and B3LYP/6-31G the difference between the two methods reaches 24% and compared the results with the addition of the polarization difference is 62%. If we look at HF/6-31G and MP2/6-31G the proportion is 22% and 10% with the addition of polarization.

Table I - Dipole moment, polarizability components, average polarizability and anisotropy (au) of bis-bp, methods HF, B3LYP, MP2 and BPE.

Method / Basis	μ	α_{xx}	α_{yy}	α_{zz}	$\langle\alpha\rangle$	$\Delta\alpha$
HF/6-31G	2.9195	323.681	155.618	49.180	176.16	239.71
6-31G*	2.6353	315.753	153.355	56.777	175.29	226.68
D95	2.8890	326.443	161.088	64.033	183.85	229.81
D95*	2.6919	320.312	158.688	71.351	183.45	218.72
6-31G**	2.6073	316.222	154.047	57.464	175.91	226.48
B3LYP/6-31G	2.8467	452.304	159.828	50.708	220.95	359.67
6-31G*	2.5720	438.546	159.633	57.666	218.61	341.51
D95	2.8764	463.756	164.393	64.698	230.95	359.73
D95*	2.6709	450.231	164.092	71.364	228.56	342.06
6-31G**	2.5468	438.478	160.298	58.301	219.03	340.82
BPE/6-31G	2.8570	515.465	163.395	43.426	240.76	424.95
6-31G*	2.5937	498.919	163.512	58.722	240.38	398.28
6-31G**	2.5701	492.842	164.210	59.338	240.80	397.58
MP2/6-31G	3.2856	372.678	160.365	50.212	194.42	283.90
6-31G*	2.9210	370.903	157.699	56.873	195.16	277.70
D95	2.6329	384.513	166.797	65.471	205.59	282.36
D95*	2.6329	382.012	163.558	71.462	205.68	276.26
6-31G**	2.4182	369.722	158.020	57.486	195.08	276.06

Table II shows the components of first hyperpolarizability and molecular first hyperpolarizability, β_{molec}.

We can note that there is a wide variation in values β_{molec} when we look at the calculations in perturbation theory. The component β_y is the main component contributing to the values most significative. Since there is no experimental results for such a structure, we believe that the MP2/6-31G ** calculation is the most significant result.

Table II - Components of the first hyperpolarizability and molecular first hyperpolarizability (au) ofbis-bp, methods HF, B3LYP, MP2 and BPE.

Method / Basis	β_x	β_y	β_z	β_{molec}
HF/6-31G	0.995	44.671	-0.042	44.68
6-31G*	0.217	27.627	0.409	27.63
D95	1.554	26.769	-0.035	26.81
D95*	0.231	10.626	-0.002	10.63
6-31G**	-0.173	24.947	0.155	24.95
B3LYP/6-31G	-3.030	15.133	-1.934	15.55

6-31G*	-4.621	38.278	-2.951	38.67
D95	-0.108	14.594	-1.023	14.63
D95*	-1.568	20.796	-0.080	20.86
6-31G**	-4.719	39.866	-0.868	40.15
BPE/6-31G	1.651	-114.416	-1.927	114.44
6-31G*	-2.704	-36.657	1.286	36.78
6-31G**	-2.532	-32.447	1.726	32.59
MP2/6-31G	-0.059	1385.476	0.007	1385.48
6-31G*	-0.834	827.416	0.045	827.42
D95	-0.028	1605.219	-0.143	1605.22
D95*	-1.023	901.743	-0.159	901.74
6-31G**	-0.057	832.390	0.139	832.39

Conclusion

In the present work, standard basis sets to reproduce accurately the values of the electric properties for the molecule bis-bp. The specific basis sets found were tested at different levels of theory, including HF, MP2, giving satisfactory results for most of methods and properties. In general, these basis sets are smaller than those reported in the literature and give values for electric properties in satisfactory agreement with experimental and others theoretical data available. In our case there are no experimental results for comparison, so our best result is the MP2/6-31G**. Thus, the basis sets reported in the present study may be used at MP2 level for calculating electric properties of larger molecules, where MP4 and CC methods are not applicable.

References

BARICATTI. R. A.; ROSA. M. F.; OLIVEIRA, J. D. S. Fotoquímica e fotofísica do ácido 1,4-bis (3-carbóxi-3-oxo-prop-1-enil) benzeno. *Eclética Quimica, Araraquara*, v. 29, n. 2, p. 15-18, 2004.

BISHOP, D. M. Additional compact formulas for vibrational dynamic dipole polarizabilities and hyperpolarizabilities. *Advances in Chemical Physics*, New York, v. 108, n. 24, p. 1013-1018, 1998.

CLARK, T.; CHANDRASEKHAR, J.; SCHLEYER, P. Efficient diffuse function-augmented basis sets for anion calculations. III. The 3-21+G basis set for first-row elements, Li-F. *Journal of Computational Chemistry,* New York, v. 4, n. 3, p. 294-391, 1983.

DILL, J. D.; POPLE, J. A. Self-consistent molecular orbital methods. XV. Extended Gaussian-type basis sets for lithium, beryllium, and boron. *Journal of Chemical Physics*, New York, v. 62, n. 7, p. 2921-2923, 1975.

DYKSTRA, C. E. *Ab initio calculations of the structures of properties of molecules.* Amsterdam: Elsevier, 1988.

ELLEUCH, S.; FEKI, H.; ABID, Y. HF, MP2 and DFT calculations and spectroscopic study of the vibrational and conformational properties of N-diethylendiamine. S*pectrochimica Acta Part A:* Molecular and Biomolecular Spectroscopy, Amsterdam, v. 68, n. 3, p. 942-951, 2007.

FRISCH, M. J.; TRUCKS, G. W.; SCHLEGEL, H. B.; SCUSERIA, G. E.; ROBB, M. A.; CHEESEMAN, J. R.; MONTGOMERY, Jr., J. A.; VREVEN, T.; KUDIN, K. N.; BURANT, J. C.; MILLAM, J. M.; IYENGAR, S. S.; TOMASI, J.; BARONE, V.; MENNUCCI, B.; COSSI, M.; SCALMANI, G.; REGA, N.; PETERSSON, G. A.; NAKATSUJI, H.; HADA, M.; EHARA, M.; TOYOTA, K.; FUKUDA, R.; HASEGAWA, J.; ISHIDA, M.; NAKAJIMA, T.; HONDA, Y.; KITAO, O.; NAKAI, H.; KLENE, M.; LI, X.; KNOX, J. E.; HRATCHIAN, H. P.; CROSS, J. B.; BAKKEN, V.; ADAMO, C.; JARAMILLO, J.; GOMPERTS, R.; STRATMANN, R. E.; YAZYEV, O.; AUSTIN, A. J.; CAMMI, R.; POMELLI, C.; OCHTERSKI, J. W.; AYALA, P. Y.; MOROKUMA, K.; VOTH, G. A.; SALVADOR, P.; DANNENBERG, J. J.; ZAKRZEWSKI, V. G.; DAPPRICH, S.; DANIELS, A. D.; STRAIN, M. C.; FARKAS, O.; MALICK, D. K.; RABUCK, A. D.; RAGHAVACHARI, K.; FORESMAN, J. B.; ORTIZ, J. V.; CUI, Q.; BABOUL, A. G.; CLIFFORD, S.; CIOSLOWSKI, J.; STEFANOV, B. B.; LIU, G.; LIASHENKO, A.; PISKORZ, P.; KOMAROMI, I.; MARTIN, R. L.; FOX, D. J.; KEITH, T.; AL-LAHAM, M. A.; PENG, C. Y.; NANAYAKKARA, A.; CHALLACOMBE, M.; GILL, P. M. W.; JOHNSON, B.; CHEN, W.; WONG, M. W.; GONZALEZ, C.; POPLE, J. A. *Gaussian 03, revision C.02*. Wallingford: Gaussian, 2004.

FRISCH, M. J.; POPLE, J. A.; BINKLEY, J. S. Self - consistent molecular orbital methods 25. Supplementary functions for Gaussian basis sets. *Journal of Chemical Physics,* New York, v. 80, n. 7, p. 3265-3270, 1984.

HARIHARAM, P. C.; POPLE, J. A. The influence of polarization functions on molecular orbital hydrogenation energies. *Theoretica Chimica Acta*, Berlin, v. 28, n. 3, p. 213-222, 1973.

HEHRE, W. J.; DITCHFIELD, R.; POPLE, J. A. Self—Consistent Molecular Orbital Methods. XII. Further Extensions of Gaussian—Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules. *Journal of Chemical Physics*, New York, v. 56, p. 2257-2262, 1972.

KRISHNAN, R.; FRISCH, M. J.; POPLE, J. A. Self - consistent molecular orbital methods. XX. A basis set for correlated wave functions. *Journal of Chemical Physics*, New York, v. 72, n. 1, p. 650-655, 1980.

MARQUES, R. N.; MELIOS, C, B.; PEREIRA, N. C. S.; SIQUEIRA, O. S.; MORAES, M.; MOLINA, M.; IONASHIRO, M. Complexation of some trivalent lanthanides, scandium(III) and thorium(IV) by benzylidenepyruvates in aqueous solution. J*ournal of Alloys and Compounds*, Lausanne, v. 249, n. 1/2, p. 102-105, 1997.

MIYANO, M. H.; MELIOS, C. B.; RIBEIRO, C. A.; REDIGOLO, H.; IONASHIRO, M. The preparation and thermal decomposition of solid state compounds of 4-dimethylaminobenzylidenepyruvate and trivalent lanthanides and yttrium. *Thermochimica Acta*, Amsterdam, v. 221, n. 1, p. 53-62, 1993.

MIYAZAKI, M.; SHIMOISHI, Y.; MIYATA, H.; TÔEI, K. The reaction of dicarboxylic acids containing ether linkages with alkaline earth metals. *Journal of Inorganic and Nuclear Chemistry*, New York, v. 36, n. 9, p. 2033-2038, 1974.

NOTARIO, R.; CASTAÑO, O.; ABBOUD, J. L. M.; GOMPERTZ, R.; FRUTOS, L. M.; PALMEIRO, R. Organic Thermochemistry at High ab Initio Levels. 1. A G2 (MP2) and G2 Study of Cyclic Saturated and Unsaturated Hydrocarbons (Including Aromatics). *The Journal of Organic Chemistry*, Easton, v. 64, n. 25, p. 9011-9014, 1999.

OLIVEIRA, L. C. S.; MELIOS, C. B.; SPIRANDELI CRESPI, M.; RIBEIRO, C. A.; IONASHIRO, M. Preparation and thermal decomposition of solid state compounds of 4-methoxybenzylidenepyruvate and trivalent lanthanides and yttrium. *Thermochimica Acta*, Amsterdam, v. 219, p. 215-224, 1993.

PEREIRA. N. C. S.; MELIOS, C. B.; MARQUES, R. N.; SIQUEIRA, O. S.; MORAES, M.; MOLINA, M.; IONASHIRO, M. 4-Dimethylaminocinnamylidenepyruvic acid: synthesis, characterization and complexation with trivalent lanthanides, yttrium(III), scandium(III), thorium(IV) and uranium(VI) in aqueous solution. *Journal of Alloys and Compounds*, Lausanne, v. 249, n. 1/2, p. 94-98, 1997.

RASERA, D. E.; OLIVEIRA, L. C. S.; MELIOS, C. B.; IONASHIRO, M. The preparation and thermal decomposition of some metal compounds of 4-dimethylaminobenzylidenepyruvate in the solid state. *Thermochimica Acta*, Amsterdam, v. 250, n. 1, p. 151-163, 1995.

SIM, F.; CHIN, S.; DUPUIS, M.; RICE, J. E. Electron correlation effects in hyperpolarizabilities of p-nitroaniline. *The Journal of Physical Chemistry, Washington*, v. 97, n. 6, p. 1158-1163, 1993.

SIQUEIRA, O. S.; MELIOS, C. B.; IONASHIRO, M.; MORAES, M.; MOLINA, M. Complexation of some trivalent lanthanides, scandium(III) and thorium(IV) by benzylidenepyruvates and cinnamylidenepyruvate in aqueous solution. *Journal of Alloys and Compounds,* Lausanne, v. 225, n. 1/2, p. 267-270, 1995.

YANG, M.; JIANG, Y. A theoretical study of second hyperpolarizabilities for donor–acceptor–donor molecules. *Physical Chemistry Chemical Physics*, Cambridge, v. 3, n. 2, p. 167-171, 2001.

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