CIENCIA 5(3), 241-248, 1997
Maracaibo, Venezuela

Density functional studies of molecular polarizabilities. Part 2: Fulvene

Alan Hinchliffe[1] *and Humberto J Soscún M.*[2,*]
[1]*Department of Chemistry, UMIST, Sackville Street, Manchester M60 1QD, UK*
[2]*Departamento de Química, Facultad Experimental de Ciencias, La Universidad del Zulia*
Apartado 526. Maracaibo, Venezuela

Recibido: 17-07-97. Aceptado: 27-11-97

Abstract

We report accurate *Ab Initio* studies of the dipole polarizabilities of fulvene at both the Hartree Fock HF and density functional (BLYP formulation) levels of theory. The molecular geometry was optimized with the following basis sets; STO-3G, 6-31G, 6-31G* and the dipole polarizability calculated with the corresponding geometry at both the HF and BLYP levels of theory. The molecular geometry was then optimized at the HF/6-311G(3d,2p) level of theory, and dipole polarizabilities were calculated using this geometry using both HF and BLYP methods. The BLYP procedure gives small but significant differences from the corresponding HF results. We also give AM1, MNDO and PM3 polarizability calculations for comparison.

Key words: *Ab initio*; density functional; dipole polarizability; fulvene.

Estudios del funcional densidad de polarizabilidades moleculares. Parte 2: Fulveno

Resumen

En el presente trabajo reportamos estudios *Ab initio* de la polarizabilidad dipolar de la molécula de fulveno utilizando los niveles de teoría Hartree Fock HF y funcional de la densidad (formulación BLYP). La geometría molecular fue optimizada con los siguientes conjuntos base: STO-3G, 6-31G, 6-31G* y la polarizabilidad molecular calculada con la corespondiente geometría de ambos niveles de teoría HF y funcional de la densidad. La geometría molecular fue luego optimizada a nivel HF/6-311G(3d,2p), y la polarizabilidad dipolar calculada usando esta geometría con los métodos HF y BLYP. El procedimiento BLYP reporta pequeñas pero significativas diferencias con respecto a los resultados obtenidos con el método HF. También reportamos la comparación de las polarizabilidades calculadas con los métodos AMI, MNDO y PM3.

Palabras clave: *Ab initio;* densidad funcional; fulveno; polarizabilidades dipolares.

Introduction

The electric dipole moment $\mathbf{p}_e$ of a molecule is a quantity of fundamental importance in structural chemistry. When a molecule is subject to an external electric field **E**, the molecular charge density rearranges and hence the dipole moment can change (1). This change is described by the equation:

---

* Author to whom the correspondence should be addressed.

$$p_e(E) = p_e(E=0) + \alpha.E + \frac{1}{2}E.\beta.E + .. \quad [1]$$

where α is a second rank tensor property called the dipole polarizability, and β is the first of a series of dipole hyperpolarizabilities. Here $\mathbf{p_e(E=0)}$ is the electric dipole moment in the absence of a field, and $\mathbf{p_e(E)}$ is the dipole moment with the field. $\mathbf{p_e(E=0)}$ is usually referred to as the permanent electric dipole moment. The hyperpolarizabilities are known to be small, and their effect is minimal for weak electric fields. They are however important quantities when the electric field is large. For a molecule such as benzene that has a centre of symmetry, the first hyperpolarizabilities are identically zero.

Because the electric dipole moment changes when an external field is applied, the molecular energy W also changes according to the equation

$$W(E) = W(E=0) - p_e.E - .. \quad [2]$$

Molecular polarizabilities and hyperpolarizabilities can be calculated from either expression. In the early days, authors used (numerical) finite difference techniques. In recent years, direct analytical differentiation of the electric dipole moment or molecular energy with respect to the applied field has become the accepted route to these properties, provide that an analytical expression has been evaluated for the particular level of theory.

It has long been known that those organic molecules that have conjugated π-electron systems show interesting non-linear optical behavior. Studies of the dipole polarizability and hyperpolarizabilities of such conjugated molecules are therefore timely because of their importance in the new experimental field of non-linear optics.

In an earlier paper, we reported our DFT results for benzene. Benzene of course obeys Hückel's 4n+2 rule and is aromatic. Fulvene I (Figure 1) is often quoted as a "non-con- jugated analogue" of benzene (2) since it has the same number of π electrons.

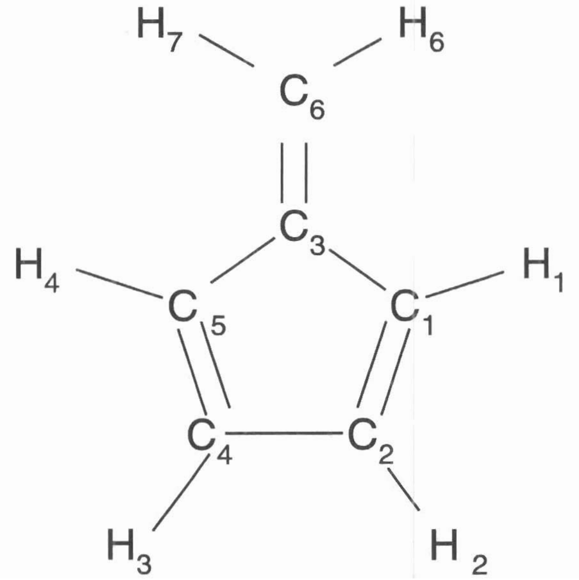

Figure 1. Fulvene I. The molecule lies in the xy plane and the y axis is the symmetry axis.

Fulvenes have been known to experimentalists for many years and they have the olefinic properties of polyenes but are characterized by a tendency of the five membered ring to carry negative charge.

Over the years, a number of authors have reported quantum mechanical studies of the dipole polarizability (and dipole hyperpolarizability) of such molecules. In view of the size of systems such as fulvene, benzene, naphthalene and anthracene, most of the calculations to date have been done at the empirical or semi-empirical level of theory. In a later section, we will report AM1, MNDO and PM3 results; some semi-empirical packages such as MOPAC have polarizability calculations built in as options, once the Hartree-Fock wavefunction has been determined.

In a series of papers, we have reported the results of good quality *Ab Initio* calculations of the dipole polarizabilities of a range of conjugated molecules (3). Our calculations were mostly made with good quality atomic orbital Gaussian basis sets and at the Hartree Fock (HF) level of theory.

It is usually possible to obtain decent agreement with experiment for the dipole polarizability α provided that a careful choice of atomic orbital basis set is made.

Until fairly recently, the most usual method of treating electron correlation in such large molecules was the Möller Plesset perturbation technique. Such calculations are labelled MPn where n is the order of perturbation. Most post-HF techniques have a common feature that they are ex-tremely expensive in computer resource. MPn calculations usually involve the semi-transformation of integrals from the atomic orbital basis set to the molecular orbital basis set, and this single step can be prohibitive in disk space.

In recent years, density functional techniques have received a great deal of attention in the literature. The idea is to start from the HF electronic energy expression (4):

$$\varepsilon_{el} = trace(\mathrm{h_1P_1}) + \frac{1}{2} trace(\mathrm{P_1J}) - \frac{1}{4} trace(\mathrm{P_1K}) \quad [3]$$

which relates the electronic energy for a one-determinant closed shell ε_{el} to the electron density matrix $\mathbf{P}_1$, the matrix of one-electron integrals $\mathbf{h}_1$, the coulomb matrix $\mathbf{J}$ and the exchange matrix $\mathbf{K}$.

Density functional theory seeks to write the energy expression as

$$\varepsilon_{el} = trace(\mathrm{h_1P_1}) + \frac{1}{2} trace(\mathrm{P_1J}) + \varepsilon_x + \varepsilon_c \quad [4]$$

where ε_X is the exchange functional and ε_C is the correlation functional, which is of course zero for HF methods. In order to calculate ε_X and ε_C it is necessary to assume some functional form for the two potentials and then calculate the contribution to the electronic energy as an integral over the electron density (and occasionally the gradient of the electron density). These calculations are usually performed numerically and tend to consume less computer resource than traditional MPn calculations.

Several different functionals are available for both ε_X and for ε_C. For example, GAUSSIAN94 has three inbuilt exchange functionals (Slater; Xα and Becke-88) and six inbuilt correlation functionals (Vosko Wilk and Nusair = VWN; Modified VWN Lee Yang and Parr; Perdew Local; Perdew 86 and Perdew/Wang 91) (5).

The application of density functional methods (6) to the study of molecular properties is a recent development, and there is no great pool of expertise to suggest that one formulation is better than any other for the calculation of a given property.

As part of a larger study, we have investigated the density functional treatment of the polarizabilities of the interesting "non-conjugated" hydrocarbon, fulvene, and the aim of this paper is to present our results.

Calculations

There are a small number of *Ab Initio* calculations of the polarizability of fulvene in the literature, ranging from minimal basis set HF calculations to large basis set MP2 and many body ones (ref, Perez). There is very little experimental data available for comparison.

The basis sets used were the standard GAUSSIAN ones. The presence of a * indicates a single d-type polarization func-tion on the heavy atoms. The notation (3d, 2p) means that each atomic centre was augmented with polarization functions as follows; 2 p-type on each hydrogen and three d-type on each carbon.

Other authors have taken a different approach and have sought to systematically develop basis sets of highly polarized functions designed to provide accurate estimates of properties such as polarizabilities (7).

For the smaller basis sets, we followed a procedure where the molecular geometry was first optimised at HF level for a given basis set, the HF polarizability was calculated and then the polarizability was also calculated using DFT theory at the same molecular geometry. For this series of calculations we used the BLYP DFT formulation (ie, we used the Becke 88 exchange functional and the Lee Yang Parr correlation functional).

Ideally one would optimize the molecular geometry using DFT theory before calculating the polarizability and if ones goal were the calculation of force constants then this step would be essential because they are calculated as the second derivatives of the energy with respect to the corresponding normal coordinate *calculated at the potential minimum.* Dipole polarizabilities are usually calculated as derivatives of the dipole (or energy) expression given above with respect to the applied electric field, and the procedure we have used is therefore acceptable (and much less costly).

For the very large basis set calculations, we optimized the geometry at the HF/6-311G(3d,2p) level of theory and then augmented this basis set with the diffuse functions "++" for HF and BLYP calculations of the dipole polarizability.

Geometries and properties

Cartesian coordinates for the HF/STO-3G and HF/6-311G(3d,2p) optimized structures are given for reference in Table 1.

Salient C-C bond length data from the HF/6-311G(3d,2p) calculation is shown as Figure 2.

This reinforces the view that fulvene is essentially olefinic in nature. Atomic population analysis indices calculated according to Mulliken's procedure are shown for the same basis set in Figure 3, and these reinforce the view of the acidic nature of the ring carbons.

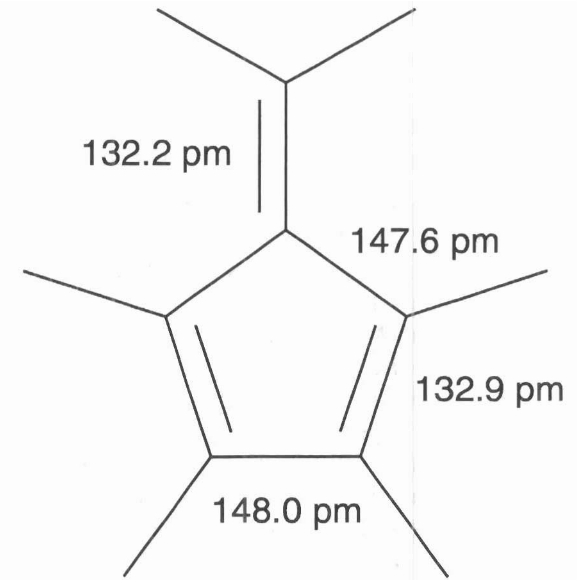

Figura 2. Salient C-C Bond Lengths.

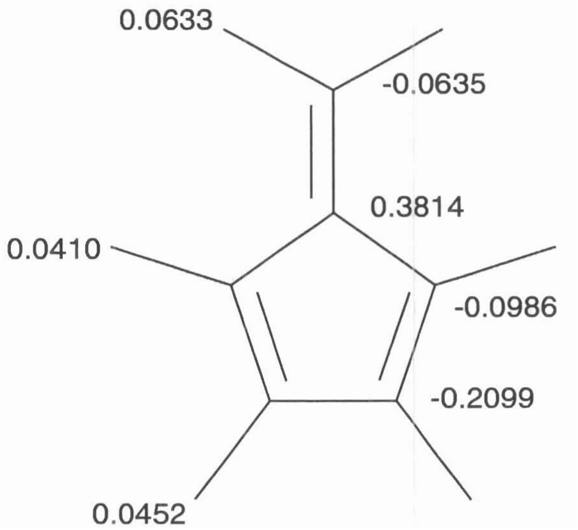

Figura 3. Mulliken Population Analysis Charges for Atoms.

Tabla 1

HF energies and cartesian coordinates for fulvene at the HF/STO-3G and HF/6-311G(3d,2p) levels of theory. The atomic unit of energie is the Hartree, E_H and it has an SI value of 4.3598×10^{-18} J

HF/STO-3G, Energy= -227.824003 E_H

Atom	x / Anstrom	y / Anstrom	z / Anstrom
C1	1.181399	-0.140864	0.0
C2	0.746124	-1.390748	0.0
C3	0.0	0.775268	0.0
H1	2.204131	0.205484	0.0
C4	-0.746117	-1.390758	0.0
C5	-1.181394	-0.1140878	0.0
C6	-0.000010	2.094080	0.0
H2	1.344155	-2.291454	0.0
H3	-1.344155	-2.291464	0.0
H4	-2.204127	0.205464	0.0
H5	-0.918433	2.667677	0.0
H6	0.918400	2.667677	0.0

HF/6-311G, Energy= -227.824003 E_H

Atom	x / Anstrom	y / Anstrom	z / Anstrom
C1	1.174948	-0.131537	0.0
C2	0.739927	-1.387776	0.0
C3	0.0	0.761850	0.0
H1	2.190685	0.205100	0.0
C4	-0.739897	-1.387791	0.0
C5	-1.174938	-0.131560	0.0
C6	-0.000035	2.084124	0.0
H2	1.345282	-2.271195	0.0
H3	-1.345223	-2.271229	0.0
H4	-2.190676	0.205062	0.0
H5	-0.915831	2.644173	0.0
H6	0.915728	2.644227	0.0

Table 2

Electric dipole moment/D. 1Debye is approximately 3.336 10^{-30} C m

Basis set	HF	BLYP
STO-3G	0.4333	0.5310
6-31G	0.5764	0.5551
6-31G*	0.4312	0.4899
6-311G(3d,2p)	0.4049	-
6-311++G(3d,2p)	0.4192	0.5162
Experiment	0.424 ± 0.001	

Table 3

Polarizability calculations at the HF level of theory. Table values are atomic units (au). The atomic unit of polarizability is $e^2 a_0^2 E_H^{-1}$ and the following conversion factors are appropriate; 1 au of polarizability = 1.6488 10^{-41} $C^2m^2J^{-1}$, and this is equivalent to 1.4818 10^{-25} cm^3

Level of theory	α_{xx}/au	α_{yy} /au	α_{zz} /au	$<\alpha>$/au	$\Delta\alpha$/au
HF/STO-3G	33.824	65.329	6.556	35.236	50.943
HF/6-31G	54.487	97.831	18.798	57.039	68.551
HF/6-31G*	55.139	96.426	21.068	57.544	65.362
HF/6-311++G(3d,2p)	65.397	105.460	45.779	72.212	52.686

The electric dipole moment has been measured by using gas-phase microwave spectroscopy (8). Table 2 below shows our calculated values for this property.

The HF calculations give reasonable agreement with experiment, but the BLYP results are unacceptably large.

Polarizabilities

Of particular importance for the calculation of dipole polarizability are the extra diffuse functions on each centre, and these are indicated by the notation ++. The largest basis set 6-311++G(3d,2p) involved 342 primitive gaussians contracted to 252 basis functions.

In the principal axis system, we write the three components of the tensor as α_{aa}, α_{bb} and α_{cc}. Quantities of interest to experimentalists are the mean polarizability $<\alpha>$ and the anisotropy $\Delta\alpha$, defined in terms of the principal values as

$$\langle\alpha\rangle = \frac{1}{3}(\alpha_{aa} + \alpha_{bb} + \alpha_{cc}) \qquad [5]$$

$$\Delta\alpha = \left(\frac{1}{3}\left((\alpha_{aa} - \alpha_{bb})^2 + (\alpha_{aa} - \alpha_{cc})^2 + (\alpha_{bb} - \alpha_{cc})^2\right)\right)^{\frac{1}{2}} \qquad [6]$$

In the case of a molecule with symmetry axes, the principal axes correspond to these (x,y,z) symmetry axes and so we will label the principal axes as x,y,z in the obvious manner. Our Hartree Fock results are shown in Table 3.

As can be seen from Table 3, the polarizability component perpendicular to the ring is the most difficult to calculate. Minimal basis sets give unacceptably small values for this polarizability component.

Table 4
Semi-empirical calculations of polarizability

Model Hamiltonian	α_{xx}/au	α_{yy} /au	α_{zz} /au
AM1	50.367	98.826	9.890
MNDO	48.750	100.572	8.940
PM3	45.590	92.073	10.470

Table 5
Polarizability calculations at the BLYP density functional level of theory

Level of theory	α_{xx}/au	α_{yy} /au	α_{zz} /au	$<\alpha>$/au	$\Delta\alpha$/au
BLYP/STO-3G	35.406	60.952	7.302	34.553	46.480
BLYP/6-31G	58.227	91.507	19.382	56.372	62.524
BLYP/6-31G*	59.395	91.767	21.337	57.500	61.060
BLYP/6-311++G(3d,2p)	71.446	103.973	46.385	73.935	50.012

As mentioned earlier, several semi-empirical packages such as MOPAC have polarizability calculations as an option. Table 4 shows the results of such calculations; in each case, the molecular geometry was optimized before calculating the polarizabilities.

The in-plane polarizabilities are competitive with those obtained from *Ab Initio* Hartree Fock calculations using (eg) a 6-31G or 6-31G* basis set, which is obviously very impressive given the vast difference in computer resource needed. But the semi-empirical calculations fail for the perpendicular component in just the same way that the minimal basis set *Ab Initio* calculation fails.

For the density functional calculations the polarizability was calculated at the optimum geometry and the results are shown in Table 5.

Comparing the HF and the BLYP results for the largest basis set we see a small decrease in the yy and the zz components but a 10% increase in the xx component.

Acknowlegments

The authors thanks to CONICIT of Venezuela and CONDES of La Universidad del Zulia for partial support, and to Javier Hernández for valuable help.

References

1. HINCHLIFFE A., MUNN R.W. ***Molecular Electromagnetism,*** John Wiley and Sons Ltd, Chichester, 1985
2. DAY J.H. ***Chem Rev*** 53:167, 1953.
3. HINCHLIFFE A., SOSCÚN-M H.J. ***J Molec Struct*** 300:1, 1993.
4. HINCHLIFFE A. ***Modelling Molecular Structures,*** John Wiley & Sons Ltd, Chichester, 1996.
5. Gaussian 94, Revision B.2,
Frisch M.J., Trucks G.W., Schlegel H.B., Gill P.M.W.,
Johnson B.G., Robb M.A., Cheeseman J.R., Keith T.,

Petersson G.A., Montgomery J.A., Raghavachari K.,
Al-Laham M.A., Zakrzewski V.G., Ortiz J.V., Foresman J.B.,
Peng C.Y., Ayala P.Y., Chen W., Wong M.W., Andres J.L.,
Replogle E.S., Gomperts R., Martin R.L., Fox D.J.,
Binkley J.S., Defrees D.J., Baker J., Stewart J.J.P.,
Head-Gordon M., Gonzalez C., Pople J.A., Gaussian, Inc., Pittsburgh PA, 1995.

6. PARR R.G., YANG W. ***Density Functional Theory of Atoms and Molecules,*** Oxford Univ. Press, Oxford, 1989.
7. PEREZ J.J., SADLEJ A.J. ***J Molec Structure (THEOCHEM)*** 371 (1996) 31 and references therein.
8. BARON P.D., BROWN R.D., BURDEN F.R., DOMAILLE P.J., KENT J.E. ***J Mol Spectrosc*** 43: 401, 1972.