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Density Functional Studies of Molecular Polarizabilities. 7. Anthracene and Phenanthrene*

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Abstract: We report accurate *Ab Initio* studies of the static dipole polarizabilities of anthracene and phenanthrene. Geometries were optimized at the HF/6-311G(3d,2p) level of theory. Dipole polarizabilities were calculated at the HF/6-311++G(3d,2p) and BLYP/6-311++G(3d,2p) levels of theory, using HF/6-311G(3d,2p) geometries. The calculated dipole polarizabilities for anthracene are compared with experiment. Inclusion of electron correlation using the BLYP procedure increases the L and M components of the dipole polarizability, but not the perpendicular (N) component. Examination of corresponding BLYP results for the polyacene series benzene, naphthalene and anthracene shows that the normal component of the dipole polarizability scales linearly with the number of benzene ring units, with an increment of 20.8 au. The medium component also scales linearly with an increment of 42.8 atomic units. The long component does not scale linearly.
Semi-emiprical AM1 calculations are also given for comparison; the normal component of the dipole polarizability tensor is poorly represented by such calculations.

Keywords: *Ab Initio*, Anthracene, phenanthrene, dipole polarizability, molecular geometry, density functional theory, AM1.

Introduction

The electric moments of a molecule are quantities of fundamental importance in structural chemistry. When a molecule with permanent electric dipole moment $\mathbf{p}_e$ is subject to an external constant electrostatic field **E**, the change in the dipole moment can be written [1]

$$p_{e,j}(\mathbf{E}) = p_{e,j}(\mathbf{0}) + \sum_{j=x}^{z} \alpha_{ij} E_j + \frac{1}{2}\sum_{j=x}^{z}\sum_{k=x}^{z} \beta_{ijk} E_j E_k + \ldots \tag{1}$$

Here $p_{e,j}$ is the jth Cartesian component of the dipole moment, $\mathbf{p}_e(\mathbf{0})$ is the dipole in the absence of a field and $\mathbf{p}_e(\mathbf{E})$ is the dipole moment in the presence of the field. The six quantities α_{ij} define the dipole polarizability tensor, the quantities β_{ijk} define the first dipole hyperpolarizability and so on.

Equation (1) is often written in tensor notation as

$$\mathbf{p}_e(\mathbf{E}) = \mathbf{p}_e(\mathbf{0}) + \alpha::\mathbf{E} + \frac{1}{2}\beta:\mathbf{EE} + \ldots \tag{2}$$

Hyperpolarizabilities are generally small and their effect is minimal for weak electric fields. They are important when the applied electric field is large. There has recently been an intense search for molecules with large non-zero hyperpolarizabilities [2], since these substances have potential as the constituents of non-linear optical materials.

Equations similar to (1) can be written for the higher electric moments, and the quantities of interest are (for example) the quadrupole polarizability and octupole hyperpolarizabilities. Such quantities are rarely encountered in Chemistry.

The energy U of the charge distribution also changes according to the equation

$$U(\mathbf{E}) = U(\mathbf{0}) - \sum_{i=x}^{x} p_{e,i}(\mathbf{0}) E_i - \frac{1}{2}\sum_{i=x}^{z}\sum_{j=x}^{z} \alpha_{ij} E_i E_j - \frac{1}{6}\sum_{i=x}^{z}\sum_{j=x}^{z}\sum_{k=x}^{z} \beta_{ijk} E_i E_j E_k - \ldots \tag{3}$$

which can again be written more compactly in tensor notation

$$U(\mathbf{E}) = U(\mathbf{0}) - \mathbf{p}_e(\mathbf{0}).\mathbf{E} - \frac{1}{2}\alpha:\mathbf{EE} - \frac{1}{6}.\beta:\mathbf{EEE} - \ldots. \tag{4}$$

The experimental determination of a molecular polarizability is far from straightforward, especially if the molecule has little or no symmetry. The mean polarizability

$$\langle\alpha\rangle = \frac{1}{3}\left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right)$$

can be determined from the refractive index n of a gas according to the equation

$$n = 1 + \frac{\langle\alpha\rangle p}{2 \in_0 k_B T} \tag{5}$$

where p is the pressure, k_B the Boltzmann constant, T the thermodynamic temperature and $\in_0$ the permittivity of free space. A key assumption in the derivation of equation (5) is that the individual mole-

cules are sufficiently far apart on average that they do not interact with each other.

In a condensed phase, the problem is more complicated because the separation between molecules is of the order of molecular dimensions and their interactions can no longer be ignored. The result is that each molecule is polarized not only by the external field but also by the field due to the surrounding molecules. The resultant field is known as the local field **F**, and it is usually written in terms of the dielectric polarization **P** as

$$\mathbf{F} = \mathbf{E} + \frac{L}{\in_0}\mathbf{P} \tag{6}$$

where L is the dimensionless Lorentz factor, which depends on the structure of the phase. L is strictly a tensor, and it can be shown that for cubic and isotropic phases the three principal values are equal to 1/3. This gives the Lorentz local field

$$\mathbf{F} = \mathbf{E} + \frac{1}{3\in_0}\mathbf{P} \tag{7}$$

The Lorenz-Lorentz equation

$$\frac{n^2 - 1}{n^2 + 2} = \frac{N\langle\alpha\rangle}{3\in_0 V} \tag{8}$$

gives a molecular expression for the polarizability, and it can be easily derived from equation (7). Here, N is the number of molecules in volume V.

In the case of molecules with a permanent dipole moment, it is necessary to take account of the orientation polarization. The resulting Debye equation

$$\frac{M}{\rho}\frac{\in_r - 1}{\in_r + 2} = \frac{N_A}{3\in_0}\left(\langle\alpha\rangle + \frac{p_e^2}{3k_B T}\right) \tag{9}$$

permits polarizabilities and dipole moments to be determined from measurements of the relative permittivity $\in_r$ and the density ρ as a function of temperature. M is the molar mass and N_A the Avogadro constant. Reliable results can only be obtained from dilute solutions [1].

The experimental techniques described above deal with infinitely dilute gases or make assumptions about the interactions between molecules in condensed phases. Laser Stark spectroscopy is a powerful experimental approach to the basic electric properties of isolated molecules in the gas phase. This type of spectroscopy utilises the interaction between a molecule and an external field. This interaction gives rise to shifts and splittings of individual rotational transitions, and an analysis of these shifts and splittings yields the tensor components of the dipole polarizability of the ground and vibronically excited states. Such a method requires a narrow band tuneable laser together with a molecular beam apparatus to produce isolated molecules, and a capacitor capable of generating an electric field of the order of 100 kV cm^{-1}. Okruss et. al [3] have recently exploited this technique to study benzene, and their paper reports the electric polarizabilities of the $S_0(^1A_{1g})$ ground electronic and the vibrationally excited 6^1 $S_1(^1B_{2u})$ state of benzene. Such accurate experimental data is hard to come by, because of the exacting

experimental requirements.

An alternative route to these properties is afforded by molecular modeling. Most dipole polarizability calculations for large molecules have been done at the empirical or semi-empirical level of theory. Indeed some semi-empirical packages such as MOPAC [4] have polarizability calculations built in as optional properties to be determined once the Hartree-Fock (HF) wavefunction has been calculated. There are a number of semi-empirical schemes in the literature and we will report later the results of AM1 calculations for the molecules under study.

Several authors have used *Ab Initio* techniques to study molecular polarizabilities. It is usually possible to obtain respectable agreement with experiment at the HF level of theory for the dipole polarizability tensor α provided that a careful choice of atomic orbital basis set is made. It is common knowledge that polarizabilities can only be calculated accurately from calculations employing extended basis sets. In particular, these basis sets have to include diffuse functions that can accurately describe the response of a molecular charge distribution to an external electric field. These diffuse (s and p) functions are needed in addition to the normal polarization functions; they are denoted by + and ++ in packages such as GAUSSIAN98 [5].

Once near the Hartree Fock limit, it is necessary to concern oneself with the correlation contribution to such properties. Until fairly recently, the most usual method of treating electron correlation in such molecules was the Muller Plesset perturbation technique. Such calculations are labelled MPn where n is the order of perturbation. Most post-HF techniques have the common feature that they are extremely 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 [6]

$$\varepsilon_{el} = trace\left(\mathbf{h}_1\mathbf{P}\right) + \frac{1}{2}trace(\mathbf{PJ}) - \frac{1}{4}trace(\mathbf{PK}) \tag{10}$$

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

Density functional theory (DFT) seeks to write the energy expression as

$$\varepsilon_{el} = trace\left(\mathbf{h}_1\mathbf{P}\right) + \frac{1}{2}trace(\mathbf{PJ}) + \varepsilon_X + \varepsilon_C \tag{11}$$

where ε_X is the exchange functional and ε_C the correlation functional, which is of course zero for HF wavefunctions. In order to calculate ε_X and ε_C it is necessary to assume some functional form to 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 performed numerically and tend to consume less computer resource than traditional MPn calculations. There are many variants on the form of the exchange and the correlation functional, most of which are based on the free-electron gas model.

The application of density functional methods to the study of molecular properties is a recent devel-

opment [7], 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. In traditional HF theory, one can increase the accuracy of a calculation by systematically extending the atomic orbital basis set, but in DFT the only way forward is to improve the basic model.

Polycyclic aromatic hydrocarbons have been the subject of very many theoretical and experimental studies. They have carcinogenic activities and they form various complexes [8].

In an earlier paper in this series [9] we reported corresponding Semi-empirical, *Ab Initio* HF and DFT studies on benzene. In the *Ab Initio* studies, we used a high quality basis set for geometry optimization and then calculated the polarizabilities at the same geometry but with diffuse functions added to the basis set. To use a common notation, we performed HF/6-311G(3d,2p) // HF/6-311++G(3d,2p) and HF/6-311G(3d,2p) // BLYP/6-311++G(3d,2p) polarizability calculations. We found that the effect of the BLYP density functional procedure was to increase the polarizability components in the molecular plane by some 5% but to leave the polarizability component normal to the molecular plane unchanged.

We reached similar conclusions for naphthalene [10].

The aim of this paper is to extend our studies to anthracene and phenanthrene.

Calculations

Geometries

All *Ab Initio* calculations were made using Gaussian98 [5] and both geometries were optimized at the HF/6-311G(3d,2p) level of theory. All AM1 semi-empirical calculations were made with MOPAC [4] and both geometries were optimized.

For the record, the *Ab Initio* total energies are given in Table 1.

Table 1. Ab Initio energies corresponding to optimized geometries.

Molecule	E/ hartree
Anthracene	-536.1323341
Phenanthrene	-536.1427035

There appears to be very little modern experimental structural data in the literature for these simple molecules. Of particular interest are the carbon-carbon bond lengths. The classic crystal data for anthracene is that of Cruickshank and Robertson [11]. Results are collected in Table 2, using the numbering scheme of Figure 1. Whilst fascinating to note that simple Huckel π-electron calculations appear to give the best agreement with experiment, it should be remembered that the experimental data refers to a crystal and the theoretical calculations refer to isolated molecules in the gas phase. *Ab Initio* calculations are generally reliable once electron correlation is included. Our *Ab Initio* geometry is the HF-optimized one.

The *Ab Initio* and AM1 results are given for phenanthrene in Table 3.

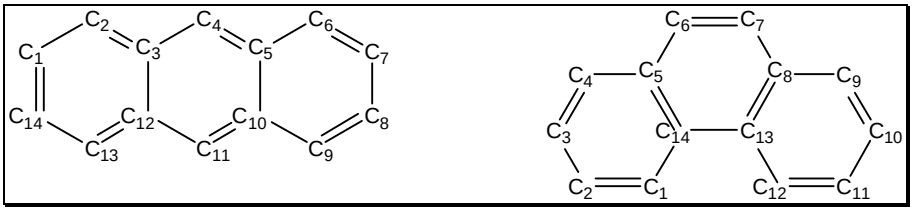

Figure 1. Numbering scheme.

Table 2. C-C bond lengths / pm for anthracene.

	HF/6-311G(3d,2p)	AM1	Huckel [12]	Experiment [11]
C_1-C_2	134.40	136.5	137.5	137.1 ± 0.6
C_2-C_3	143.47	143.3	141.4	142.4 ± 0.5
C_3-C_4	138.69	139.9	140.0	139.6 ± 0.4
C_3-C_{12}	142.18	142.9	142.4	143.6 ± 0.7
C_1-C_{14}	143.20	142.6	140.4	140.8 ± 1.0

Table 3. C-C bond lengths / pm for phenanthrene.

	HF/6-311G(3d,2p)	AM1
C_1-C_2	136.49	138.1
C_2-C_3	140.00	140.6
C_3-C_4	136.28	138.0
C_4-C_5	140.66	141.3
C_5-C_6	143.90	143.5
C_6-C_7	133.55	135.7
C_5-C_{14}	140.11	141.6
C_{13}-C_{14}	145.92	144.6
C_{14}-C_1	140.85	141.4

Polarizabilities

Early calculations of polarizability made use of the so-called finite field technique. Examination of equation (3) suggests that the way to include the effect of an external electrostatic field in a conventional Hartree Fock calculation is to add a perturbation $-\mathbf{p}_e(\mathbf{0}).\mathbf{E}$. to the HF Hamiltonian and then proceed with the HF calculation in the usual way. This defines the finite field method, which was widely used in early calculations of polarizabilities.

In recent years, gradient techniques have appeared and these are now the usual method for performing geometry optimisations. Examination of equation (3) shows that the first derivative of the energy with respect to a component of the electric field gives that component of the electric dipole moment, whilst the second derivative gives the polarizability and so on. In symbols

$$p_{e,x} = -\left(\frac{\partial U}{\partial E_x}\right)_0$$
$$\alpha_{xx} = -\left(\frac{\partial^2 U}{\partial E_x^2}\right)_0 \qquad (12)$$

where the subscript 0 means "evaluated at zero electric field **E** = **0**". Equally, the polarizability can be deduced as the gradient of the induced dipole

$$\alpha_{xx} = \frac{\partial p_{e,x}}{\partial E_x}$$

Modern calculations of electric properties therefore make use of gradient techniques, and packages such as Gaussian98 have this as an option.

For molecules with molecular symmetry, the principal axes of the polarizability tensor correspond to the symmetry axes. It is conventional in studies of the dipole polarizability of conjugated molecules to label these principal axes L (for "long"), M (for "medium") and N ("normal to the plane of the conjugated system"). The dipole polarizability tensor components are referred to as α_{LL}, α_{MM} and α_{NN}.

Dipole polarizability data for anthracene is given in Table 4. There are two other Ab Initio calculations in the literature, those of Hinchliffe and Chablo (HF/STO-4G) [13], and those of Perez et. al (who performed Hartree-Fock studies using two double zeta basis sets, referred to as DZ and DZ') [14]. There are several condensed-phase experimental studies in the literature and two typical ones are also shown in the Table.

Table 4. Polarizability data / au for anthracene. Atomic unit of polarizability is $e^2 a_0^2 E_h^{-1}$ (approximately 1.649×10^{-41} C^2 m^2 J^{-1}).

	α_{LL}	α_{MM}	α_{NN}	$\langle\alpha\rangle$
HF/STO-4G [13]	176	109	13	99
HF/DZ [14]	239	142	65	149
HF/DZ' [14]	254	152	75	160
HF/6-311++G(3d,2p)	264.6	157.2	86.2	169.3
BLYP/6-31++G(3d,2p)	293.8	166.7	86.3	182.3
AM1	251.5	147.4	20.2	139.7
Experiment [15] Cotton Mouton effect in benzene	238	173	103	171
Experiment [16] Kerr effect in CCl_4	367	174	154	232

The experimental values are generally in poor agreement with each other. The STO-4G results are in poor agreement with the other *Ab Initio* studies and with experiment. Minimal basis sets cannot be used for polarizability calculations. It is reassuring to see an immense improvement in the calculated values once a double zeta basis set is used, although the perpendicular (α_{NN}) component is again relatively poorly represented. AM1 results for the in-plane components are quite reasonable bearing in mind the relative cost of semi-empirical and *Ab Initio* studies. The perpendicular component is poorly represented by the AM1 method, due to the small number of basis functions inherent in the AM1 methodology.

The inclusion of electron correlation using density functional theory results in significant improvements in the long and medium components but has no effect on the normal component. This behaviour was noted in our earlier studies on benzene and naphthalene.

Dipole polarizability data for phenanthrene is given in Table 5.

Table 5. Polarizability data /au for phenanthrene.

	α_{LL}	α_{MM}	α_{NN}	$<\alpha>$
HF/6-311++G(3d,2p)	233.2	164.9	86.0	161.4
BLYP/6-31++G(3d,2p)	258.1	177.4	86.0	173.8
AM1	223.1	151.4	19.9	131.5

On the basis of the corresponding results for anthracene, the *Ab Initio* data for phenanthrene is likely to give a very good prediction of the true values.

Discussion

There has been some discussion in the literature [3] as to correlation between the dipole polarizabilities of the polyacenes. In Table 6 we collect together our results at the BLYP/6-311++G(3d,2p) level for benzene, naphthalene and anthracene.

Table 6. Polarizability data /au for the polyacenes.

	α_{L}	α_{M}	α_{N}	$<\alpha>$
Benzene	81.1	81.1	44.7	68.9
Naphthalene	170.5	123.9	65.7	120.0
Anthracene	293.8	166.7	86.3	182.3

The normal component is seen to scale as the number of benzene ring units, with an increment of 20.8 atomic units. The M component scales as the number of benzene rings, with an increment of 42.8 atomic units. The L component does not scale linearly with the number of benzene ring units.

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