Density functional studies of the dipole polarizabilities of the linear polyacenes benzene through nonacene

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Abstract: We report \textit{Ab Initio} studies of the electric dipole polarizability of the linear polyacene series benzene through nonacene. A number of \textit{Ab Initio} studies were done at different levels of theory for benzene, with all remaining \textit{Ab Initio} calculations being at the B3LYP/6-311G(2d,1p)//B3LYP/6-311+G(2d,1p) level of theory. We find that the NN tensor component shows a constant increment of 20 atomic units per ring. AM1 and QSAR-quality empirical calculations show poor absolute agreement with the \textit{Ab Initio} results, but give excellent statistical correlation coefficients with the \textit{Ab Initio} values. This implies that the results of such cheaper calculations can be suitably scaled for predictive purposes.

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1 Introduction

The electric dipole moment $p_e$ 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 will usually rearrange and so the dipole moment and the molecular mutual potential energy $U$ will also change \cite{1}. This change can be described

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by the equations

\[ p_e = p_{e,0} + \alpha : E + \frac{1}{2} \beta : EE + \ldots \]  
\[ U = U_0 - p_e : E - \frac{1}{2} \alpha : EE - \frac{1}{6} \beta : EEE - \ldots \]  

(1)  

(2)

Here \( \alpha \) is a second rank tensor property called the (dipole) polarizability, and \( \beta \) is the first of an infinite series of dipole hyperpolarizabilities. The electric dipole moment in the absence of an external field is written \( p_{e,0} \).

The principal routes to dipole polarizability are through studies of refractive index and relative permittivities, through Rayleigh and Raman scattering and through the quadratic Stark effect. Mention must also be made of various non-linear optical phenomena such as hyper-Raman scattering and the electro-optic Kerr effect. The most easily derived quantity is the mean value

\[ \langle \alpha \rangle = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \]  

(3)

The individual components and anisotropies are harder to come by [1].

Polarizabilities are also of great interest in the field of non-linear optics since they show interesting frequency dependencies for time-dependent fields [2, 3]. They are also used in QSAR studies, along with other indicators such as log (P), surface area and atomic partial charges [4].

Spectroscopists have long been interested in benzenoid hydrocarbons, but a satisfactory theory of their spectra was not developed until there had been a detailed classification of their absorption bands. This important task was first undertaken by E. Clar in his classic work *Aromatische Kohlenwasserstoffe* [5]. The linear polyacene series is defined as \( n \) fused rings, shown in Figure 1 (with \( n = 9 \)).

![Nonacene](image)

Fig. 1 Nonacene

There have been a good number of experimental studies of the polarizability of benzene, a few for naphthalene (often reported together with azulene), and significantly fewer for anthracene (sometimes reported with phenanthrene). There have also been a good number of theoretical studies of these three systems.

It is traditional to label the Cartesian axes of such linear polyacene molecules L (long), N (normal to the molecular plane) and M (medium), and so the mean polarizability is written

\[ \langle \alpha \rangle = \frac{1}{3} (\alpha_{LL} + \alpha_{MM} + \alpha_{NN}) \]  

(4)

Representative experimental data is shown in Table 1. The SI unit of dipole polarizability is \( \text{F m}^2 \) (\( = \text{C}^2 \text{m}^2 \text{J}^{-1} \)) and the atomic unit is therefore \( e^2 a_0^2 E_0^{-1} \). It follows that
1 atomic unit = $1.6488 \times 10^{-41}$ C$^2$ m$^2$ J$^{-1}$. For historical reasons, dipole polarizabilities are sometimes quoted as \textit{polarizability volumes} and an atomic unit is therefore equivalent to $1.4818 \times 10^{-25}$ cm$^3$.

| Molecule | Technique | $<\alpha>$/atomic unit |
|----------|-----------|---------------------|
| Benzene [6] | Static DC-Kerr effect | 66.80 |
| | Static Rayleigh Scattering (RS) | 67.48 |
| | Dynamic RS at 632.8 nm | 70.05 |
| Naphthalene | Combination of various electro-optic measurements [7] | 118.7 |
| | Anisotropic refraction of light from crystal [8] | 117.4 |
| Anthracene | Cotton Mouton effect in benzene [9] | 171 |
| | Kerr effect in CCl$_4$[10] | 232 |

\textbf{Table 1} Representative experimental data.

It seems clear from Table 1 that there is a qualitative relationship between $<\alpha>$ and the number of rings for these compounds. The aim of this paper is to investigate this relationship using state-of-the-art \textit{Ab Initio} results.

## 2 Calculations

The principles involved in \textit{Ab Initio} polarizability calculations are well understood [4] and can be illustrated by our results for benzene shown in Table 2. The calculations here refer to an isolated gas-phase molecule at 0 K. Naturally, such a molecule has zero-point energy and there is a small but finite contribution to the polarizability from this effect [11]. No attempt was made to estimate the vibrational contributions in this paper.

| Level of Theory | Energy/au | $\alpha_{LL}/au$ | $\alpha_{MM}/au$ | $\alpha_{NN}/au$ | $<\alpha>/au$ |
|-----------------|-----------|------------------|------------------|------------------|---------------|
| HF/6-31G(2d,1p) | -230.767200 | 72.14 | 30.81 | 58.36 |
| HF/6-311+G(2d,1p) | -230.764895 | 75.56 | 43.07 | 64.68 |
| HF/6-311++G(2d,1p) | -230.764966 | 75.59 | 43.17 | 64.80 |
| B3LYP/6-311G(2d,1p) | -232.319983 | 75.60 | 30.75 | 60.60 |
| B3LYP/6-311+G(2d,1p) | -232.317426 | 79.43 | 42.98 | 67.28 |
| B3LYP/6-311++G(2d,1p) | -232.317492 | 79.49 | 43.07 | 67.35 |
| B3LYP/aug-cc-pVDZ | -232.317492 | 82.83 | 45.04 | 70.23 |
| B3LYP/aug-cc-pVTZ | -232.317492 | 81.63 | 44.79 | 69.35 |
| 'Standard' | -232.317492 | 79.38 | 42.97 | 67.24 |

\textbf{Table 2} Representative Ab Initio static polarizability calculations for benzene.

All calculations were done using Gaussian 03W [12], with internal basis sets, integration points, cutoffs etc. With the exception of the final row labelled ‘Standard’, all calculations were begun by optimizing the molecular geometry at the level of theory specified; polarizabilities were then calculated at the same level of theory using the stan-
standard Gaussian 03W keyword ‘Polar’. This keyword means that the polarizabilities were obtained analytically rather than by numerical differentiation.

Examination of the values shown in Table 2 illustrates the following well-known conclusions.

- Extended, polarized basis sets are needed for polarizability calculations.
- A treatment of electron correlation is essential.
- Diffuse functions (+, ++ or aug) need to be included in the basis set.

A compromise always has to be made between the expected accuracy of a calculation and the availability of computer resource. It was therefore decided that the following procedure would be adopted for the larger molecules in the series.

- Geometry optimization at the B3LYP/6-311G(2d,1p) level of theory
- Polarizability calculation at this geometry but including a single set of diffuse functions.

This model can be summarized B3LYP/6-311G+(2d,1p)//B3LYP/6-311G(2d,1p) and is referred to as ‘Standard’ in Table 2.

### 3 Results and discussion

#### 3.1 Ab Initio Calculations

Table 3 summarizes our results for the series benzene (n = 1) through nonacene (n = 9). All calculations were done at the ‘Standard’ level of theory discussed above.

| n  | Energy/au | α_{LL}/au | α_{MM}/au | α_{NN}/au | <α>/au |
|----|-----------|------------|------------|------------|---------|
| 1  | -232.31427 | 79.38      | 79.38      | 42.97      | 67.24   |
| 2  | -385.99534 | 168.59     | 121.70     | 63.58      | 117.96  |
| 3  | -539.67032 | 291.56     | 164.63     | 83.83      | 180.01  |
| 4  | -693.34279 | 447.60     | 209.00     | 103.97     | 253.52  |
| 5  | -847.01407 | 634.65     | 255.01     | 124.00     | 337.89  |
| 6  | -1000.69368| 849.55     | 302.79     | 143.94     | 432.09  |
| 7  | -1154.35507| 1089.77    | 352.27     | 163.90     | 535.31  |
| 8  | -1308.02521| 1351.94    | 403.40     | 183.85     | 646.40  |
| 9  | -1461.69524| 1632.98    | 456.11     | 203.81     | 764.30  |

**Table 3 Ab Initio Polarizabilities for the title molecules.**

The mean value

\[ <\alpha> = \frac{1}{3} (\alpha_{LL} + \alpha_{MM} + \alpha_{NN}) \]  

(which is invariant to rotation of coordinate axes) can be determined from the refractive index \( n \) of a gas of non-interacting particles according to the equation

\[ n = 1 + \frac{\langle\alpha\rangle p}{2\varepsilon_0 k_B T} \]
where $p$ is the pressure, $k_B$ the Boltzmann constant, $T$ the thermodynamic temperature and $\varepsilon_0$ the permittivity of free space [1].

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. As a result both the external field and the field due to the surrounding molecules polarize each molecule. The Lorenz-Lorentz equation

$$\frac{n^2 - 1}{n^2 + 2} = \frac{\langle \alpha \rangle N}{3\varepsilon_0 V}$$

applies to non-polar molecules in condensed phases and it can be derived from a detailed consideration of these ideas [1]. Here, $N / V$ is the number density.

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

$$\frac{M}{\rho} \frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{N_A}{3\varepsilon_0} \left( \langle \alpha \rangle + \frac{p_r^2}{3k_BT} \right)$$

permits polarizabilities and dipole moments to be determined from measurements of the relative permittivity $\varepsilon_r$ and the density $\rho$ as a function of temperature.

Rewriting equation (5) in terms of molar quantities defines the molar refractivity

$$R_M = \frac{M}{\rho} \frac{n^2 - 1}{n^2 + 2} = \frac{N_A}{3\varepsilon_0} \langle \alpha \rangle$$

Here $M$ is the molar mass, $N_A$ the Avogadro constant and $\rho$ the density. It is an experimental fact that molar refractivities are additive properties at the molecular level, and a view has long prevailed that the molar refractivity of a molecule is a sum of the molar refractivities of the constituent parts (atoms/groups). Extensive tables of additive atom and group molar refractivities are available [13]. These tables have been extended to molecular polarizabilities with the compilations of Denbigh [14] and others.

One might therefore expect that the various components of the $\alpha$ tensor would show interesting incremental behaviour as the number $n$ of rings increases. The increments are shown in Table 4.

The interesting feature of Table 4 is the constant increment for the NN component.

3.2 Semi-empirical calculations

Ab Initio calculations on large molecules are expensive in computer resource, and semi-empirical models such as AM1 generally offer a cheaper route [4]. The well-known shortcoming of such calculations for the polarizabilities of conjugated molecules is that they give unrealistically small values for $\alpha_{NN}$. In the case of benzene we find

$$\alpha_{AM1/au} = \begin{pmatrix} 68.60 & 0 & 0 \\ 0 & 68.60 & 0 \\ 0 & 0 & 9.03 \end{pmatrix}$$
with \(<\alpha> = 48.75\) au.

\[
\begin{array}{cccccc}
 n & \Delta \alpha_{LL}/au & \Delta \alpha_{MM}/au & \Delta \alpha_{NN}/au & \Delta<\alpha>/au \\
\hline
1 & 0.00 & 0.00 & 0.00 & 0.00 \\
2 & 89.21 & 42.32 & 20.61 & 50.71 \\
3 & 123.97 & 42.94 & 20.25 & 62.05 \\
4 & 156.05 & 44.37 & 20.14 & 73.52 \\
5 & 187.94 & 46.01 & 20.04 & 84.36 \\
6 & 214.90 & 47.78 & 19.93 & 94.20 \\
7 & 240.23 & 49.48 & 19.96 & 103.22 \\
8 & 262.17 & 51.13 & 19.96 & 111.09 \\
9 & 281.04 & 52.71 & 19.96 & 117.90 \\
\end{array}
\]

\textbf{Table 4} Increments for \(\alpha\).

\[
\begin{array}{ccccccc}
 n & \alpha_{LL}/au & \alpha_{MM}/au & \alpha_{NN}/au & \Delta\alpha_{NN}/au & <\alpha>/au \\
\hline
1 & 68.60 & 68.60 & 9.03 & 0.00 & 48.75 \\
2 & 147.24 & 106.04 & 14.57 & 5.54 & 89.29 \\
3 & 251.51 & 147.43 & 20.18 & 5.60 & 139.70 \\
4 & 378.13 & 192.81 & 25.80 & 5.62 & 198.91 \\
5 & 555.21 & 274.74 & 31.96 & 6.16 & 287.30 \\
6 & 726.66 & 337.84 & 37.68 & 5.72 & 367.39 \\
7 & 911.44 & 403.20 & 43.44 & 5.75 & 452.69 \\
8 & 1118.05 & 468.79 & 49.14 & 5.70 & 545.33 \\
9 & 1327.18 & 539.23 & 54.96 & 5.83 & 640.46 \\
\end{array}
\]

\textbf{Table 5} AM1 polarizabilities for the title molecules.

AM1 results for the title molecules are collected in Table 5. The interesting feature is again the constant increment for \(\alpha_{NN}\). There is poor absolute agreement between the \textit{Ab Initio} values and the AM1 results, but they give a correlation coefficient of 0.99 which means that AM1 results can be accurately scaled for such molecules.

### 3.3 QSAR-quality calculations

Dipole polarizabilities are often used in QSAR studies, where the aim is to give a reliable but quick estimate of \(<\alpha>\), as part of the process of high-throughput screening. \textit{Ab Initio} polarizability calculations are prohibitively expensive in a QSAR context, even for such simple molecules. One therefore looks to less rigorous but reliable procedures.

The definitive reference in this field appears to be that due to K J Miller [15]. Miller pointed out the need to take account of the atomic environment in molecular calculations, and this is usually done by assigning parameters in which each atom is characterized by
its state of atomic hybridization. Miller and Savchik [16] proposed a functional form

\[ \langle \alpha \rangle = 4\pi \varepsilon_0 \frac{4}{N} \left( \sum_A \tau_A \right)^2 \]

where \( \tau_A \) is an atomic hybrid component for each atom \( A \) in a given state of hybridization. \( N \) is the total number of electrons. In fact, Miller and Savchik omitted the factor \( 4\pi \varepsilon_0 \) and so most computer packages quote the results as polarizability volumes (typically \( \text{Å}^3 \)).

These are shown in Table 6.

| \( n \) | \( \langle \alpha \rangle / \text{Å}^3 \) |
|---|---|
| 1 | 10.43 |
| 2 | 17.70 |
| 3 | 24.97 |
| 4 | 32.24 |
| 5 | 39.51 |
| 6 | 46.78 |
| 7 | 54.05 |
| 8 | 61.32 |
| 9 | 68.59 |

**Table 6** Miller polarizabilities.

Whilst there is poor absolute agreement between these values and the *Ab Initio* ones, there is an excellent correlation coefficient of 0.98 between the two sets of data. This is to be expected, since the method was first parameterized for hydrocarbons.

### 4 Conclusions

Molecular polarizabilities (and hyperpolarizabilities) are of current interest in the field of nonlinear optics, but are notoriously difficult to measure with any degree of accuracy for molecules in the gas phase. The best that can be done in solution is a measurement of the mean polarizability \( \langle \alpha \rangle \). Polarizabilities can be accurately calculated for molecules of modest size, and it is generally accepted that *Ab Initio* calculations can effectively replace experiment. The field has recently been reviewed by Maroulis [17]. It is therefore likely that our polarizability tensors are the most accurate available.

We note that

- *Ab Initio* polarizability calculations on the title molecules demonstrate a constant increment of 20 atomic units per ring unit in \( \alpha_{NN} \), but there are no such constant increments for the other two tensor components.

Polarizabilities are routinely calculated as QSAR indicators, but obviously *Ab Initio* runs on large pharmaceutical molecules are out of the question. It was initially believed that distinct chemical groups make relatively constant contributions to \( \langle \alpha \rangle \), but a more detailed analysis of the tensor components has been hindered by lack of experimental data.
The Miller scheme is widely used for such purposes and we find that
- Miller QSAR-quality polarizability calculations give a correlation coefficient of 0.98 when compared with the \( Ab \) \( Initio \) values. which means that the Miller \( <\alpha> \)'s can be suitably scaled to match the best \( Ab \) \( Initio \) results, for this series of molecules. Finally,
- AM1 polarizability calculations are in poor quantitative agreement with the \( Ab \) \( Initio \) results, and the NN tensor component is particularly poorly represented. Nevertheless, \( <\alpha> \) gives a correlation coefficient of 0.99 when compared to the \( Ab \) \( Initio \) results.

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