Theoret. chim. Acta (Berl.) 6, 159—166 (1966)

Self-consistent Perturbation Theory for Conjugated Molecules

II. Anisotropic Electric Polarizabilities of Conjugated Molecules

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Received June 20, 1966

Since an external field produces a drift of the mobile π-electrons in the plane of a conjugated molecule the electric polarizability of these molecules is anisotropic. The S.C.F. perturbation theory is used to calculate the π-electron contribution to the polarizability tensor for a number of conjugated molecules. Using previous theoretical and semi-empirical values for the polarizabilities of C – C and C – H bonds the σ contribution is estimated and total polarizabilities for the molecules obtained as the sum of the σ and π contributions. There is reasonable agreement between these theoretical values and the available experimental ones.

Ein äußeres elektrisches Feld verschiebt die π-Elektronen in der Molekülebene, so daß die elektrische Polarisierbarkeit von Molekülen mit konjugierten Bindungen anisotrop ist. Mittels SCF-Störungsrechnung wurde der Beitrag der π-Elektronen zum Tensor der Polarisierbarkeit für eine Anzahl von Molekülen berechnet und der Beitrag des σ-Bindungsgerüstes aus semiempirischen Größen ermittelt. Die Übereinstimmung mit gemessenen Werten ist zufriedenstellend.

La polarisabilité électrique des molécules conjuguées est anisotrope car un champ extérieur provoque un déplacement des électrons π mobiles dans le plan moléculaire. La théorie des perturbations SCF est utilisée pour le calcul de la contribution des électrons π au tenseur de polarisabilité d'un certain nombre de molécules conjuguées. En utilisant des valeurs théoriques et semi-empiriques antérieures concernant les polarisabilités des liaisons C – C et C – H on peut évaluer la contribution des électrons σ. Les polarisabilités totales sont obtenues comme la somme des contributions σ et π. L'accord avec les données expérimentales disponibles est raisonnable.

1. Introduction

When an electric field acts on a molecule the change in energy to first order is the product of the field and the molecular dipole moment. There is also a second order effect due to the dipole moment induced by the field itself. This effect is quadratic in the components of the field and the coefficients, which are the electric polarizabilities, transform as a second order tensor.

Saturated molecules can be considered as systems of localized bonds and the polarizabilities of these molecules can be obtained as tensor sums of the polarizabilities of the various CC and CH bonds in the molecule. In a conjugated molecule, however, only the σ electrons will occupy localized bonds and so only the σ-contribution to the polarizability can be obtained in this way. The π electron contribution has to be calculated using perturbation theory and, since the π electrons are delocalized and are moved freely by the field, this contribution can be at least as large as that due to the σ electrons. Moreover the π electron contribution is highly anisotropic and, in fact, vanishes when the field is perpendicular to the molecular plane. Thus in order to calculate the polarizability anisotropy, which is related to the molar Kerr constant and the depolarization factor of scattered light, it is clear that it is important to compute the π contribution accurately.

The purpose of this note is to use the self-consistent perturbation theory described in paper I of this series to calculate the π electron contribution to the electric polarizabilities of a number of conjugated hydrocarbons. These SCF polarizabilities are compared with those obtained in previous calculations using Hückel theory and they turn out to be smaller than the Hückel ones. A recent preprint by Dierksen and McWeeny [*10*] also includes values of the SCF polarizability components but for fewer molecules than we consider here.

The σ part of the polarizabilities can be estimated using theoretical and empirical estimates for the polarizabilities of the CH and CC bonds and in this way the total polarizabilities can be obtained as the sum of the σ and π contributions. Unfortunately there are widely differing estimates for the polarizabilities of the C–H bonds but by comparing the final results with experiment it is possible to obtain some indication as to which of the various values are the most satisfactory.

2. Perturbation due to an Electric Field

In the presence of a constant external electric field the potential of a molecule changes by

$$\mathrm{e}X \sum_i x_i \tag{1}$$

where X is the field strength and x_i the coordinate of the i th electron measured from some arbitrary origin in the direction of the field. The σ electrons can be considered separately from the π electrons since, even when the electric field is taken into account, $\sigma - \pi$ interaction will probably be small. Considering only π orbitals, therefore, the matrix element of the perturbation becomes

$$z_{rs} = eX \int \omega_r x \omega_s \, d\tau \tag{2}$$

in the notation of paper I [*1*]. Since the atomic orbitals $\{\omega_r\}$ are localized, z_{rs} vanishes unless $r = s$ when the integral reduces to the x-coordinate of the atom r.

With these values of the z_{rs} the first order changes, P'_{rs}, in the bond order matrix can be computed using the method described in paper I. The α_{xx} component of the polarizability tensor will then be twice the second order energy change due to this perturbation when $X = 1$ and will be given by

$$\begin{aligned} \alpha_{xx} &= -e \sum_r z_{rr} P'_{rr} \\ &= -e \sum_r x_r P'_{rr} \end{aligned} \tag{3}$$

where x_r is the x coordinate of atom r. Note that α_{xx} is independent of the choice of origin of coordinates because $\sum_r P'_{rr}$ is identically zero.

Since the first order effects of several perturbations acting simultaneously are additive it follows from paper I that P'_{rr} can be written in terms of the atom-atom polarizabilities, π_{rs}, obtained in that paper. We have that

$$P'_{rr} = -e \sum_s \pi_{rs} x_s \tag{4}$$

so that (3) becomes

$$\alpha_{xx} = -e^2 \sum_{rs} x_r x_s \pi_{rs} . \tag{5}$$

This is an equation identical in form to that obtained by Cohen, Coulson and Jamieson [*7*]. The only difference is that in (5) the π_{rs} are the self-consistent atom-atom polarizabilities whereas in their equation the Hückel ones were used.

There are, therefore, two methods of calculating α_{xx}. The first of these is based on Eq. (5) and requires the π_{rs} to be known. The second method is based on Eq. (3) and involves finding the P'_{rr} directly using the numerical method described in paper I.

Table 1. *π contribution to electric polarizability components* ($\text{cm}^3 \cdot 10^{-25}$)

Molecule	Hückel Theory		Self-consistent Theory	
	α_L	α_S	α_L	α_S
Benzene	59.0	59.0	61.6	61.6
Naphthalene	166	114	152	100
Anthracene	298	202	272	149
Phenanthrene	276	168	243	144
Azulene	245	129	198	110
Butadiene	129	16.5	92.7	16.3
Hexatriene	380	26.1	208	25.7

α_L and α_S are the components along the long and short axes in the molecular plane. Note that for the two polyenes these axes do not coincide with the principal axes of the polarizability tensor.

The results of using the latter method to compute the π contribution to the components of the polarizability tensor along the long and short axes in the molecular plane for a number of conjugated molecules are given in Tab. 1. For comparison the polarizabilities obtained using Hückel-theory are also included. The parameters used in the calculation were those discussed in paper I with the unit of energy taken to be $\beta = -4.78$ eV. With x_r in units of Å the units of α_{xx} in (3) and (5) are $\text{Å}^2 e^2 |\beta|^{-1}$ and these were converted to the more usual $\text{cm}^3\ 10^{-25}$ for the results given in Tab. 1.

The Hückel values in Tab. 1 are slightly different from those obtained in previous calculations [*2*, *7*, *8*, *11*]. This is due to the different parameters used, especially the different values for β.

The results in Tab. 1 show the relatively large values of the polarizabilities and their dependance on the size of the molecule. Generally the self-consistent values are smaller than the Hückel ones. The results for butadiene and hexatriene indicate that the rapid increase in the polarizability component along the long axis of the polyenes as predicted by Davies [*8*] using simple molecular orbital theory and Bolton [*2*] using free electron theory becomes rather less pronounced when self-consistent perturbation theory is used.

3. σ-Contribution

In order to find the total electric polarizabilities of the conjugated molecules considered here we need to know the σ-contribution. This can be deduced from the polarizability components of the C–C and C–H bonds and these can be estimated empirically. The wide range of values thus obtained testifies to the difficulty involved in making such estimates. For an account of some of these values which have been used and their reliability see references [*20*] and [*25*].

VICKERY and DENBIGH [*23*] have obtained for the mean polarizabilities of the C–C and C–H bonds the values

$$\alpha_{\mathrm{Av}}^{\mathrm{CC}} = 5.14 \times 10^{-25}\,\mathrm{cm}^3\,,$$
$$\alpha_{\mathrm{Av}}^{\mathrm{CH}} = 6.64 \times 10^{-25}\,\mathrm{cm}^3\,.$$

Since they are derived from the refraction indices of a large number of alkanes we accept these values as reasonably correct.

The anisotropy of the polarizability of the C–H bond is, in principle, deducible from the Raman intensities of methane and a value of $3.12 \times 10^{-25}\,\mathrm{cm}^3$ was obtained in this way by YOSHINO and BERNSTEIN [*25*]. However, only the magnitude of $\alpha_{\parallel}^{\mathrm{CH}} - \alpha_{\perp}^{\mathrm{CH}}$ can be found by this method and so, when the value of the anisotropy is used with the value of $\alpha_{\mathrm{Av}}^{\mathrm{CH}}$ to find the components, there are two possible solutions:

$$\begin{aligned} \alpha_{\parallel}^{\mathrm{CH}} &= 8.72 \times 10^{-25}\,\mathrm{cm}^3 \quad \text{(A)} \\ \alpha_{\perp}^{\mathrm{CH}} &= 5.60 \times 10^{-25}\,\mathrm{cm}^3 \end{aligned}$$

$$\begin{aligned} \alpha_{\parallel}^{\mathrm{CH}} &= 4.56 \times 10^{-25}\,\mathrm{cm}^3 \quad \text{(B)} \\ \alpha_{\perp}^{\mathrm{CH}} &= 7.68 \times 10^{-25}\,\mathrm{cm}^3\,. \end{aligned}$$

The first of these has $\alpha_{\parallel} > \alpha_{\perp}$ in agreement with most of the previous estimates [*9, 18, 24*]. However, a recent evaluation of the experimental data on polarizabilities and magnetic susceptibilities has led ZÜRCHER [*25*] to conclude that $\alpha_{\parallel} < \alpha_{\perp}$ and, indeed, he has deduced values in agreement with the set we have denoted as B.

Empirical estimates of $\alpha_{\parallel}^{\mathrm{CC}}$ and $\alpha_{\perp}^{\mathrm{CC}}$ are very variable (compare, for example [*5*] and [*18*]). We, therefore, prefer to use the values calculated by BOLTON [*3*] particularly since his computed values for $\mathrm{C{=}C}$ and $\mathrm{C{\equiv}C}$ agree well with the empirical estimates and these are likely to be quite reliable. BOLTON finds $\alpha_{\parallel}^{\mathrm{CC}} = 7.0 \times 10^{-25}\,\mathrm{cm}^3$ and $\alpha_{\perp}^{\mathrm{CC}} = 3.8 \times 10^{-25}\,\mathrm{cm}^3$ but these give an average $\alpha_{\mathrm{Av}}^{\mathrm{CC}}$ rather smaller than that of VICKERY and DENBIGH. To correct for this we have increased $\alpha_{\parallel}^{\mathrm{CH}}$ slightly and we shall use

$$\alpha_{\parallel}^{\mathrm{CC}} = 7.8 \times 10^{-25}\,\mathrm{cm}^3\,,$$
$$\alpha_{\perp}^{\mathrm{CH}} = 3.8 \times 10^{-25}\,\mathrm{cm}^3\,.$$

In addition to the polarizabilities of the C–C and C–H bonds some allowance should be made for the polarizability of the $2\,p_z$ carbon orbitals occupied by the π electrons. However, since this is, in fact, a type of $\sigma - \pi$ interaction effect and there seems to be no obvious way to estimate it we shall neglect it. It should, in any event, be quite small.

With the values we have quoted for $\alpha_{\parallel}^{\mathrm{CC}}$ and $\alpha_{\perp}^{\mathrm{CC}}$ and the two sets of values for $\alpha_{\perp}^{\mathrm{CH}}$, $\alpha_{\parallel}^{\mathrm{CH}}$ we calculate two sets of results for the σ contribution to the polarizability components of the molecules considered in the previous section. The σ-contribution is added to the π contribution in Tab. 1 to give the total polarizabilities. The final results for the total polarizabilities are in Tab. 2.

Table 2. *Electric polarizability components* ($\mathrm{cm}^3 \cdot 10^{-25}$)

Molecule	Computed using A values			Computed using B values		
	α_L	α_S	$\alpha_\perp$	α_L	α_S	$\alpha_\perp$
Benzene	139	139	56.4	133	133	68.9
Naphthalene	272	222	86.6	270	208	103
Anthracene	434	316	117	436	293	138
Phenanthrene	406	310	117	402	293	138
Azulene	318	232	86.6	316	218	103
Butadiene	151	78.3	45.0	155	62.7	57.5
Hexatriene	292	115	63.8	299	90.9	80.4

α_L and α_S are the components along the long and short axes in the molecular plane and $\alpha_\perp$ is the component perpendicular to this plane.

4. Comparison with Experiment

In principle it is possible to deduce the values of the individual components of the polarizability tensor from experimental values of the molar refractivity, the molar Kerr constant and the depolarization factor of scattered light. For a discussion see, for example, ref. [13] and [14].

Benzene is one case where this has been done and the results are given in Tab. 3. The discrepancies between the values point to difficulties of obtaining accurate and consistent experimental data. The major disagreement, however, is between the values of Briegleb [4] and the Le Fèvres [13, 14] on one hand and those of Parthasarathy [16] and of Stuart and Volkmann [21] on the other. This is due to different values for the anisotropy of the polarizability tensor and we shall discuss this point later. For nonpolar molecules the experimental quantities we have mentioned will only give the ratio between the principal polarizability components and to determine their absolute values further experimental results are needed. In naphthalene, for example, Krishnan [12] has used measurements

Table 3. *Experimental values for the polarizability components* ($\mathrm{cm}^3 \cdot 10^{-25}$)

Molecule	α_1	α_2	α_3	Ref.
Benzene	117	117	78	Briegleb [4]
	128	128	64.7	Parthasarathy [16]
	123	123	63.5	Stuart and Volkmann [21]
	111	111	73.7	Le Fèvre and Le Fèvre [13]
Naphthalene	215	176	103	Le Fèvre and Le Fèvre [14]
	268	141	115	Krishnan [12]

of the Cotton-Mouton effect and has made calculations of the principal susceptibilities of the naphthalene crystal to obtain the results shown in Tab. 3. LE FÈVRE and LE FÈVRE [*14*], on the other hand, have, for the same molecule, used experimental information on the crystalline state together with a calculation of the effect of dipole induction to find the values given in Tab. 3. Clearly both the results for naphthalene should be regarded as rather tentative. In addition to benzene and naphthalene, LE FÈVRE and SUNDARAM [*15*] have estimated the polarizability components for anthracene and phenanthrene but since their values for $\alpha_\perp$ are computed by assuming it varies linearly with the number of C–C bonds we do not consider that their results can properly be described as experimental.

Table 4. *Average polarizabilities* ($cm^3 \cdot 10^{-25}$)

Molecule	Calculated		Experiment [*19*]		Experiment [*15*]	
	Absolute	Relative	Absolute	Relative	Absolute	Relative
Benzene	111	(1.00)	103	(1.00)	99.2	(1.00)
Naphthalene	194	1.74	175	1.69	166	1.67
Anthracene	289	2.60	259	2.51	253	2.55
Phenanthrene	278	2.50	247	2.39	235	2.36
Azulene	212	1.90	—	—	—	—
Butadiene	91.5	0.82	—	—	—	—
Hexatriene	157	1.41	—	—	—	—

We, therefore, have only the values given in Tab. 3 to compare with our calculated values in Tab. 2. In view of the experimental uncertainties we can be reasonably satisfied that the overall pattern of both the theoretical and experimental results is the same. For benzene, where the experimental values are the most satisfactory, the agreement is as good as can be expected. The best agreement is between the theoretical values computed using the estimates B for the CH bond and the experimental values of PARTHASARATHY [*16*] and of STUART and VOLKMANN [*21*].

The most accurate experimental results are available for the molar refractivity which is related to the average polarizability $\bar{\alpha} = \frac{1}{3}(\alpha_1 + \alpha_2 + \alpha_3)$. Calculated and experimental values $\bar{\alpha}$ are given in Tab. 4. In this table both the absolute quantities $\bar{\alpha}$ and the values relative to benzene are given. The calculated absolute values are about 10% higher than the experimental ones. This could be because the π contribution is 10% too large or because the VICKERY and DENBIGH [*19*] values of $\alpha_{\mathrm{Av}}^{\mathrm{CC}}$ and $\alpha_{\mathrm{Av}}^{\mathrm{CH}}$ are too large. In this context it is interesting that Bolton's calculations on the polarizabilities of the CC bond lead to a value of $\alpha_{\mathrm{Av}}^{\mathrm{CC}}$ smaller than that of VICKERY and DENBIGH by about 7%. If the $\alpha_{\mathrm{Av}}^{\mathrm{CH}}$ were similarly reduced the calculated values of $\bar{\alpha}$ would be only about 5% higher than the experimental ones. A comparison of the relative values of $\bar{\alpha}$ in Tab. 4 shows the theory and experiment to be in excellent agreement.

The molar Kerr constant and the depolarization factor of scattered light are related to the anisotropy, a, of the polarizability tensor which is defined by:

$$a = (\alpha_1 - \alpha_2)^2 + (\alpha_2 - \alpha_3)^2 + (\alpha_3 - \alpha_1)^2 .$$

We have calculated a for the molecules considered in this paper and the results are shown in Tab. 5.

Experimental values of a can be obtained by combining results from the depolarization factor of scattered light and $\bar{\alpha}$. For benzene one then obtains $a \sim 68$ Å^6 (c.f. [*13*]) in fair agreement with our value for calculation B. STUART and VOLKMANN [*12*] in a similar way have found an experimental value of $a = 71$ Å^6 in slightly better agreement with our calculation. For naphthalene, the experimental evidence on the depolarization factor points to $a \sim 370 - 460$ Å^6 [*6, 17*] which again agrees quite well with our calculations. The most recent work in this context by UNANUÉ and BOTHOREL [*22*] leads to a value of 72 Å^6 for benzene and 390 Å^6 for naphthalene and again the agreement with the calculated values is satisfactory.

Table 5. *Anisotropy of the polarizability tensor* (cm$^6 \cdot 10^{-46}$)

Molecule	Computed with values A	Computed with values B
Benzene	1.36	0.82
Naphthalene	5.52	4.27
Anthracene	15.40	13.32
Phenanthrene	13.00	10.56
Azulene	8.21	6.82
Butadiene[a]	1.76	1.80
Hexatriene[a]	8.60	9.12

[a] Computed on the basis that the molecular long and short axes coincide with the principal axes of the polarizability tensor.

Experimental values of a can also be deduced from data on Kerr constants. Strictly speaking the Kerr constants should be for gases but the Kerr constants of solutes extrapolated to infinite dilution have been used by LE FÈVRE and his co-workers [*13, 14, 15*] to find values for a. The values thus obtained for the first four molecules in Tab. 5 are 29, 192, 732, 314 Å^6. These clearly disagree with both the calculated values and the experimental values obtained from the depolarization factor. It may be necessary, therefore, to reconsider the use of Kerr constants of solutes to find values for the anisotropy a.

To sum up, it seems that our computed values for the components of the polarizability tensor and associated quantities agree quite well with the experimental results currently available. It is, however, a great pity that there are so few of these and that they are not very reliable. A final point we should like to make concerns the values for the polarizability components of the CH bond. We have generally found better agreement between theory and experiment when the set of values marked B were used in the calculations. There is, therefore, some slight indication from the results presented in this paper in favour of ZÜRCHER's [*23*] conclusion that $\alpha_{\parallel}^{\text{CH}}$ is smaller than $\alpha_{\perp}^{\text{CH}}$.

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