Theoret. chim. Acta (Berl.) 29, 139 – 150 (1973)

Dispersion Interactions and Solvent-Shift Effects

A. T. Amos
Department of Mathematics, University of Nottingham

B. L. Burrows
Department of Mathematics, The Polytechnic, Stafford

Received October 13, 1972

The problem of relating solvent-shift effects to excited-state polarizabilities is discussed. It is found that the chief difficulty is that of estimating the dispersion term in the interaction energy between a solvent molecule and a solute molecule, and it is shown that the differences in the values of excited-state polarizabilities which have been deduced from solvent-shift data are due to widely differing estimates of this dispersion term. In order to obtain meaningful results it is found necessary to assume that the change in the dispersion term is related to the change in the polarizability of a solute molecule on excitation. On the basis of this assumption, the use of a semi-empirical formula which connects solvent-shifts with these changes in the polarizability is discussed and it is found that the accuracy is such that very little useful information can be obtained.

Das Problem, Lösungsmittelverschiebungen mit der Polarisierbarkeit angeregter Zustände in Verbindung zu bringen, wird diskutiert. Dabei zeigt sich, daß die Hauptschwierigkeit im Abschätzen des Dispersionsterms der Wechselwirkung Solvent-Solut-Molekül liegt und daß die Unterschiede in den Polarisierbarkeiten, die sich aus Daten für Lösungsmittelverschiebungen ergeben, auf die sehr unterschiedliche Abschätzung dieses Dispersionsterms zurückgehen. Um sinnvolle Resultate zu erhalten, muß angenommen werden, daß die Änderung des Dispersionsterms mit der Änderung der Polarisierbarkeit eines angeregten Solutmoleküls zusammenhängt. Auf dieser Grundlage wird eine entsprechende semiempirische Formel diskutiert; jedoch deren mangelnde Genauigkeit läßt keine eindeutigen Aussagen mehr zu.

1. Introduction

When a conjugated molecule – the solute molecule – is placed in a solvent there will be interaction effects between the solute and the surrounding solvent molecules. These effects will change the solute energy levels and, since they are not all changed by equal amounts, there will be a change in the excitation energies between the ground and excited states, which can be observed in the spectrum. These changes, called solvent shifts, can clearly be related to the basic interaction terms between the solute and the solvent molecules, and these, to a certain degree of approximation, can be expressed as electrostatic type terms depending on the dipole moments and polarizabilities of the solute molecule in both ground and excited states and the solvent molecules in their ground state. In this way the solvent shifts can, so it is believed, give information on the difference in the dipole moment and polarizability of the solute molecule in its ground and excited states.

Unfortunately, while this seems to work none too badly for dipole moments, the results have been interpreted in very different ways in the case of polarizabilities so that, for example, one authority believes that the polarizability change between the ground and the lowest excited state of naphthalene is small [1] while another believes it is very large indeed [2]. The purpose of this note is to try to examine how far the solvent-shift effects can be related to polarizability changes and, in passing, to resolve these apparent contradictions. Although in a fairly *ad hoc* way it is possible to find a rough correlation between theoretical values of excited-state polarizabilities and solvent-shift effects the approximations involved are so dubious that we tend to doubt whether any really convincing evidence on the magnitude of polarizability changes can be obtained in this way.

2. Electrostatic Interpretation of Solvent-Shift Effects

There have been many reviews and original papers (Refs. [3–8] are a small selection) giving detailed quantum-mechanical derivations of the equations relating solvent shifts to the electric properties of the solute and solvent molecules, so we shall only quote the main results here. However, in passing, we ought to point out that these results are based on quite a severe approximation, namely that solvent and solute molecules are sufficiently far apart for exchange of electrons to be neglected and for the interaction potential to be expressed as a truncated dipolar expansion. In many cases this will hardly be the case and one can only hope that any errors due to this fortuitously cancel.

If $\boldsymbol{\mu}_u^s$, $\boldsymbol{\mu}_v$, $\boldsymbol{\alpha}_u^s$, $\boldsymbol{\alpha}_v$ refer to the dipole moments and the polarizability tensors of the solute molecule in the state s and the pth solvent molecule $v(p)$ in its ground state, the change in the energy of the s state of the solute due to the interaction with the solvent is

$$\begin{aligned}\Delta E_s = & \sum_{p=1}^{N} R_p^{-3} \boldsymbol{\mu}_u^s \cdot \boldsymbol{\theta}^{uv(p)} \cdot \boldsymbol{\mu}_{v(p)} \\ & -\tfrac{1}{2} \sum_{p=1}^{N} R_p^{-6} \boldsymbol{\mu}_u^s \cdot \boldsymbol{\theta}^{uv(p)} \cdot \boldsymbol{\alpha}_{v(p)} \cdot \boldsymbol{\theta}^{uv(p)} \cdot \boldsymbol{\mu}_u^s \\ & -\tfrac{1}{2} \sum_{p,q=1}^{N} R_p^{-3} R_q^{-3} \boldsymbol{\mu}_{v(p)} \cdot \boldsymbol{\theta}^{uv(p)} \cdot \boldsymbol{\alpha}_u^s \cdot \boldsymbol{\theta}^{uv(q)} \cdot \boldsymbol{\mu}_{v(q)} + D_s\end{aligned} \tag{1}$$

where the solute is assumed to be placed with its mean centre of charge at the origin and R_p is the distance from the origin to the mean centre of charge of the pth solvent molecule, $\boldsymbol{\theta}^{uv(p)}$ is an angular term taking into account the relative orientations of the solute and solvent molecule and the sums are over all N solvent molecules in the system. In (1) terms which depend on solvent molecules only have been omitted since they cancel when the solvent shift is calculated and terms depending on higher powers of R^{-1} than the sixth are ignored.

In Eq. (1) D_s is the dispersion-interaction term and is given by

$$D_s = -\sum_{p=1}^{N} \sum_{e \neq 0} \sum_{t \neq s} R_p^{-6} \frac{\langle 0|\boldsymbol{\mu}_{v(p)}|e\rangle \cdot \boldsymbol{\theta}^{uv(p)} \cdot \langle t|\boldsymbol{\mu}_u|s\rangle \cdot \langle s|\boldsymbol{\mu}_u|t\rangle \cdot \boldsymbol{\theta}^{uv(p)} \cdot \langle e|\boldsymbol{\mu}_{v(p)}|0\rangle}{\varepsilon_v^e - \varepsilon_v^0 + \varepsilon_u^t - \varepsilon_u^s} \tag{2}$$

where, for example, $\langle 0|\boldsymbol{\mu}_{v(p)}|e\rangle$ is the transition dipole moment between the pth solvent molecule ground state $|0\rangle$ of energy ε_v^0 amd the excited state $|e\rangle$ of energy ε_v^e and similarly for $\langle s|\boldsymbol{\mu}_u|t\rangle$.

As it happens many conjugated hydrocarbons have zero dipole moments in their ground and lowest excited states. Therefore Eq. (1) will simplify considerably because the first two terms will vanish. Even with this simplification, however, Eq. (1) is not yet ready for use. This is because it it obtained on the basis that all the molecules are rigidly fixed in position and orientation, as is indicated by the presence of the R_p and the $\boldsymbol{\theta}^{uv(p)}$ in the formulae. The true energy change of the liquid system ought, therefore, to be computed by a statistical averaging over the various possible configurations, each weighted by the appropriate Boltzmann factor. In practice, of course, this is too difficult so one can either use an approach in which the solvent is replaced by a continuous dielectric or else use a semi-classical result and compute $\langle V \exp(-V/kT)\rangle$ where V is the angular-dependent interaction term [9]. The latter, which will not be valid for low temperatures but should be reasonably accurate for normal laboratory temperatures, gives:

$$\Delta E_s = -\sum_{p=1}^{N} R_p^{-6}\{(\boldsymbol{\mu}_{v(p)})^2\,\alpha_u^s + d_{uv}^s\} \tag{3}$$

where $\alpha_u = \frac{1}{3}$ trace $\boldsymbol{\alpha}_u$ and d_{uv}^s is the van der Waals coefficient between the solute molecule and a solvent molecule:

$$d_{uv}^s = \frac{2}{3} \sum_{t \neq s} \sum_{e \neq 0} \frac{|\langle e|\boldsymbol{\mu}_v|0\rangle|^2\,|\langle t|\boldsymbol{\mu}_u|s\rangle|^2}{\varepsilon_e^v - \varepsilon_0^v + \varepsilon_t^u - \varepsilon_s^u}\,. \tag{4}$$

In (3) we have assumed the molecules are isotropic so that both α_u and d_{uv}^s represent average values. This actually, is neither necessary nor true, but the approximations made in the theory are, in our view, too drastic to allow anisotropic effects to be estimated with any sort of accuracy so that we prefer not to include them.

There remains the evaluation of the sum $\Sigma\, R_p^{-6}$. It is probably simplest to assume that the solvent molecules are distributed uniformly outside a spherical cavity of radius a (the cavity radius) which contains the solute molecule. This gives the result

$$\Sigma\, R_p^{-6} = 4\,\pi A d/3\, M a^3 \tag{5}$$

where M and d are the mass and density of the solvent molecules and A is Avogadro number. Alternatively one can use the method of Abe [10] who places each solvent molecule inside a sphere of radius $r_v = (4\,\pi A d/3\, M)^{\frac{1}{3}}$ which are closely packed around the sphere of radius $r_u = (4\,\pi A d_u/3\, M_u)^{\frac{1}{3}}$ containing the solute molecule, where M_u and d_u denote the mass and density of the solute. As we have pointed out elsewhere [4] the two approaches give much the same results if one assumes not that $r_u = a$, as might be expected, but rather that $a \approx r_u + \frac{1}{2}\, r_v$. The basic reason for this is that the sum $\Sigma\, R_p^{-6}$ dies off so quickly with distance that only the solvent molecules close to the solute contribute strongly. In fact more than 90% of the whole solvent-shift effect arises from interactions between the solute molecule and the solvent molecules forming the first "layer" around it.

This gives, therefore,

$$\Delta E_s = -\frac{4\,\pi A d}{3\, M}\, a^{-3}\{d_{uv}^s + \alpha_u^s(\mu_v)^2\}\,. \tag{6}$$

Table 1. Experimental values for the solvent-shifts of the two lowest excited states of naphthalene in a number of solvents

Solvent	Solvent shift in cm^{-1} [13]	
	$^1B_{1u}$	$^1B_{2u}$
n-pentane	−258	−870
n-hexane	−288	−912
n-heptane	−287	−917
n-nonane	−322	−951
Cyclohexane	−296	−954
Cyclopentane	−296	−950
Ethyl ether	−236	−919
Ethanol	−256	−979
Acetronitrile	−266	−1189

The solvent shift between the ground state G and the excited state E will be

$$\begin{aligned}\Delta_{EG} &= \Delta E_E - \Delta E_G \\ &= -\frac{4\pi A d}{3 M a^3}\left[\Delta d + (\mu_v)^2\,\Delta\alpha\right]\end{aligned} \tag{7}$$

where Δd represents the change in the dispersion term between ground and excited state, and $\Delta\alpha$ the similar quantity for the polarizability. Clearly if (7) is to be used to estimate $\Delta\alpha$ from the experimental values of Δ_{EG}, some method of estimating the change in the dispersion term Δd must be found. We now turn to this problem.

3. The Dispersion Term

The contribution of dispersion forces to the solvent-shift effect is most difficult to estimate since we require the dispersion interaction between a solvent molecule and the solute molecule. Even for very small atomic systems the calculation of the d_{uv}^s term is by no means easy and any hope of computing it accurately for the type of complex molecules we are interested in must be abandoned. This is particularly so since we require it not only for the ground state of the solute but also for its excited state, and, as far as we know, there has been no attempt to compute d_{uv}^s for excited states even for small systems except, that is, for degenerate excited states where the problem is altogether different [11]. Thus if we are not to give up the problem as altogether intractable, there are only three reasonable ways to proceed.

Firstly we could try to eliminate the dispersion term from the problem. This is basically what is done by Suppan in order to estimate excited state dipole moments [1, 12] and he does this by the simple expedient of subtracting the solvent shift for two separate solvents. On the assumption that the dispersion term is the same for both it is eliminated from the problem. To examine how this would work for naphthalene consider the data given in Table 1. For the three solvents, ethyl-ether, ethanol and acetronitrile with non-zero dipole moments, there will be, according to Eq. (7), two terms in the solvent shift, the dispersion term and the term involving $(\mu_v)^2\,\Delta\alpha$. If we assume that the dispersion term is more or less the same in all three polar solvents then taking the difference of any two X and Y say will give

$$\Delta^X_{EG} - \Delta^Y_{EG} = \frac{4\pi A}{3}\left\{\frac{d_Y}{M_Y a_Y^3}\mu_Y^2 - \frac{d_X}{M_X a_X^3}\mu_X^2\right\}\Delta\alpha \tag{8}$$

Now these differences $\Delta^X_{EG} - \Delta^Y_{EG}$ are of the order of 20 cm^{-1} for the $^1B_{1u}$ excited state of naphthalene and 60–200 cm^{-1} for the $'B_{2u}$ excited state. (Results given by Weigang [13] show the same trend of results for phenanthrene and azulene.) However, if we now examine the non-polar solvents where the solvent shift is caused entirely by the dispersion term, we see that here, too, there are differences of the order of 20 cm^{-1} for the lowest state and 40–80 cm^{-1} for the $^1B_{2u}$ excited state. Thus the errors involved in assuming the dispersion terms cancel, so that Eq. (8) is obtained, are the same order of magnitude as the differences $(\Delta^X_{EG} - \Delta^Y_{EG})$ themselves. For this reason we do not believe that the dispersion term can be eliminated from the problem in such a way as to enable estimates of $\Delta\alpha$ to be made. [The case of dipole-moment changes is, of course, entirely different since the differences between solvent shifts of a polar solute in different polar solvents is much greater than those for non-polar solutes so that the error in cancelling the dispersion term is relatively unimportant.]

The second possible way to proceed is to use semi-empirical methods to estimate the value of d^s_{uv}. By this we mean that the wave functions for the solute and solvent molecules could be divided up into bond-orbitals and pi-type orbitals. The dispersion forces could then be written as the sum of bond interaction terms, pi-sigma and pi-pi terms [14]. Such a procedure would be difficult but by no means impossible. However, one thing is quite clear: such semi-empirical estimates could only give order of magnitude results and the errors would be quite large. Since the estimated dispersion term would have to be substituted into (7) and the difference between this and the experimental shift used to determine $\Delta\alpha$, the value of $\Delta\alpha$ thus determined would be subject to such possible error as to be practically useless.

In fact both the two methods just discussed fail for very similar reasons. In Eq. (7) the two terms which together contribute to the solvent shift are of very different orders of magnitude, the term proportional to $\Delta\alpha$ being, in our view, only about 10% of the dispersion term. Thus, if Eq. (7) is to be used to determine $\Delta\alpha$, then either the dispersion term must be estimated accurately to within a few percent, which we have shown to be impractical or else, and this is the third possible method of procedure, the dispersion term must be related to polarizability changes.

Almost from the first introduction of the idea of dispersion interaction, it has been believed that they can be approximately related to the polarizabilities of the molecules involved. In their recent book on Intermolecular Forces [11], Margenau and Kestner list various of these approximations and show how they can be derived. The more important and most useful of these when applied to the interaction between a solvent molecule and the solute molecule in the state s take the forms:

$$\text{(i)}\ d^s_{uv} = \frac{3}{2}\,\frac{\bar{\varepsilon}^s_u \bar{\varepsilon}_v}{\bar{\varepsilon}^s_u + \bar{\varepsilon}_v}\,\alpha^s_u \alpha_v \tag{9}$$

where $\bar{\varepsilon}^s_u$ and $\bar{\varepsilon}_v$ are "average" (or Unsöld) energy denominators which are often identified with ionization potentials.

$$\text{(ii)}\ d^s_{uv} = \frac{3}{2}\,\frac{\alpha^s_u \alpha_v}{\left(\dfrac{\alpha^s_u}{N_u}\right)^{\frac{1}{2}} + \left(\dfrac{\alpha_v}{N_v}\right)^{\frac{1}{2}}} \tag{10}$$

where N_u and N_v are the "average" number of electrons in closed shells. This is the Slater-Kirkwood formula. A modification of this is

$$\text{(iii)}\ d^s_{uv} = \frac{6}{B}\,\frac{\alpha_v \alpha^s_u}{\alpha^s_u/\chi^s_u + \alpha_u/\chi_v} \tag{11}$$

where χ^s_u and χ_v are the diamagnetic susceptibilities.

Equations (10) and (11) can be considered as modifications of (9) in which the average energies $\bar{\varepsilon}^s_u$ and $\bar{\varepsilon}_v$ are related to the polarizabilities and susceptibilities. In particular it should follow that

$$\bar{\varepsilon}^s_u : \left(\frac{N_u}{\alpha^s_u}\right)^{\frac{1}{2}} : \left(\frac{\chi^s_u}{\alpha^s_u}\right). \tag{12}$$

This equation shows quite clearly that to a large extent the results for the change in α_u between the ground and excited state depends on the assumption made concerning the variation in the value of $\bar{\varepsilon}_u$ between these two states. Since N_u will remain constant, the first proportionality sign indicates that a decrease in $\bar{\varepsilon}_u$ in going from the ground to excited state implies an increase in α_u. The second proportionality sign indicates that the change in α_u is proportional to the change in the square of the diamagnetic susceptibility. The latter should be proportional to the mean value of r^2 for the molecule, i.e. should vary with molecular size. Generally the bond lengths of a conjugated molecule increase on excitation but not by very much [15]. This suggests a small increase in $(\chi^s_u)^2$ on excitation and hence a small increase in α^s_u. On the other hand if the $\bar{\varepsilon}^s_u$ is approximated by ionization potentials there will be a large change in $\bar{\varepsilon}_u$ in going from the ground to the lowest excited states.

To summarize, therefore, the results obtained from solvent shift data using these approximate forms for the dispersion energy will depend on how the 'average' energy denominators are varied from the ground to the excited state. A small change will lead to a small change in the polarizability whereas a large change will lead to a large change in the polarizability.

In the theory developed by Abe [10] it is assumed that large changes in the $\bar{\varepsilon}^s_u$ do occur and that is why calculations based on Abe's method do indeed give rise to such large values of excited-state polarizabilities [2, 16]. On the other hand those calculations which obtain relatively small excited-state polarizabilities [1, 12, 18] in one way or another are assuming the dispersion terms are not very different in the ground and excited states which is equivalent to the assumption that the $\bar{\varepsilon}_u^s$ are roughly the same in the two states. If simple dispersion formulae like (9) are to be used in this field, therefore, it is essential to decide whether the average energies are changed by large or small amounts in going from the ground to the excited state.

To resolve this crucial point let us set out the arguments for the two possible choices. Firstly the reasons for making a small change in $\bar{\varepsilon}_u^s$:

(a) Equation (12) suggests that $\Delta\bar{\varepsilon}_u$ should depend on $\Delta\chi_u$ and since the molecular size varies only slightly on excitation so should χ_u and, hence, α_u.

(b) Equation (12) also suggests $\Delta\bar{\varepsilon}_u$ should change with $(\alpha_u)^{-\frac{1}{2}}$ and theoretical calculations imply relatively minor changes in α_u.

(c) A large change in α_u would imply that the assumption that polarizability terms could be ignored, which is made in deriving dipole-moment changes from solvent-shift data, would have to be revised. Yet the dipole-moment results seem consistent and acceptable (c.f. Ref. [12]).

(d) Attempts made to find excited-state polarizabilities from the electrostatic terms by considering non-polar solvents and also non-polar solutes in non-polar solvents suggest that d_{uv}^s is roughly proportional to the polarizability change and that this is relatively small [1].

The main arguments for making a large change in $\bar{\varepsilon}_u$ are:

(a) For atoms in their ground states, $\bar{\varepsilon}_u^s$ is often replaced by the ionization potential and the ionization potential of a conjugated molecule in its excited state is much less than in its ground state.

(b) An examination of (4) shows that the energy denominators are decreased in going from the ground to the excited state.

We believe these last two points are not really valid. Point (a) assumes that the results for atoms will apply equally to molecules which may well not be the case. Even if the result does hold for most molecules, conjugated hydrocarbons provide a special case where there are relatively low-lying excited states with large transition moments connecting them to the ground state. Point (b) is valid only if the energy denominators are the determining quantity, i.e. only if the numerators remain the same for the ground and excited state which is not the case since the transition dipoles $|\langle t|\boldsymbol{\mu}_u|s\rangle|^2$ will vary depending on whether s is the ground or excited state. The effect of this is almost impossible to determine which is why the whole problem is so difficult.

Our opinion at the moment is that what evidence there is suggests that the energy denominators $\bar{\varepsilon}_u^s$ should be given approximately the same values for both the ground and excited states. Further evidence that this is so can be obtained by comparing values of excited-state polarizabilities obtained from solvent-shift data with theoretical values. There have been two sets of theoretical calculations of the polarizabilities of the p-excited states of a number of conjugated hydrocarbons. Those of Trsic et [16] were made for quite a large number of molecules and were based on the Hückel method. We ourselves [17] have made calculations on a restricted number of molecules but have used relatively sophisticated methods. The results obtained in the two sets of calculations are given in Table 2 and are in quite good agreement. (Note that the values of Trsic *et al.* are given in units of $e^2 d^2 \beta^{-1}$ and a conversion factor of 100 was used to bring them into units

Table 2. Polarizabilities of the ground and excited states of a number of conjugated molecules (units of 10^{-25} cm^3)

Molecule	Excited state polarizabilities obtained from solvent-shift data		Theoretical excited state polarizabilities		Ground state polarizabilities	
	$\bar{\varepsilon}^s = \bar{\varepsilon}$ (ground)[a]	$\bar{\varepsilon} = $ I.P.	[16]	[17]	Experiment[e]	Theory [20]
Naphthalene $^1B_{1u}$	223	346[c]	—	206	175	194
Naphthalene $^1B_{2u}$	337	556[c]	257	256	175	194
Anthracene	391	685[b]	429	461	259	289
Phenanthrene	332	[d]	488	322	247	278
Azulene	[d]	201[b]	224	229	180	212

[a] Computed from experimental data in [13] and [19].
[b] Quoted in [16].
[c] Quoted in [2].
[d] Not available.
[e] For experimental references see [20].

of 10^{-25} cm^3, the reasons for this choice being discussed in Ref. [17]). In Table 2 we also give the values of the excited-state polarizabilities for the same molecules (in the case of naphthalene results are given for the two lowest excited states) computed from solvent-shift data using formula (9) for the dispersion interaction. In column 1 the energy denominators are assumed to be the same for the excited state as for the ground state (i.e. to be the ground-state ionization potentials) while in column 2 the values of $\bar{\varepsilon}_u^s$ for the excited states are the ionization potentials of those states and are, therefore, much smaller. Thus the second column results are based on Abe's formula [10] without any qualification. The table makes explicit the point we have made earlier that the use of the same $\bar{\varepsilon}_u^s$ in the ground and excited states leads to excited-state polarizabilities which are relatively close to the groundstate values (these are quoted in columns 5 and 6 of Table 2) while the very different values for $\bar{\varepsilon}_u^s$ used in Abe's formula leads to large changes. Clearly the former case gives "experimental" values in better agreement with the calculated ones (columns 3 and 4).

However, although, at least on empirical grounds, it seems that the average energies in the formula (9) for the London coefficient should be the same or approximately the same in the ground and excited states, we are not entirely happy with the choice of the ground-state ionization potentials for these average energies. This may not be too bad an approximation for the solvent molecules where the ground state is well separated from the excited state but the solute conjugated hydrocarbons have many low-lying excited states so that it is not so clear what would be a reasonable value of ε_u^s in this case. Another difficulty is the proper choice for the cavity radius. Although the choice $a \approx r_u + \frac{1}{2} r_v$ is the proper one for spherical molecules which are well separated; in practice we have large planar molecules with certain regions of the solute and surrounding solvent molecules very much closer together than the distance, a, between the molecular centres. On the whole, therefore, it would seem better to try and replace both by some

Table 3. Comparison of *n*-pentane solvent shifts of a number of conjugated molecules and the Hückel polarizability changes between the ground and the excited *p*-states

Molecule	N	Experimental Δ_{EG} (cm^{-1}) [19]	Theoretical $\Delta\alpha(10^{-25}\text{cm}^3)$[16]	$C\Phi(n^2)=\frac{N\Delta_{EG}}{\Delta\alpha}$	$C\Phi(n^2)=\frac{N^2\Delta_{EG}}{\Delta\alpha}$
Naphthalene	2	902	68.5	26.3	52.6
Anthracene	3	866	138.2	18.8	56.4
Naphthacene	4	854	266.9	12.8	51.2
Phenanthrene	3	1012	215.5	14.1	42.3
Pyrene	4	1061	73.3	57.9	289.5
Chyrene	4	1030	383.4	10.8	42.4
1–2 Benzanthracene	4	884	284.3	12.4	49.6
1, 2, 5, 6 Dibenzanthracene	5	3706	509.9	36.3	181.7

type of semi-empirical parameter. Certainly it is the case [13] that the dispersion part of the solvent shift of any particular solute molecule in a number of solvents can be represented quite well by the relation

$$\Delta_{EG}=C_u\Phi(n^2)\,\Delta\alpha \tag{13}$$

where

$$\Phi(n^2)=\frac{n^2-1}{n^2+2}=\frac{4\pi Ad}{3M}\alpha_v \tag{14}$$

represents the solvent property and C_u depends only on the solute and is equal to

$$\frac{3}{2}\,\frac{\bar{\varepsilon}_u^s\bar{\varepsilon}_v}{\bar{\varepsilon}_u^s+\bar{\varepsilon}_v}a^{-3}\,. \tag{15}$$

We say that C_u depends on only the solute even though (15) contains $\bar{\varepsilon}_v$ and a which actually do depend on the solvent because this dependence, at least for commonly used solvents, is so slight that it can be ignored. An examination of the solvent-shift data for a number of molecules shows that Eq. (13) gives a good representation of the dispersion effect. However to use this equation to obtain $\Delta\alpha$ from the experimental Δ_{EG} values an estimate of C_u must be found.

It would clearly be most satisfactory if the same value of C_u could be used for all solute molecules but this cannot be correct, for, even if the $\bar{\varepsilon}_u^s$ were independent of the solute molecule, the cavity radius would not be. If we use the ground-state ionization potentials for $\bar{\varepsilon}_u^s$ the quality $\bar{\varepsilon}_u^s\bar{\varepsilon}_v/\bar{\varepsilon}_u^s+\bar{\varepsilon}_v$ shows some relatively slight dependence on the particular solute. For polyenes and polyacenes there is a slight decrease as the size of the molecule increases. Similarly, since a^3 depends on the size of the molecule, the term a^{-3} decreases as the molecular size increases. Therefore, the value of C_u varies inversely with molecular size. If N is the number of rings in a solute molecule and we take no account of the variation of the average energies, we would expect C_u to be proportional to $1/N$. This suggests that a reasonable procedure is to try and fit the experimental Δ_{EG} and the theoretical $\Delta\alpha$ by a relationship of the form:

$$\Delta_{EG}=\frac{C}{N}\Phi(n^2)\,\Delta\alpha \tag{16}$$

Table 4. Predictions of $\Delta\alpha$ from Eqs. (16) and (17)

Molecule	$\Delta\alpha$ $[C\Phi(n^2)=16$ (from (16))]	$\Delta\alpha$ $[C\Phi(n^2)=50$ (from (17))]	$\Delta\alpha$ (theoretical [16])
Naphthalene	112.0	72.1	68.5
Anthracene	162.4	155.9	138.2
Naphthacene	213.5	273.3	266.9
Phenanthrene	189.8	182.2	215.5
Chyrene	257.5	329.6	383.4
1–2 Benzanthracene	221.0	282.9	284.3

where C is some constant more or less independent of solute and solvent. C should be fixed empirically and, for this to be done in a satisfactory way, it is clearly best to use a large number of molecules. Unfortunately, self-consistent calculations of $\Delta\alpha$ have been done only for a very few conjugated molecules so for the theoretical values we have used the Hückel calculations of Trsic *et al.* [16]. We have assumed that these theoretical values correspond to the p-bands. For the Δ_{EG} values we have considered only the solvent-shift effects in n-pentane. We do not anticipate that the choice of one solvent only is very significant since variations in Δ_{EG} for different solvents will be adequately taken care of by the $\Phi(n^2)$ term.

In Table 3 we compare values of the experimental Δ_{EG} with theoretical $\Delta\alpha$ and the measure N of molecular size. The ratio $N\Delta_{EG}/\Delta\alpha$, which should be a constant $C\Phi(n^2)$ if the expression (16) is correct, is also computed and the values given in Table 3. Even if we exclude the two highly anomalous results of pyrene (where $\Delta\alpha$ seems anomalous) and 1, 2, 5, 6 dibenzanthracene (where Δ_{EG} seems anomalous), the values of $C\Phi(n^2)$ for the different solute molecules are not by any means constant.

The problem is clearly that while the values of Δ_{EG} do not vary in any significant way with the size of the solute molecule and indeed are fairly constant for all of them, the values of $\Delta\alpha$ display a size dependence greater than $\Delta\alpha$ proportional to N which is implied by Eq. (16). Indeed, if we replace (16) by

$$\Delta_{EG}=\frac{C}{N^2}\,\Phi(n^2)\,\Delta\alpha\,, \tag{17}$$

then as Table 3 shows the resulting values of $C\Phi(n^2)$ are very much more constant.

Using these two different formulae, Eqs. (16) and (17), with the value of $C\Phi(n^2)=16$ in the first and $C\Phi(n^2)=50$ in the second we have used the experimental values of Δ_{EG} to find values of $\Delta\alpha$ to compare with the theoretical ones. These values are given in Table 4. It is fairly clear from that table that the second formula (17) gives decidedly better results. Taking the average energy $\bar{\varepsilon}_u$ for naphthalene to be its ground state ionization potential these values of C correspond to a cavity radius of 5.35 Å and 4.607 Å respectively. These are not out of line with previously used values.

The results in Tables 3 and 4 are not very encouraging. Provided we use Eq. (17) there is a correlation between Δ_{EG} and $\Delta\alpha$ but not a good one. Essentially, since the Δ_{EG} do not vary very much, the formula is really giving a correlation between $\Delta\alpha$ and N^2 rather than $\Delta\alpha$ and the solvent shift. A better test of this type of relationship could be made if values of $\Delta\alpha$ were available for the α and β bands of the solute molecules since Δ_{EG} for the α band is smaller (approximately 300 cm^{-1}) than for the other two bands. Actually we do have a calculated value for the α band of naphthalene of $\Delta\alpha = 12.10^{-25}\,\text{cm}^3$ which does fit the expression (17) (c.f. $20.64 \times 10^{-25}\,\text{cm}^3$) reasonably well but it would be unwise to draw any conclusion from this one value. On the whole therefore one would have to conclude that Table 4 shows that very little useful information on excited state polarizabilities can be gleaned from solvent shift data.

4. Summary and Conclusions

We have examined the possibility of using solvent-shift data to obtain "semi-experimental" values for the polarizabilities of excited states of conjugated molecules. We decided that for this to be done in a satisfactory way the dispersion-interaction term had to be related to the polarizability changes of the solute molecule between its ground and excited state. This can only be done by assuming that the dispersion interaction can be approximated by a London-type formula involving average excitation energies. The use of this formula involves the crucial decision of whether the average solute excitation energy should have approximately the same value for the solute in its ground state as in its excited state or whether the values in the two states should be very different. This is crucial since the former choice will inevitably mean that the polarizability changes deduced from the solvent-shift data will be small while the latter choice will lead to large changes. This explains the very different values which can be found in the literature. For a number of reasons, the most important of which was comparison with theoretical values, we decided that the average energies ought to be taken the same for both ground and excited state. When this is done the final relation between the experimental solvent shift Δ_{EG} and the polarizability change $\Delta\alpha$ takes the form

$$\Delta_{EG} = \frac{C}{f(N)}\,\Phi(n^2)\,\Delta\alpha \tag{18}$$

where $f(N)$ is a function of the solute molecular size (measured by the number of benzene rings N) which takes account of the cavity volume occupied by the solute and the variation of the average energy between the different molecules. One might expect that the dominant term in $f(N)$ depends on the cavity volume which, in turn, should vary as N. However, we have found that this choice of $f(N)$ proportional to N does not lead to very good agreement between Δ_{EG} and the Hückel values of $\Delta\alpha$. It turned out to be much better to take $f(N)$ proportional to N^2. It is difficult to see, using the usual cavity-field type arguments, why the volume should depend on a higher power of N than the first. The extra power of N could come from the average energy, which, since it is something of an unknown quantity might perhaps vary in this way, although it is rather unlikely. It may well be, however, that with increasing size of the solute molecules the whole basis of the usual theory of solute-solvent interaction breaks down. It is not, after all, very realistic to replace the interaction between two large molecules by a dipolar expansion in terms of the distance between their centres when, in fact, the periferies of the two molecules are in closer contact than either perifery to their respective centres. The rather odd variation with molecular size which we appear to have found may well be an indication that these considerations are becoming important. Using Eq. (18) with theoretical values of excited-state polarizabilities and experimental solvent-shift values it has proved possible to obtain at least some indication of the empirical status of the relationship between solvent shift effects and polarizability changes. It seems quite clear that for the *p*-bands of conjugated hydrocarbons the relationship is not very good. The solvent shifts do not vary very much for the different solute molecules, whereas the polarizabilities vary considerably more or less as the square of the molecular size. This is why, in order to get any sort of correlation, we are forced to include a term proportional to N^2 in the formula relating Δ_{EG} and $\Delta\alpha$ and this is not easy to justify theoretically.

Our general conclusion is that, while it is possible to find a rough correlation between theory and experiment, the exact basis of this relationship is hard to understand. Moreover, the crudity of the correlation is such that the values of $\Delta\alpha$ obtained from the solvent-shift data are very approximate indeed. Thus such values are not very useful for confirming and comparing theoretical calculation. As a final point, however, we recognise that these disappointing conclusions are based only on results for the *p* excited states. It would be useful to have more theoretical values of excited state polarizabilities, particularly of the α and β excited states, available to make a more extensive comparison in order to try to confirm our findings. However, there are beginning to become available direct measurements of excited state polarizabilities [18] which can be used to confirm the theoretical calculations directly and so make it unnecessary to use the solvent-shift data in this way. There will, of course, still remain the problem of estimating the dispersion contribution to the solvent shift theoretically. The results in this paper certainly suggest that the use of the London approximation is not a suitable way to do this.

References

1. Suppan, P.: Spectrochim. Acta **24**, 1161 (1964).
2. Abe, T., Amako, Y., Nishioka, T., Azumi, H.: Bull. chem. Soc. Japan **39**, 845 (1966).
3. Liptay, W.: In: Modern quantum chemistry, Part II p. 173. New York: Academic Press 1965.
4. Amos, A. T., Burrows, B. L.: Advances in quant. Chemistry, in press (1973).
5. Suppan, P.: J. chem. Soc. (A), 3126 (1968).
6. Ooshika, Y.: J. physic. Soc. Japan **9**, 594 (1954).
7. MacRae, E. G.: J. physic. Chem. **61**, 562 (1957).
8. Liptay, W., Walz, G.: Z. Natur **26**a, 2007 (1971).
9. Margenau, H.: Rev. mod. Physics **11**, 1 (1939).
10. Abe, T.: Bull. chem. Soc. Japan **38**, 1314 (1965).
11. Margenau, H., Kestner, N.: Theory of intermolecular forces. Oxford: Pergamon Press 1969.
12. Ledger, M. B., Suppan, P.: Spectrochim. Acta **23**, 641 (1967).
13. Weigang Jr., O. E.: J. chem. Physics **33**, 892 (1960).
14. Haugh, E. F., Hirschfelder, J. O.: J. chem. Physics **23**, 1778 (1955).
15. Dixon, R. N.: Spectroscopy and structure. London: Methuen 1965.
16. Trsic, M., Uzhinov, B. M., Matzke, P.: Molecular Physics **18**, 851 (1970).
17. Amos, A. T., Burrows, B. L.: Theoret. chim. Acta (Berl.) **23**, 327 (1972).
18. Eisenthal, K. B., Rieckhoff, K. E.: J. chem. Physics **55**, 3317 (1971). Liptay, W., Walz, G., Baumann, W., Schlosser, H. J., Deckers, H., Detzer, N.: Z. Natur **26**a, 2020 (1971).
19. Weigang Jr., O. E., Robertson, W. W., Matsen, F. A.: J. molecular Spectroscopy **1**, 1 (1959).
20. Amos, A. T., Hall, G. G.: Theoret. chim. Acta (Berl.) **6**, 159 (1966).

Dr. A. T. Amos, Department of Mathematics,
University of Nottingham, Nottingham NG 7 2RD, England