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Van der Waals Interactions in Molecular Complexes of Tetracyanoethylene

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The interaction energy of complexes formed between methylbenzenes and tetracyanoethylene is calculated by two procedures. The first one is the "monopoles-bond polarizabilities" procedure previously described, while the second is derived from the semi-empirical treatment proposed by Kitaygorodsky. A satisfactory agreement is obtained between the calculated energies and the observed energies of formation in the gas phase. The dipole moment induced by mutual electronic polarization of the components is calculated for the Durene-Tetracyanoethylene complex, and is found to account for the major part of the observed dipole.

Die Wechselwirkungsenergie von Komplexen, die aus Methylbenzenen und Tetracyanäthylen gebildet werden, wird mit Hilfe von zwei Verfahren berechnet. Das erste ist das Verfahren der „Monopol-Bindungs Polarisierbarkeiten", welches bereits beschrieben wurde. Das zweite Verfahren wird aus der halbempirischen Methode, die durch Kitaygorodsky vorgeschlagen wurde, hergeleitet. Eine befriedigende Übereinstimmung zwischen den berechneten und beobachteten Formationsenergien in der Gasphase wird erzielt. Das Dipolmoment, welches durch die gegenseitige elektrische Polarisation der Komponenten induziert wird, wird für den Durol-Tetracynäthylen-Komplex ausgerechnet. Es stimmt im wesentlichen Teil mit dem beobachteten Dipolmoment überein.

L'énergie d'interaction des complexes formés entre les methylbenzenes et le tétracyanoéthylène est évaluée au moyen de deux procédés: le premier est le procédé dit «monopoles-polarisabilités de liaison» tandis que le second est dérivé du traitement semi-empirique proposé par Kitaygorodsky. Un accord satisfaisant est obtenu entre les valeurs calculées et les énergies expérimentales de formation en phase gazeuse. Le dipole induit par polarisation électronique mutuelle des constituants est calculé dans le cas du complexe durene-tetracyano éthylène et rend compte de la majeure partie du dipole observé.

Introduction

The exact structure of the so-called "charge transfer complexes", i.e. molecular associations, which present in their UV spectra a new characteristic band (undoubtly due to a charge-transfer transition [1]) has recently given rise to some controversy.

During the last fifteen years, these complexes have been generally regarded as a special kind of association, and their ground state properties were explained in terms of a resonance between two structures of the type (D, A) and (D^+A^-). Recently, Dewar and Thompson [2], then Malrieu and Claverie [3], pointed out that this commonly accepted picture of "charge transfer complexes" was open to discussion and they showed that: i) the strictly speaking charge transfer contribution does not differ in kind from other Van der Waals interactions (such as polarization, dispersion ...) as can be seen from a second order perturbation treatment;

ii) in the various ground state properties of these complexes, the contribution of these Van der Waals-London interactions can be expected to play the dominant role.

We have able to demonstrate [7], with a procedure of calculation described elsewhere [4, 5, 6] that Van der Waals-London interactions do play a significant role in the stabilization energy of π-π molecular complexes – as well as in the appearance of a dipole moment. In particular, in the case of complexes formed between tetracyanoethylene (TCNE) and aromatic hydrocarbons, a good parallelism was obtained between the calculated Van der Waals interaction energy and the experimental free energy, measured at 25° C in chloroform as a solvent [2]. But, in fact, the proper thermodynamic quantity which corresponds to the theoretical intermolecular energy is the *internal energy* of the complex, as measured in the gas phase. Unfortunately, experimental values of this quantity were rather scanty, until Kroll [8] recently determined the values of the internal energies of a series of four complexes formed between TCNE and methylbenzenes[1].

1. Method of Calculation of the Interaction Energy — 1st Procedure

The calculation of the Van der Waals-London energies are carried out in the so-called "monopole-bond polarizabilities approximation" [5, 6], i.e. the intermolecular energy is built up from four contributions:

1. the electrostatic interaction E_{el} between the ground state distributions (point charge approximation);

2. the polarization energy E_{pol} of each molecule by the charge distribution of its partner;

3. the dispersion term, evaluated by the London expression – the usual form of which is:

$$E_{\text{disp}} = -\frac{3}{2}\frac{\bar{U}_{\text{A}}\bar{U}_{\text{B}}}{\bar{U}_{\text{A}}+\bar{U}_{\text{B}}}\frac{\alpha_{\text{A}}\alpha_{\text{B}}}{r^6} \tag{1}$$

where r is the distance between the two interacting systems A and B; α their mean polarizability and $\bar{U}$ the "average excitation energy" resulting from the closure approximation, and generally approximated by the ionization potential; in fact, in our procedure the bond polarizability tensors are introduced, so that our expression becomes:

$$E_{\text{disp}} = -\frac{1}{4}\frac{\bar{U}_{\text{A}}\bar{U}_{\text{B}}}{\bar{U}_{\text{A}}+\bar{U}_{\text{B}}}\sum_{n_{\text{A}}=1}^{\text{NA}}\sum_{n_{\text{B}}=1}^{\text{NB}}\frac{1}{r^6}\,Tr[\bar{\bar{\boldsymbol{T}}}\bar{\bar{\alpha}}_{n_{\text{A}}}\ \bar{\bar{\boldsymbol{T}}}\bar{\bar{\alpha}}_{n_{\text{B}}}] \tag{2}$$

where N is the number of bonds, r the distance between their midpoints, and $\bar{\bar{\boldsymbol{T}}}$ the tensor: $3\frac{\boldsymbol{r}\otimes\boldsymbol{r}}{r^2}-1$;

4. a repulsive contribution E_{rep}. As no perturbation treatment is reliable for large molecules, it is evaluated by the semi-empirical formula used by Favini and

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[1] The free energies of these complexes in solution had been previously measured by Merrifield and Philips [9].

Simonetta [1]:

$$E_{\text{rep}} = 3 \times 10^4 \exp\left(-13 \frac{r}{R_1 + R_2}\right) \tag{3}$$

giving the repulsion (in kcal/mole) between two atoms distant from r; R_1 and R_2 are the atomic radii as given in Pauling's table [11]. This formula is derived from a treatment proposed by Kitaygorodsky for hydrocarbons [12], but it should be noticed that it does not yield numerical values identical to those obtained by the initial Kitaygorodsky's treatment, since the sums of Pauling's values of atomic radii are smaller than the set of equilibrium distances adopted by Kitaygorodsky for each pair of atoms.

This repulsive term [3] is added to the attractive first and second order perturbation terms E_{el}, E_{pol} and E_{disp}. As previously noted [5], in the case of stacked aromatic compounds, where two p orbitals point toward one another, we use slightly increased values of atomic radii (1.70, 1.59 and 1.49 Å for aromatic carbon, nitrogen and oxygen respectively instead of 1.60, 1.50 and 1.40 Å) and a constant of 8.1×10^4 instead of 3×10^4 kcal/mole. For the intermediate case of methyl benzenes stacked with TCNE, it seems reasonable to distinguish the ring carbons for which the radius 1.7 Å and the constant 8.1×10^4 are used from the hydrogens and methylcarbons for which the constant 3×10^4 is used.

Electronic Structures of the Components

Methylbenzenes

The σ charges are evaluated by the procedure of Del Re [13] adapted for conjugated molecules [14]. The π atomic charges are calculated in the Pariser-Parr-Pople approximation of the SCF method, with parameters recently adapted [15] for methylated compounds. (In the case of o-xylene, these total net $\sigma + \pi$ charges give a dipole of 0.64 D, in excellent agreement with the observed value 0.62 D.)

Tetracyanoethylene

The SCF Pariser-Parr-Pople method and the procedure of Del Re for π and σ atomic charges respectively give total net charges equal to -0.446, $+0.383$ and $+0.126$ for the nitrogens, sp carbons and sp^2 carbons respectively. The same procedure used for H—C≡N leads to a dipole of 3.5 D, the observed value being around 3 D.

Bond Polarizabilities

The bond longitudinal and transverse polarizabilities α_L and α_T used in Eq. (2) are taken from Le Fèvre's data [16] when available. For the C≡N bond, we assume $\alpha_L = 3.1$ and $\alpha_T = 1.4$ Å [3], from data known for C–N and C=N. On the other hand, in London's formula, the average excitation energies $\bar{U}$ are approximated by the ionization potentials; the values used are 8.6, 8.5, 8.4 and 8.2 eV for o-xylene, p-xylene, mesitylene and durene respectively – and 8.6 eV for TCNE.

Results

The equilibrium distance between the planes of the two interacting molecules is found to be 3.30 Å. For this distance, the calculations are carried out for a number of relative orientations of the two partners. For the most favourable configuration, the values of each of the four contributions and their sum are given in Table 1 and compared with the experimental energies of formation in the gas phase. The fair agreement between the theoretical and experimental energies is illustrated in Fig. 1.

Table 1. *Calculated interaction energies (procedure 1) for the equilibrium distance 3.30 Å. Units are kcal/mole*

Complex formed with TCNE	E_{el}	E_{pol}	E_{disp} (London)	E_{rep}	Sum	E_{exp}
p-xylene	−3.1	−1.8	−4.6	+2.9	−6.6	−7.4 ± 0.5
o-xylene	−3.1	−1.9	−4.9	+3.2	−6.7	−8.0 ± 0.5
mesitylene	−3.2	−2.0	−5.2	+3.2	−7.2	−9.2 ± 0.5
durene	−3.5	−2.2	−6.0	+3.7	−8.0	−10.1 ± 0.8

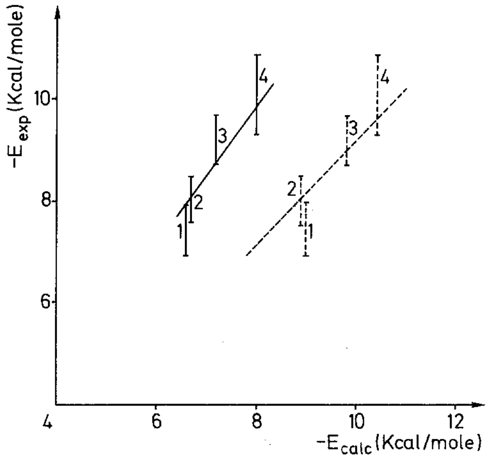

Fig. 1. Experimental energies of formation E_{exp} against calculated interaction energies (full lines, 1st procedure; dashed lines, 2nd procedure). *1* = p-xylene, *2* = o-xylene, *3* = mesitylene, *4* = durene, stacked with TCNE. The two indicated lines pass through the origin

2nd Procedure

Kitaygorodsky proposed in 1961 [12] a semi-empirical treatment of the interaction between saturated and insaturated hydrocarbons, in which the attractive and repulsive contributions are represented by expressions of the form:

$$E_{disp} = -C_1\left(\frac{r_0}{r}\right)^6 \tag{4}$$

and

$$E_{\mathrm{rep}} = C_2 \exp\left(-\alpha \frac{r}{r_0}\right). \tag{5}$$

This treatment has been very successfully applied to the determination of heats of sublimation, strain energies, *etc.* of various hydrocarbons. The quantities r_0 are "contact distances" chosen for each pair of atoms. With the Kitaygorodsky's values: $r_0 = 3.8$, 3.15 and 2.6 Å for C...C, C...H and H...H respectively, the constants are fixed at $C_1 = 0.14$ kcal/mole, $C_2 = 3 \times 10^4$ kcal/mole and $\alpha = 13$.

The term (4) represents the only dispersion term (i.e. the only non vanishing attractive term for non polar hydrocarbons[2]). For the present case, we have to add two classical (electrostatic and polarization) terms. To remain faithful to the initial treatment of Kitaygorodsky, we should, (in contrast to the procedure used by Favini and Simonetta [10]) compensate for the modification made in replacing the Kitaygorodsky's "contact distances" by the sum of Pauling's atomic radii, by making an appropriate correction of the constants C_1 and α in the Eq. (4) and (5). As the ratio between the distances of Kitaygorodsky and the sum of these atomic radii is in the neighbourhood of 1.18 (it is for example 3.8/3.2 for a pair of saturated carbon atoms), we can adopt the values $C_1 = 0.38$ kcal/mole and $\alpha = 11$.

The calculation of the total energy of interaction composed of the two Kitaygorodsky's terms (4) and (5), and of electrostatic and polarization contributions, yields an equilibrium distance between the planes of methylbenzenes and TCNE equal to 3.50 Å.

For this equilibrium distance, calculations are carried out for a number of relative orientations. For the most favourable configurations obtained (which are generally found to be quite similar to those obtained in the first procedure), the values of each of the four contributions and their sum are indicated in Table 2 and in Fig. 1 (dashed line).

Table 2. *Calculated interaction energies (procedure II) for the equilibrium distance 3.50 Å. Units are kcal/mole*

Complex formed with TCNE	E_{el}	E_{pol}	E_{disp} (Kit.)	E_{rep} (Kit.)	Sum	E_{exp}
p-xylene	−2.70	−1.39	−10.20	+5.23	−9.05	−7.4 ± 0.5
o-xylene	−2.69	−1.43	−10.70	+5.92	−8.90	−8.0 ± 0.5
mesitylene	−2.75	−1.51	−11.51	+5.97	−9.79	−9.2 ± 0.5
durene	−2.99	−1.67	−12.93	+7.19	−10.39	−10.1 ± 0.8

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[2] It can be noticed that the semi-empirical formula (4) is not unrelated to the London's expression [1] for the dispersion energy. In effect, the atomic polarizabilities are approximatively proportional to R^3 (R being the atomic radius). The term $\frac{\alpha_1 \alpha_2}{r^6}$ is therefore approximatively proportional to $\frac{(R_1 R_2)^3}{r^6}$, which is proportional to the term $\left(\frac{r_0}{r}\right)^6$ since the "contact distances" of Kitaygorodsky vary as the geometric mean $(R_1 R_2)^{1/2}$ of the atomic radii.

Clearly the experimental values are seen to fall between the two theoretically determined sets of values. However, the magnitude of the individual dispersion and repulsion contributions are significantly different in the two procedures. For example, for the distance 3.50 Å, the dispersion energy calculated by the Kitaygorodsky formula is $\frac{12.93}{4.50} \cong 2.9$ times larger than the dispersion energy calculated by the London formula.

In comparing these two theoretical approaches, it should be noted that some results reported in the literature seem to indicate that London's expression (1), where $\bar{U}$ is approximated by the ionization potential, underestimates strongly the dispersion energy.

It has been possible to check the dispersion energy only in the case of rare gas atoms and small non polar molecules. For these systems, various experimental data – such as second virial coefficients, viscosities, or sublimation energies – are available. Pitzer [17] and Salem [18] compared theoretical and experimental dispersion energies, and found that the various approximated theoretical formulae, such as the London, Slater-Kirkwood, and Kirkwood-Müller formulae, are rather unsatisfactory. In particular London's expression gives energies which are always too small. Thus, for small systems with *sp* closed shells, this London's expression should be multiplied by a factor of 2 (it is 2.4 for two methanes; an average factor of 2.25 was proposed by Pitzer [17]). Moreover, the situation can be expected to be worse for unsaturated systems, since, in this case, the excitation energies U of the whole system of σ and π electrons are replaced by an ionization potential which concerns strictly the π electrons, and is smaller than the ionization potential of the σ electrons: for example, $I_D = 13$ eV for methane while $I_D = 9.2$ eV for benzene.

Therefore, if for small σ systems such as CH_4, the dispersion energy is found to be about twice the value given by London's expression, it would be approximatively $2 \times \frac{13}{9} \cong 3$ times larger for benzenoid compounds[3].

This is perhaps an argument in favour of the second procedure, which also yields a dispersion energy about 3 times that obtained by London's formula.

2. Polarization Contribution to the Dipole Moment of the Durene-TCNE Complex

It has been shown recently [3, 20, 21] that, contrary to the commonly accepted view that the existence of a dipole moment in a "charge transfer complex" between two non polar components is due entirely to the contribution of the dative form ($D^+ A^-$), the mutual electronic polarization of the partners can generate a non-negligible, or even significant, dipole moment.

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[3] The fact that the London expression underestimates strongly the dispersion energy calls the following remark: calculations of the Van der Waals-London interaction energies between various purines and pyrimidines have shown [19] that associations involving very polar bases – such as cytosine – do not follow the observed order of the energies. For example, the self association of cytosine is predicted to be stronger than that of purine, while in fact it is weaker. But one can notice that while the electrostatic energy of the associations involving purine is much weaker than those involving cytosine, their London dispersion energy is found to be stronger. So if this London dispersion contribution was increased by a factor of about 3, the associations involving polar compounds such as cytosine would follow the observed relative order of the energies.

Table 3. *Induced dipole in the* DURENE-TCNE *complex (Debyes)*

Intermolecular distance (Å)	Dipole induced by TCNE	Dipole induced by DURENE	Total dipole	Experimental dipole
3.30	1.08	0.14	1.22	1.26
3.50	0.98	0.13	1.11	

An experimental determination of the dipole moment is available for the Durene-TCNE complex. The observed value is 1.26 D [22].

The induced dipole moment in this complex is calculated by the previously described procedure [20] i.e. by summation of the dipoles induced at the midpoint of the bonds by the net atomic charges of the partner. The mean values obtained for the two intermolecular distances 3.30 and 3.50 Å are indicated in Table 3.

Conclusion

The two procedures used for the calculation of the interaction energy of methylbenzenes stacked with TCNE lead to similar *total* energies, both of which are in satisfactory agreement with the experimental energies of formation in the gas phase.

In addition, further evidence is provided that the major part of the dipole moment appearing in complexes formed between two non-polar compounds, such as durene and TCNE, can be interpreted in terms of mutual electronic polarization between the partners.

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