Stabilization energies in charged tetracene clusters Quantum chemical and microelectrostatic calculations[*]

A. EILMES[**]

Jagiellonian University, Department of Computational Methods in Chemistry,
Ingardena 3, 30-060 Cracow, Poland

Theoretical calculations of the stabilization energy for an excess electron in tetracene clusters are presented. Vertical detachment energies were calculated for small clusters (up to 7 tetracene molecules) using the quantum-chemical DFT method. For larger clusters and an infinite 2D layer of tetracene molecules, the self-consistent polarization field (SCPF) method was used to calculate the polarization energy for a tetracene anion. Both DFT and SCPF results show that the charge stabilization energy increases rapidly with the cluster size and, even for clusters of less than 10 tetracene molecules, amounts to more than 50% of the bulk crystal value, which is in agreement with the conclusions of a recent experimental work.

Key words: *tetracene; polarization energy; electron detachment energy*

1. Introduction

Linear oligoacenes (anthracene, tetracene or pentacene) are commonly used in research on fundamental physical properties of organic molecular crystals. Studies on charge-carrier localization and transport in such systems attract significant attention owing to possible applications in molecular electronics. The major research effort is focused on crystals, while small aggregates are of lesser interest. Molecular clusters, however, offer new possibilities for the study of microscopic charge localization phenomena and allow one to trace the evolution of physical properties of aggregates towards bulk crystals.

Recently, a study on tetracene cluster anions has been reported [1]. Photoelectron spectroscopy (PE) combined with mass spectrometry was used to measure the values

of electron vertical detachment energy (VDE) for a series of clusters $(\text{tetracene})_n^-$, ($n = 1–100$). It has been found that for $n > 50$, two bands of almost constant VDE were observed. One band appeared at about 1.8 eV; its intensity gradually decreased with the cluster size, and for $n > 60$ the other band, at 2.0 eV, was more prominent. The former band was attributed to a 2-dimensional cluster of tetracene molecules, while it was argued that the higher-energy band originates from a double- or multilayered structure. The authors of [1] concluded that a large part of the polarization energy of bulk tetracene crystal is reached in surprisingly small clusters.

In this paper, a theoretical study of electron binding energy in small tetracene aggregates is presented. Two complementary approaches are used to estimate the electron detachment energies from charged tetracene aggregates. For small clusters, the detachment energy may be obtained from standard quantum-chemical calculations as the difference between energies of electrically neutral and negatively charged clusters. As the computational cost increases rapidly with the number of tetracene molecules, this method is feasible only for the smallest aggregates. The other approach is the self consistent method of microelectrostatic calculations easily capable of computing the polarization energy for an excess charge in a cluster consisting of thousands of molecules. Polarization energy calculations will therefore provide information about the increase in the charge stabilization energy in large clusters.

2. Quantum chemical calculations

The Gaussian 03 program [2] was used for the density functional theory calculations with B3LYP functional. Single point energy calculations were performed for input geometries of tetracene clusters taken from the crystallographic data [3]. To reduce the time of calculations, the basis set was limited to 3-21G. The calculated detachment energies are therefore significantly underestimated, however, the energy change upon increasing cluster size should be less affected by the basis set size.
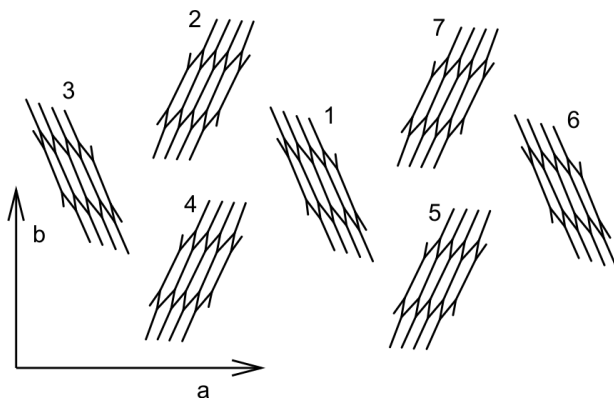

Fig. 1. Geometry of the largest tetracene cluster used in calculations

The DFT calculations were performed for clusters of up to seven tetracene molecules cut from the *ab* plane of the crystal. Figure 1 presents the geometry of the largest aggregate, the numbers give the sequence in which the molecules were added to the cluster. The geometries measured for two molecules [3] at the (0,0,0) and (1/2,1/2,0) crystallographic positions differ slightly, which leads to differences in the calculated energies. Results were therefore averaged over two choices of cluster position in the tetracene lattice.

The electron detachment energy VDE was calculated as a difference of two single-point energies:

$$\text{VDE} = E^0 - E^- \tag{1}$$

where E^0 and E^- are the energies of clusters with charge 0 and –1, respectively.
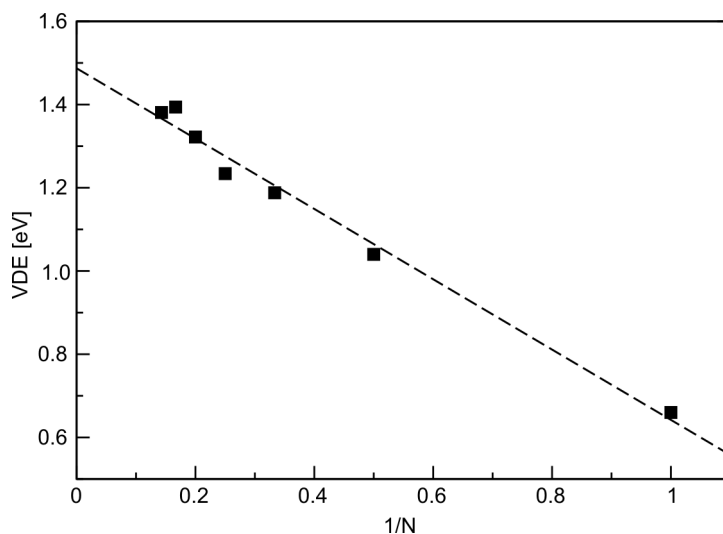

Fig. 2. Vertical detachment energy for electrons in tetracene clusters calculated at the B3LYP/3-21G level vs. reciprocal of the number of tetracene molecules in the cluster. The line is the linear fit to the data

Electron detachment energy calculated at the B3LYP/3-21G level for a single tetracene molecule at the crystal geometry is 0.66 eV, i.e. ca. 0.4 eV lower than the electron affinity of tetracene (1.06 eV) [1]. The dependence of the calculated VDE values on the reciprocal value of cluster size is shown in Fig. 2. Linear data fitting provides an estimate of 1.49 eV for the detachment energy corresponding to an infinite number of molecules. The increase in the VDE from one tetracene molecule to the infinite *ab* plane amounts, therefore, to 0.83 eV. This value can be compared with the experimental data. Assuming (as in [1]) that the peak at 1.8 eV in the photoelectron spectra of tetracene clusters corresponds to the limit of an infinite monomolecular layer, we obtain 0.74 eV as the experimentally determined estimate for the increase in VDE if the number of tetracene molecules increases from 1 to infinity. In spite of the low level of

theory applied in calculations, the quantum-chemically computed value is in good agreement with measurements. It should be noted that preliminary results of calculations employing a larger basis set suggest that with increase in the cluster size, the VDE values change more slowly than at the 3-21G level, which opens up prospect of an even better agreement with the experimental data.

Although the VDE of 0.66 eV calculated for a single molecule is only 44% of the value extrapolated for an infinite system, for a cluster consisting of only seven tetracene molecules about 93% of the electron detachment energy for the *ab* crystallographic plane is reached. This agrees with the PE spectra of tetracene clusters (Fig. 3 of Ref. 1), indicating increase of the detachment energy for small clusters which saturates for about 10 molecules. The results of DFT calculations support, therefore, the conclusions of Ref. 1, namely that for a relatively small tetracene cluster the detachment energy approaches the bulk crystal value.

3. Microelectrostatic calculations

The self-consistent polarization field (SCPF) method [4] was used to calculate polarization energies for an excess charge in tetracene clusters. The SCPF method solves iteratively the problem of local fields and induced dipoles. Given a system of polarizable points (which may be molecules or parts of molecules in submolecule treatment [5]) and external charges, the first approximation of induced dipoles is calculated and used to update local fields. Local fields are then used to obtain a better approximation of the induced dipoles and these steps are repeated until a satisfactory convergence is reached. Final estimates of the induced dipoles are used to calculate the polarization energy. Calculations are performed for systems of increasing size. Such procedure has been applied in the past for calculations of the polarization energy in fullerene microcrystals and polymers [6–9]. It differs from the method described in [4] by omitting the contribution to the polarization energy arising from the dielectric continuum surrounding the system. It is therefore applicable to calculations for microclusters but the polarization energy for bulk crystal may also be estimated by data extrapolation [6]. Microelectrostatic SCPF calculations are also useful for imperfect crystals, as demonstrated by recent calculations on energies of electronic states at grain boundaries in pentacene [10].

The input data necessary for SCPF calculations are the positions of polarizable points (molecules or submolecules) and their polarizabilities.

Polarizability of the tetracene molecule was obtained from quantum-chemical B3LYP/6-31+G** calculations. The polarizability tensor is diagonal in the (L, M, N) molecular axis system[*] and its α_{LL}, α_{MM} and α_{NN} components read 66.12, 31.03 and

---

[*]L and M are the long and middle axis of the molecule, respectively and N is the axis normal to the molecular plane.

15.05 Å^3, respectively. These values may be compared with the tetracene polarizability tensor extrapolated by Eisenstein and Munn [11] from effective (in crystal environment) molecular polarizabilities of shorter oligoacenes. Quantum chemical calculations predict a larger α_{LL}/α_{NN} ratio (4.39 compared with 2.88 from Ref. [11]), nevertheless the calculated value of the mean isotropic polarizability, i.e. 37.4 Å^3, is only a little higher than the value of 36.25 Å^3 obtained for the extrapolated effective tensor [11]. The anisotropy of the polarizability is therefore more pronounced for the quantum-chemically computed tensor.

Geometries of the systems (positions and orientations of tetracene molecules) were constructed based on the crystallographic data [3]. Each tetracene molecule was represented as four polarizable points (submolecules) located at the centres of benzene rings. Accordingly, the total molecular polarizability and the excess charge on the molecular ion were equally distributed over the four points, with the standard assumption that the submolecule does not polarize other submolecules belonging to the same molecule [5]. Without such polarizability partitioning, SCPF calculations would not converge. Such problems are related to the large anisotropy of the molecule and the submolecule treatment is necessary for longer oligoacenes, in order to avoid physically unrealistic results [12].

Two series of SCPF calculations were performed. In each series an excess charge was located at the tetracene molecule located in the centre of the cluster. The cluster size was increased either in all three dimensions (3D clusters) or in the *ab* plane only (2D clusters).
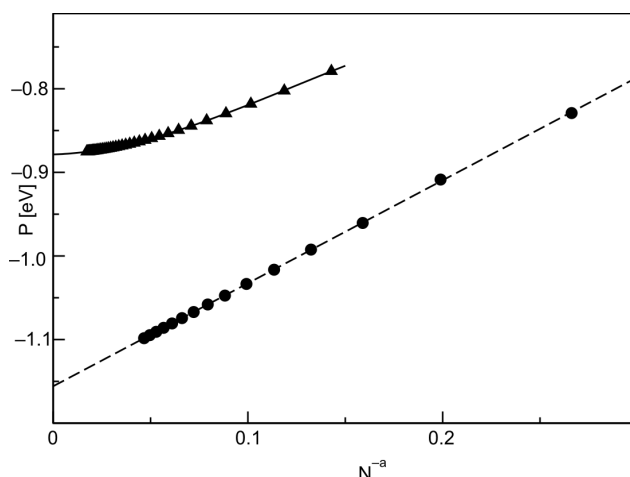

Fig. 3. Dependence of the polarization energy *P* on the number of tetracene molecules *N*. Circles – 3D clusters (*a* = 1/3), triangles – 2D clusters (*a* = 1/2). Lines are the best fits to the data (3D – linear, 2D – cubic)

The resulting dependence of the polarization energy *P* on the number of tetracene molecules *N* is displayed in Fig. 3. Apparently, the dependence of *P* on $N^{-1/3}$ is linear and the extrapolation to infinitely large *N* yields –1.156 eV. As shown in [6], this

value corresponds to the polarization energy for the charge in the bulk crystal. The polarization energy calculated by the Fourier transform method [11] was –1.144 eV; the difference reflects mainly a slight difference in the mean polarizability used in calculations.

Similar extrapolation of P versus $N^{-1/2}$ by cubic regression gives –0.88 eV as the polarization energy for a charge in the infinite ab plane of tetracene crystal. This means that a single layer of tetracene molecules gives rise to about 76% of the polarization energy for the infinite 3D crystal. Such a result is a consequence of crystal structure: the distances between planes are larger than within a plane, which weakens the electrostatic interactions, and although the largest component of the polarizability tensor is oriented roughly perpendicular to the plane, the first effect prevails.

Additional SCPF calculations were performed for a planar cluster of 30 tetracene molecules (as proposed in Ref. 1 Fig. 2b) as well as for such a cluster "sandwiched" between two smaller clusters of 14 molecules, each located in the neighbouring crystal ab planes. For the planar 30-mer, the polarization energy is –0.72 eV, i.e. ca. 82% of the value for an infinite layer and more than 60% of the polarization energy for the bulk crystal. For the system of 14–30–14 molecules, the P value of –0.84 eV was obtained (about 70% of the bulk value). The above results show that in the aggregate of several tens of molecules, a major part of the electrostatic stabilization corresponding to charged molecules in the bulk crystal is reached.

5. Conclusions

Quantum-chemical and microelectrostatic calculations of the stabilization energy for a charge in a tetracene cluster were performed. Both methods show that even in relatively small clusters the stabilization may exceed half the stabilization experienced by a charged molecule in bulk crystal.

The "vertical" total charge stabilization energies obtained in [1] from the photoelectron spectra are –0.74 and –0.94 eV for an infinite 2D layer and an infinite 3D crystal, respectively. SCPF microelectrostatic calculations yield –0.88 eV for the 2D system and –1.16 eV for the bulk crystal. Quantum-chemical calculations of the electron detachment energy provide an estimate of the electron stabilization in a planar layer ca. –0.83 eV. Although the computed values of the stabilization energy are larger than the experimental values, they are of the same order of magnitude and the agreement is surprisingly good taking into account all the approximations made in the calculations.

Theoretical predictions will be supposedly improved at the cost of more detailed or applying higher level of theory calculations. Increase of the basis set in the quantum-chemical calculations will greatly reduce the underestimation of the absolute values of electron detachment energies and, as suggested by some test calculations, will yield a better agreement between the computed and the measured dependence of VDE on the cluster size. In addition, some kind of analysis of the relative stability of tetracene clusters would be desirable. However, as the weak dispersion interactions play an important role in the stabilization of oligoacene molecular crystals, such an analysis

will require a higher level of theory (MP2 calculations) and the computational time will become prohibitive.

In the electrostatic calculations reported in this paper, the charge–quadrupole energy was not taken into account. It has been shown [11] that this interaction reduces the stabilization energy for negative charges in tetracene crystals, therefore when it is included in the SCPF calculations (e.g., by introducing permanent charges located on the atoms) the agreement with experimental estimates is likely to improve. Similar, although not so significant, may be the effect of spreading the polarizability onto more points (e.g. assigning polarizability tensors to individual atoms in the molecule).

To conclude, it has been shown that even approximate theoretical methods can provide a reasonable estimate of changes in the electron stabilization energy upon increase in the tetracene cluster size, and thereby confirm the experimental findings [1]. For a better description more computational effort has to be invested in the calculations.

References

[1] MITSUI M., ANDO N., NAKAJIMA A., J. Phys. Chem. A, 111 (2007), 9644.
[2] FRISCH M.J., TRUCKS G.W., SCHLEGEL H.B., SCUSERIA G.E., ROBB M.A., CHEESEMAN J.R., MONTGOMERY J.A. Jr., VREVEN T., KUDIN K.N., BURANT J.C., MILLAM J.M., IYENGAR S.S., TOMASI J., BARONE V., MENNUCCI B., COSSI M., SCALMANI G., REGA N., PETERSSON G.A., NAKATSUJI H., HADA M., EHARA M., TOYOTA K., FUKUDA R., HASEGAWA J., ISHIDA M., NAKAJIMA T., HONDA Y., KITAO O., NAKAI H., KLENE M., LI X., KNOX J.E., HRATCHIAN H.P., CROSS J.B., BAKKEN V., ADAMO C., JARAMILLO J., GOMPERTS R., STRATMANN R.E., YAZYEV O., AUSTIN A.J., CAMMI R., POMELLI C., OCHTERSKI J.W., AYALA P.Y., MOROKUMA K., VOTH G.A., SALVADOR P., DANNENBERG J.J., ZAKRZEWSKI V.G., DAPPRICH S., DANIELS A.D., STRAIN M.C., FARKAS O., MALICK D.K., RABUCK A.D., RAGHAVACHARI K., FORESMAN J.B., ORTIZ J.V., CUI Q., BABOUL A.G., CLIFFORD S., CIOSLOWSKI J., STEFANOV B.B., LIU G., LIASHENKO A., PISKORZ P., KOMAROMI I., MARTIN R.L., FOX D.J., KEITH T., AL-LAHAM M.A., PENG C.Y., NANAYAKKARA A., CHALLACOMBE M., GILL P.M.W., JOHNSON B., CHEN W., WONG M.W., GONZALEZ C., POPLE J.A.,*Gaussian 03*, Gaussian, Inc., Wallingford CT, 2004.
[3] ROBERTSON J. M., SINCLAIR V. C., TROTTER J., Acta Cryst., 14 (1961), 697.
[4] KNOWLES D. B., MUNN R. W., J. Mater. Sci.: Mat. Electr., 5 (1994), 89.
[5] BOUNDS P. J., MUNN R. W., Chem. Phys., 59 (1981), 47.
[6] EILMES A., Synth. Metals, 109 (2000), 129.
[7] EILMES A., Chem. Phys. Lett., 326 (2000), 580.
[8] EILMES A., MUNN R. W., GÓRA A., J. Chem. Phys., 119 (2003), 11467.
[9] EILMES A., MUNN R. W., J. Chem. Phys., 120 (2004), 7779.
[10] VERLAAK S., HEREMANS P., Phys. Rev. B, 75 (2007), 115127.
[11] EISENSTEIN I., MUNN R. W., Chem. Phys., 77 (1983), 47.
[12] BOUNDS P.J., MUNN R.W., Chem. Phys., 44 (1979), 103.