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THEORETICAL INVESTIGATION OF THE STRUCTURAL AND SPECTROSCOPIC PROPERTIES OF ANTHRACENE DIMERS

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Equilibrium geometries of the ground electronic state of anthracene dimers are obtained using the density functional level of theory with the B97D hybrid functional and the TZVP basis set and their electronic absorption spectra are simulated.

Keywords: thin films, anthracene dimers, density functional theory.

INTRODUCTION

Knowledge of the structural and spectroscopic properties of luminophore films is of great scientific and practical interest for the development of optical systems of information recording and displaying in micro- and nanooptoelectronics, solution of problems of solar energy converters, design of sensors, etc. [1, 2]. Organic dye molecules are densely packed in thin solid films; therefore, their optical properties are complicated by intermolecular interactions. All photoprocesses in this case proceed in supramolecular systems comprising molecular and aggregated dye species. Unlike monomer molecules, the photoprocesses in aggregates have been studied insufficiently. On the other hand, these investigations are very urgent and promising for synthesis of nanocomposite materials with preset photophysical properties. Limited ranges of luminophore molecule orientations in thin films allow the researchers to form molecular complexes with the known geometry using molecules with definite chemical composition and hence to predict the physical and chemical properties of these systems. For this reason, in the first stages of studying the photophysical and spectroscopic processes in luminophore complexes it becomes urgent to investigate their possible geometrical orientation. The inverse problem of retrieval of the luminophore geometry from the spectroscopic characteristics is also urgent.

Nowadays the geometrical characteristics of large molecules and of their complexes are investigated both experimentally and theoretically. X-ray structural analysis and magnetic nuclear resonance spectroscopy are sufficiently reliable experimental methods of investigation of spatial arrangement of atoms in molecules [3]. The methods of quantum chemistry provide the basis for theoretical investigations of the geometrical structure of molecules. Results of recent calculations demonstrate that such methods of quantum chemistry as the density functional theory (DFT) and *ab initio* calculation methods allow the geometrical structure of molecules and of their complexes to be calculated with sufficiently high accuracy often not worse than the accuracy of measurements by experimental methods [4–6].

The anthracene dimers as objects of research were chosen due to the fact that in most cases, the anthracene dimers were used as luminophores in thin films [7]. At the same time, investigations of the spectral and geometrical properties of these complexes are poorly reflected in the scientific literature. Works devoted to calculations of the geometry by the methods of symmetry adapted perturbation theory (SAPT) [8] and second-order Moller–Plesset theory (MP2) [9] are few in number. However, in these works the small 6–31G Pople basis set was used. The geometrical

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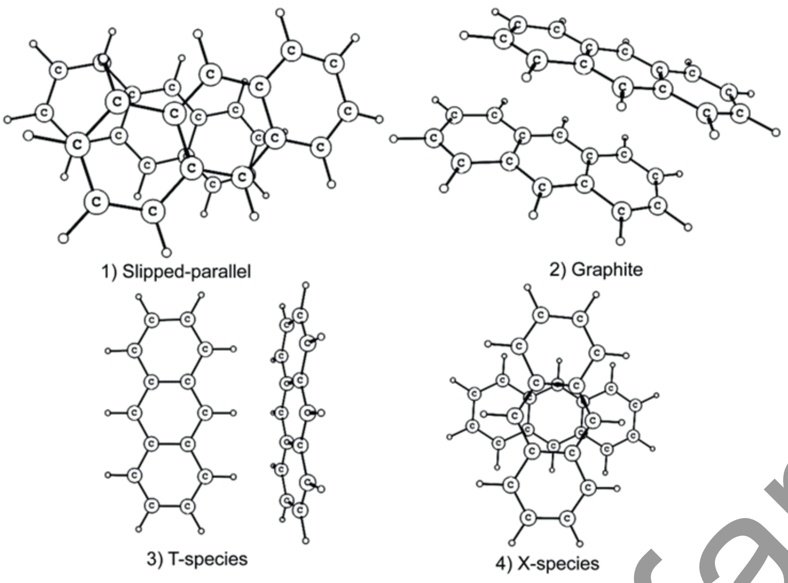
1) Slipped-parallel
2) Graphite
3) T-species
4) X-species

Fig. 1. Equilibrium geometries of the ground electronic state for four anthracene dimers.

characteristics of the anthracene dimers can be calculated more exactly by the DFT method using the hybrid functional with dispersion correction and expanded basis set.

In this regard, the present work is aimed at investigation of the geometrical and spectroscopic characteristics of the stable anthracene dimers by the method of density functional theory.

COMPUTING DETAILS

Equilibrium geometries of anthracene dimers in the ground electronic state were obtained using the density functional level of theory in the TZVP basis set [10]. In so doing, we took advantage of the hybrid Grimme functional with B97D dispersion correction [11]. The dispersion correction in the B97D dispersion correlation functional allows us to take into account correctly the intermolecular interaction of anthracene monomers.

The energies of the excited singlet electronic states were calculated using the method of time-dependent density functional level of theory (TDDFT) [12]. We note that all calculations were performed using the software package Gaussian 09 [13].

RESULTS AND DISCUSSION

Equilibrium Geometry

Results of quantum-chemical calculation demonstrate that there are four equilibrium configurations for two anthracene molecules. Figure 1 shows that four anthracene dimers: slipped–parallel (SP), graphite (G), t–shaped (T), and so-called crossed (X). Below these dimers are designated by the corresponding letters. It should be noted that our results on the existence of four stable anthracene dimer structures and on their kinds are in agreement with the results presented in [8]. We note also that the bond lengths of anthracene molecules change only slightly (within 0.02 Å) for all dimer species.

Table 1 gives the minimum distances between atoms in the molecules forming anthracene dimers and the binding energy for each of four dimers. From Table 1 it follows that the minimum distance between the molecules in the anthracene dimers is observed for the T-kind dimer. In addition, this dimer has the minimum binding energy. Therefore, we can conclude that it is most unstable of all dimers studied in the present work.

TABLE 1. Minimum Distances between the Molecules Forming the Anthracene Dimer and Binding Energies

Dimer	Distance, Å	Bond energy, cm^{-1}
SP	3.47	–4170
G	3.63	–4390
T	2.76	–3300
X	3.39	–4000

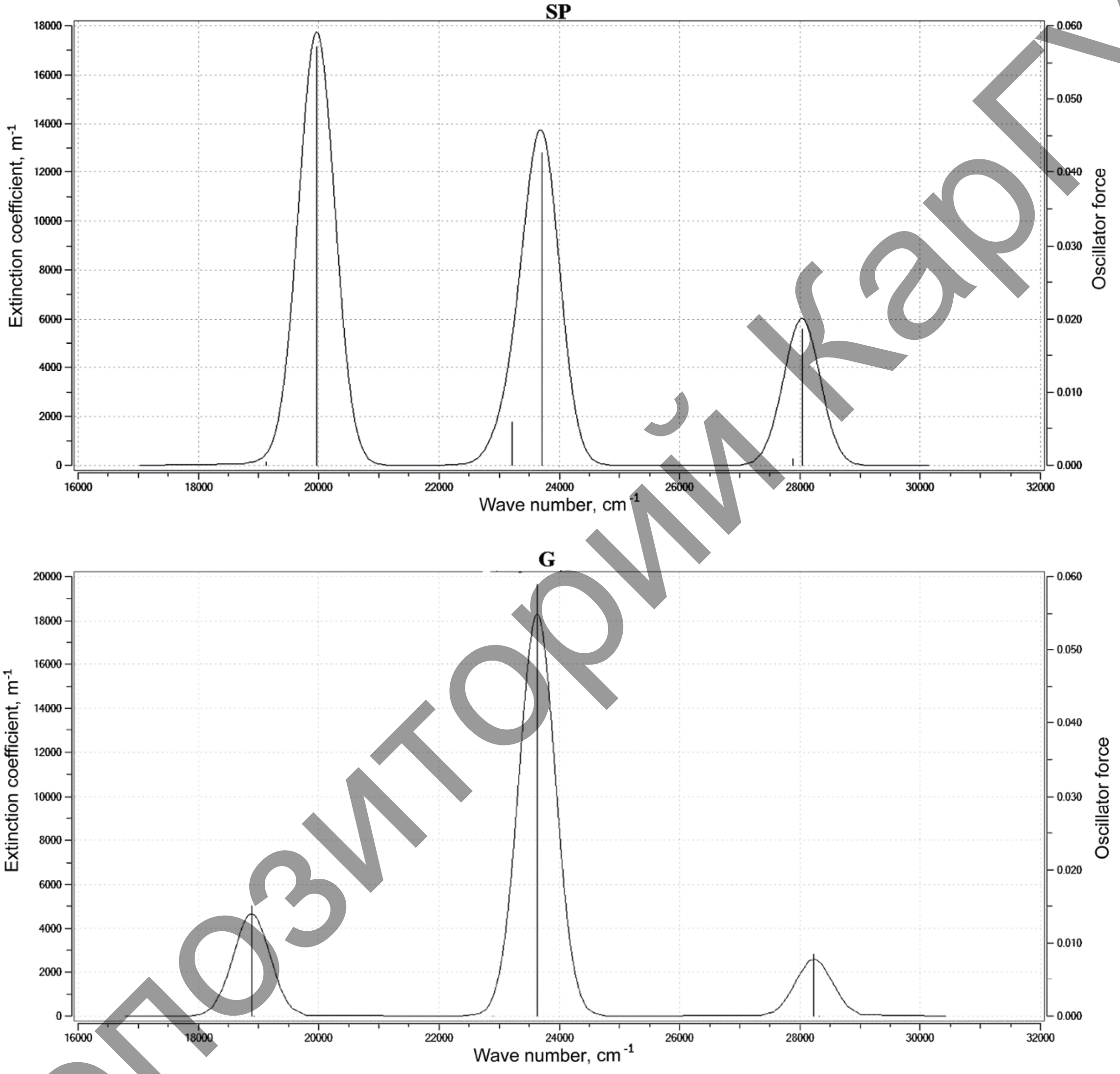

Fig. 2. Calculated electronic absorption spectra of the SP and G kinds of the anthracene dimer. Electronic transitions forming bands are indicated by vertical straight lines.

Electronic Absorption Spectra

Figures 2 and 3 show the electronic absorption spectra of the anthracene dimers that were simulated using the TDDFT/B97D/TZVP method. We note that for the theoretical absorption spectra, the half width of spectral line was equal to 350 cm^{-1}, and the Gaussian line shape was used. Three absorption bands are observed in the electronic

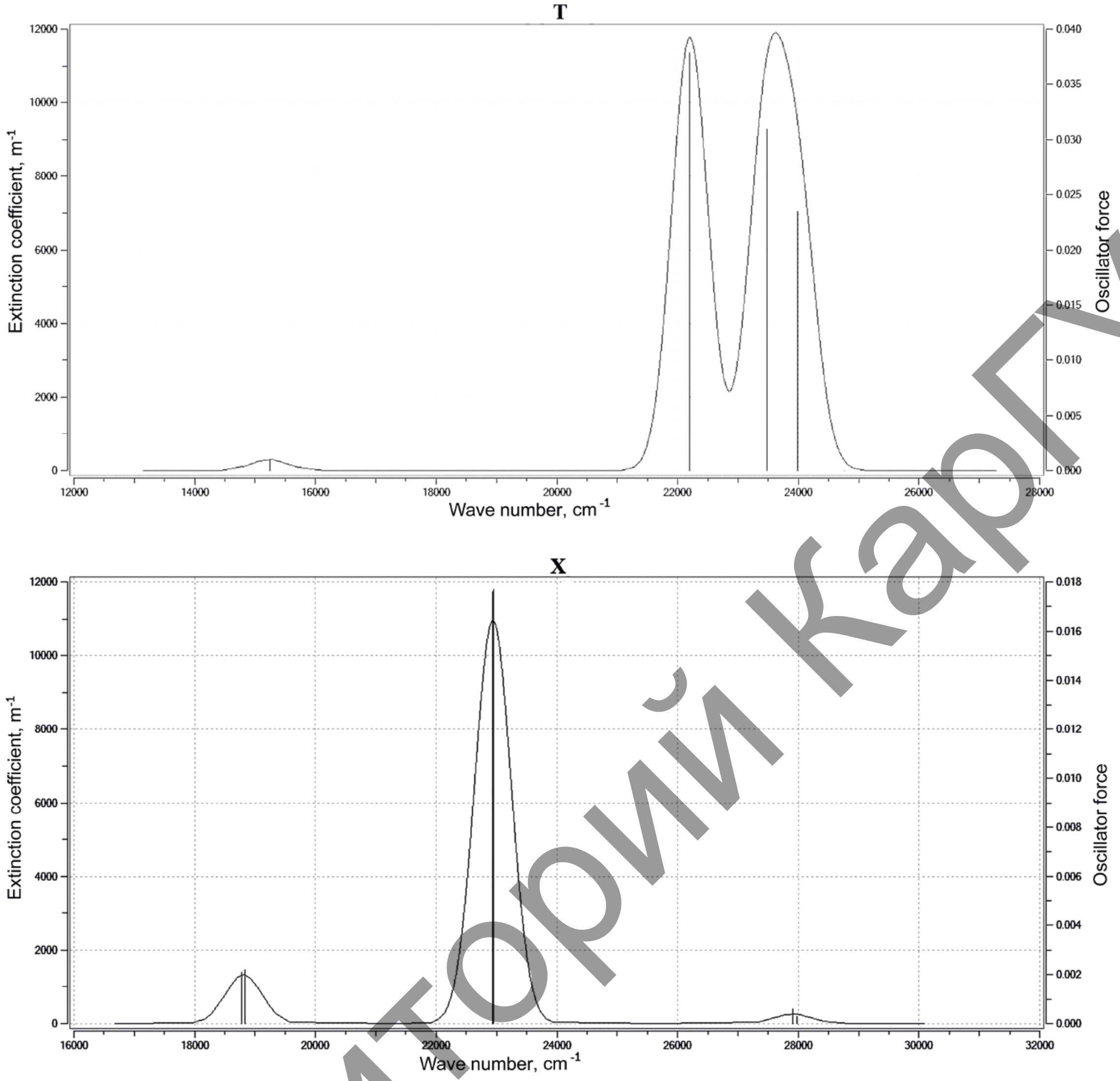

Fig. 3. Calculated electronic absorption spectra of the T- and X-species of the anthracene dimer. The electronic transitions forming bands are denoted by vertical straight lines.

absorption spectra of all four anthracene dimers in the spectral range from 14000 to 30000 cm^{-1}. These bands are formed by six lower electronic transitions. We note that the oscillator strength is equal to zero for some of the six electronic transitions. In addition, the bands in the electronic absorption spectra differ by their positions and intensities. Therefore, the considered kind of dimers can be identified based on their electronic absorption spectra. It should be noted that the G-kind of the dimer was considered in [7]. In that work the electronic absorption spectrum was presented, and it was demonstrated that the most intensive absorption band is observed at a wave number of 24875 cm^{-1}. In the present work, the second band for the graphite kind of dimer is also the most intensive band; it is formed by the electron transition with a wave number of 23700 cm^{-1}, which is in agreement with experiment [7].

CONCLUSIONS

The structural and spectroscopic properties of the anthracene dimers have been investigated theoretically. Results of calculations demonstrate that there are four stable kinds of the anthracene dimer. The positions and intensities of the absorption bands in the electronic absorption spectra of the examined anthracene dimers differ. The obtained theoretical electronic absorption spectra can be used to identify concrete anthracene structures in thin solid films.

REFERENCES

1. R. Evans and P. Douglas, Appl. Mater. Interfac., **1**, No. 5, 1023 (2009).
2. R. Evans, P. Douglas, and Ch. Winscom, Coord. Chem. Rev., **250**, 2093 (2006).
3. P. G. Gassman, J. Ghosh, and J. Almlöf, J. Am. Chem. Soc., **114**, No. 25, 9990 (1992).
4. R. R. Valiev, V. Ya. Artyukhov, V. N. Cherepanov, and D. Sundholm, Phys. Chem. Chem. Phys., **14**, No. 32, 11508 (2012).
5. R. R. Valiev, E. G. Ermolina, Yu. N. Kalugina, *et al*., Spectrochimica Acta, **A87**, 40 (2012).
6. R. R. Valiev and V. N. Cherepanov, Int. J. Quantum. Chem., DOI 10.1002/qua.24523 (2009).
7. E. A. Chandross, J. Ferguson, and E. J. McRae, J. Chem. Phys., **44**, No. 5, 419 (1966).
8. P. Podeszwa and K. Szalewicz, Phys. Chem. Chem. Phys., **10**, No. 19, 2735 (2008).
9. C. Gonzalez and E. C. Lim, Chem. Phys. Lett., **32**, 382 (2000).
10. F. Weigend and R. Ahlrichs, Phys. Chem. Chem. Phys., **7**, No. 18, 3297 (2005).
11. S. Grimme, J. Comp. Chem., **27**, No. 15, 1787 (2006).
12. M. Casida, Recent Advances in Density Functional Methods. Part I, World Scientific, Singapore (1999).
13. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09, Revision A.1, Gaussian, Inc., Wallingford CT (2009).