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Electron density analysis of aromatic complexes in excited electronic states: The benzene and naphthalene excimers

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ABSTRACT

This paper presents an energetic and electron density analysis of intermolecular complexes in excited states. The electron distributions of the benzene and the naphthalene dimers, $(C_6H_6)_2$ and $(C_{10}H_8)_2$, are studied at selected intermolecular configurations in the ground and first singlet excited states. The electrostatic contribution to the interaction energy of the benzene and the naphthalene excimers is analyzed in terms of changes on the electron density accompanying the transitions related to their electronic spectra. Some descriptors from the quantum theory of atoms in molecules and the NCI index are analyzed for these complexes in both states. These properties reveal that whereas the first order density does not explain the larger stability of the excimers compared to the ground state complexes, the intermolecular electron delocalization, a second order property, shows definite trends. The increase of intermolecular electron sharing can thus be considered a measure of the delocalization of the excitation energy in the electronic transitions.

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1. Introduction

Complexes formed by the interaction between two monomers, one of them in an excited electronic state and the other in the ground state, are called excimers if both monomers correspond to the same molecule or exciplexes when they are different species [1–5]. The pyrene excimer is probably the most representative of all excimers. Since its experimental observation in the 1950s and of the benzene and naphthalene excimers in the 1960s, intermolecular complexes in excited states have been of increasing scientific and technological interest. The applications of excimers are illustrated by the use of pyrene as a fluorescent probe in polymer reactions or in organic semiconductors in material science [6,7]. Moreover, research on the role of excimers as precursors in DNA base-pair stacking stabilization has been an active field for a long time [8–11].

The term excimer often refers to dimers that are associated in excited electronic states having dissociative ground states. The structureless emission electronic spectra of excimers are in agreement with the potential energy curves represented schematically in Fig. 1 in which the excited state S_1 of $(MM)^*$ is an associated species and MM in the ground state S_0 can either be dissociative

or weakly bonded. Hence, the definition can be extended to encompass systems regardless of the nature of the ground state [4]. The characterization of the interactions between a monomer M in the ground electronic state with another M^* in the excited state to form an excimer $(MM)^*$ is of interest from the experimental and theoretical points of view. The term resonance interaction has been defined as the migration of the excitation energy between molecules [12]. The stability of excimers is usually attributed to configurational mixing of exciton and charge resonance states involving a delocalization of the electronic excitation over both molecules of the pair plus a charge transfer contribution [1,4].

Concerning the ground state complexes, the benzene dimer, $(C_6H_6)_2$, has been the subject of a large number of studies [13–16]. In most of these, a parallel-displaced and a T-shaped structures are found to be the most stable orientations with the former being the preferred one. The information about the ground state naphthalene complex, $(C_{10}H_8)_2$, is more scarce [17–21] but a parallel-displaced and several stacked configurations, either parallel or crossed, are among the most stable structures. In particular, symmetry adapted perturbation theory (SAPT) studies of these complexes [15,18], reveal a dominant role of the stabilizing dispersion contribution and a small electrostatic component that is offset by exchange terms which within SAPT turn out to be of a repulsive nature.

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The benzene and naphthalene excimers have been less studied theoretically than their ground state counterparts and most of the efforts have been oriented to the description of their fluorescence spectra. The benzene excimer, $(C_6H_6)_2^*$, has been more investigated than that of naphthalene, $(C_{10}H_8)_2^*$, and the reported theoretical calculations involve the use of a variety of computational approaches such as semiempirical approximations, time dependent density functional theory, linear response methods, and multiconfigurational perturbation theory [21–28]. Among these, probably the latter provides the best description because of its accurate account of both static and dynamic correlation which is necessary to describe the intermolecular interactions involved in aromatic excimers (AEs). As for the $(C_{10}H_8)_2^*$ excimer, only a few reports have been published [21,27] using time-dependent density functional theory and multiconfigurational calculations with small active spaces.

Apart from electronic structure calculations, the topological analysis of the electron density, $\rho(\vec{r})$, by means of the quantum theory of atoms in molecules (QTAIM) [29–31], is a useful tool for the study of molecular structure and chemical reactivity. There is a wealth of information that has been obtained for ground state atoms, molecules and solids as opposed to electronic excited states for which the number of studies is rather limited. Some investigations about the topology of $\rho(\vec{r})$ in excited states include the analysis of transition densities, the quantum dynamics of $\rho(\vec{r})$, proton transfer reactions, chemical bonding in metallocenes, and the relationship between QTAIM and the molecular orbital analysis of electronic structure [32–36]. The topological analysis of the charge distributions of AEs provides an opportunity to explore the role of $\rho(\vec{r})$ in the transannular interactions stabilizing the complexes and to understand the charge redistribution taking place during excitation processes. This is the motivation behind this work wherein $(C_6H_6)_2^*$ and $(C_{10}H_8)_2^*$, the simplest AEs, are used as a source of information concerning π - π interactions in excited electronic states by means of the topological properties of their electron distributions.

2. Methodology

The electronic structure calculations were carried out with the complete active space second-order perturbation theory (CASPT2). The ANO basis set of Ross et al. [37] was used with the contraction scheme (C,4s3p2d/H,3s2p). The active space of both the benzene and naphthalene dimers comprised 12 electrons in 12 active orbitals. The use of a more appropriate active space made up of

20 electrons in 20 orbitals for the naphthalene complexes was precluded by the high computational cost required. Nevertheless, the CASPT2(12,12) level of theory used here correctly reproduced the fluorescence spectra of both excimers. Graphical representations of the active orbitals used for each case are given in Figs. S1 and S2 of the Supplementary Information. All the calculations included the IPEA modification [38,39] to the zero-order Hamiltonian with a value of 0.20 because of the presence of intruder states. Fig. 2 shows the geometrical arrangements and the R and D parameters used for the construction of the potential energy surfaces (PES) of the ground and first singlet excited electronic states of the benzene complex. For the naphthalene dimer, only the R variable was used to obtain the corresponding potential energy curves (PECs). The energetic information obtained allows to follow the transitions involved in the electronic spectra of the complexes and will be used for the analysis of the charge distribution. The monomers were frozen to the D_{6h} and D_{2h} CASPT2 ground state optimized geometries, respectively, and the corresponding nuclear coordinates are given in Table S1 of the Supplementary Information. With regard to the stacked eclipsed complexes, single point calculations for a set of R values were carried out using the D_{2h} point group. In a separate test for the stacked eclipsed benzene excimer, in addition to the intermolecular separation, the C–C and C–H internuclear distances within the monomers were optimized restricted to the C_{2v} point group. As a result, a small geometry relaxation takes place but both moieties remain indistinguishable from each other. In addition, Table S2 of the Supplementary Information shows that these changes have a small effect on the properties of the electron density. This is a justification for freezing the monomers to their isolated ground state geometries throughout this study. The basis set superposition error (BSSE) was corrected by means of the counterpoise [40] method. The static dipole polarizabilities of the ground and excited state benzene and naphthalene molecules were calculated as energy derivatives by the finite difference approximation at the CASPT2 level using the Sadlej's triple-zeta basis set [41]. These basis functions were devised for the calculation of molecular dipole moments and polarizabilities. All these quantum chemical calculations were carried out using the Molpro [42–44] program.

In addition, the exact electrostatic energy was obtained in terms of the basis-set representation of the first order density matrices of the unperturbed interacting molecules and the one- and two-electron integrals using the Molpro program following a procedure described in Ref. [45].

The topological properties of $\rho(\vec{r})$ were calculated using the AIMALL program [46] with formatted information of the natural orbitals obtained from single-point CASPT2 calculations at selected intermolecular arrangements with the Molcas [47] program. Finally, the NCI index of Yang et al. [48,49] was computed with the NCIPLOT software.

3. Results and discussion

3.1. Energetic analysis of excimer formation

The B_{1g} benzene excimer results from the interaction of a molecule in the A_{1g} ground state with another in the B_{2u} first excited state. The most stable intermolecular arrangement of the ground state benzene dimer is the parallel-displaced conformation, PD, shown in Fig. 2(a). The stacked-eclipsed arrangement, SE, displayed in Fig. 2(b), is a saddle point c.a. 0.1 eV higher in energy than the connected PD structures. In contrast, the SE orientation is the most stable arrangement of the $(C_6H_6)_2^*$ excimer. The SE geometry shown in Fig. 2(c) is stable for both the ground state naphthalene dimer and the corresponding B_{3g} excimer which results from the

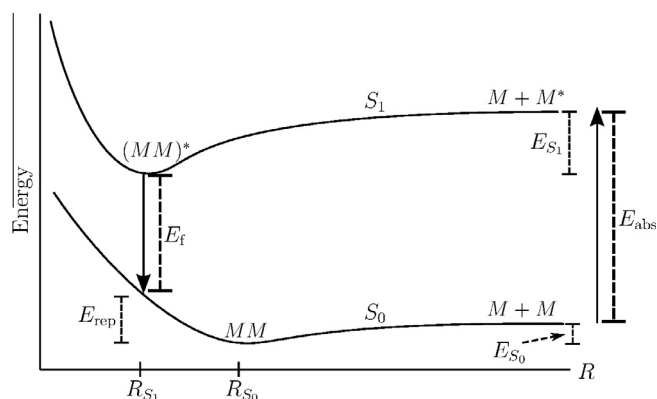


Fig. 1. Schematic potential energy curves for the dissociation of an MM complex in the ground and first excited states. The spectroscopic excimer transition to the repulsive branch of the ground state (left downward arrow) and the monomer absorption (right upward arrow) are also displayed.

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