

## On the role of van der Waals interactions in organic chemistry

Rudolf Zahradník and Pavel Hobza

J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, 121 38 Prague 2, Czechoslovakia and Institute of Hygiene and Epidemiology, 100 42 Prague 10, Czechoslovakia

**Abstract** - The interest of organic chemists in van der Waals (vdW) intermolecular interactions is increasing. There are numerous systems where these interactions play a key role: charge-transfer complexes, transannular interaction and stacking complexes, inclusion complexes, hydrogen-bonded systems, molecules with chiral discrimination, real vdW molecules, and multimolecular clusters. Moreover, the conformation of organic molecules is significantly influenced by vdW interactions. Also the role of vdW species in bimolecular reactions and in some catalytic processes is discussed. Quantum chemical and other methods suitable for the treatment of small and large vdW systems are outlined.

### INTRODUCTION

Until recently experimental chemists were usually not interested in noncovalent intermolecular interactions. Also theorists were mostly not particularly keen on the subject. The forces responsible for noncovalent interaction were considered within the framework of physical chemistry by J.D. van der Waals more than a century ago. But the first references to these forces can be traced back to the middle of the 18th century. As far as understanding the nature of these forces is concerned, the first real step forward was made in the early days of quantum mechanics by F. London. Systematic studies were begun in the thirties of this century and dealt with noncovalent interactions between atoms and molecules as well as between colloid particles. It must be admitted that these two realms of noncovalent interaction (which we shall call van der Waals interactions) have been developed with very weak mutual interaction. It is also true that their role for some areas of classical physical chemistry has been appreciated for a long time (ref. 1).

The significance of vdW interactions for chemistry was first acknowledged not a very long time ago (ref. 2). In colloid chemistry, the theory of vdW interactions has played a distinctive role for decades (ref. 3 & 4). No doubt, vdW interactions are very important for the interactions between biopolymers, and between the supermolecular constituents of living systems (ref. 2, 3 & 5).

It is the purpose of this article to outline systems and processes which are important for organic chemistry and which are intimately connected with vdW interactions. Theoretical procedures suitable for investigation of organic vdW systems will be reviewed briefly; more attention will be paid to utilization of quantum chemical methods. Phenomena which are closely connected with the great role of vdW interactions but which are not specific for organic chemistry will, in general, not be included. This concerns, for example, behaviour in solutions and solvent effects and surface chemistry.

### VAN DER WAALS INTERACTIONS

**Systems and processes.** The systems and processes under study are outlined in the following Chart.

- Chart**
- A INDIVIDUAL MOLECULES: Conformation**
- B INTERMOLECULAR COMPLEXES**
- (a) charge-transfer complexes
  - (b) transannular interaction and stacking complexes
  - (c) inclusion complexes
  - (d) hydrogen-bonded systems
  - (e) chiral discrimination
  - (f) real vdW molecules
  - (g) multi-molecular clusters
- C CHEMICAL TRANSFORMATIONS**
- (a) bimolecular reactions
  - (b) catalytic ability of vdW species

**Theoretical tools.** In order to correctly describe energy change,  $\Delta E$ , accompanying the formation of a vdW complex (Eq. 1) highly accurate methods



must be used (see Fig. 1). We shall limit ourselves to only the most productive methods. Therefore, special attention will be paid to the MO-LCAO approximation at various levels of sophistication and to the variation method. It is expedient to distinguish four categories of organic systems regardless their structural type. For computational and economic reasons, the usefulness of the most accurate methods of quantum chemistry (beyond H.F., see Fig. 1 and group 1 in Table 1) is limited to systems with not more than 20 to 25 electrons. This requirement is fulfilled in organic chemistry with systems like  $\text{CH}_2 + \text{H}_2$ ,  $\text{CH} + \text{CH}$ ,  $\text{CH} + \text{H}_3^+$ ,  $\text{CH}_2 + \text{H}_3^+$ ,  $\text{CH}_3 + \text{CH}_2$ ,  $\text{C}_2\text{H}_4 + \text{CH}_3^+$ . Before dealing with some computational details, it should be noted that  $\Delta E$  in Eq. 1 is mostly expressed as a superposition of two contributions, namely the Hartree-Fock (H.F.) SCF energy change ( $\Delta E^{\text{SCF}}$ ) and the correlation energy change ( $\Delta E^{\text{COR}}$ ):

$$\Delta E = \Delta E^{\text{SCF}} + \Delta E^{\text{COR}} \quad (2)$$

A really accurate calculation of both these parts is a complex task. Special care must be paid to equally good description of the subsystems and of the supersystem; the basis set superposition error (BSSE) should be included (e.g., by applying the function counterpoise method (ref. 6)) at both the SCF and beyond SCF levels. In order to obtain reliable values of  $\Delta E^{\text{SCF}}$  and  $\Delta E^{\text{COR}}$ , extended basis sets must be used. Reasonable values of  $\Delta E^{\text{SCF}}$  (but not  $\Delta E^{\text{COR}}$ ) can be also obtained with moderate or even minimal (but well balanced) basis sets. In this case, however, the  $\Delta E^{\text{COR}}$  term will be strongly

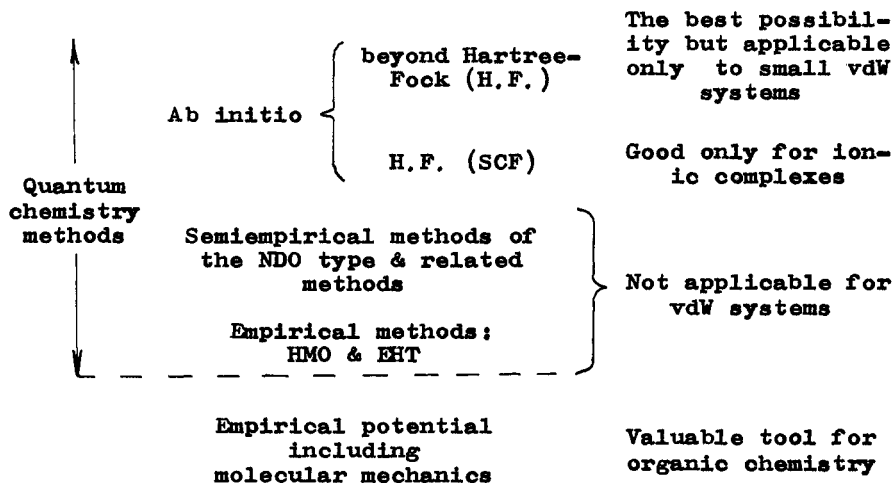


Fig. 1.

underestimated; this term can be successfully approximated by the dispersion energy obtained on the basis of, e.g., the modified London expression. It has been shown that the dispersion energy is a very good approximation to the change in the intersystem correlation energy. It is worth mentioning that recently a procedure was developed, using a "chemical Hamiltonian", which avoids the BSSE (ref. 7). At present this procedure is critically tested.

## APPLICATIONS

### Individual molecules: conformation

It is useful to realize that steric phenomena (hindrance, acceleration) are usually due to vdW interactions. Frequently, H.F. SCF calculations combined with an efficient molecular geometry optimization are satisfactory; the DZ basis set is mostly reliable sufficiently. To attain high accuracy, the DZ+P basis set or even beyond SCF level should be considered. It is fair to add that the popular STO-3G basis set, which is not suitable for intermolecular interactions, is rather good for conformation analysis of very large organic molecules (ref. 8). If, however, two ends of a large molecule, which are usually far apart, approach one another at least approximation 3 (Table 1) should be used.

A broad spectrum of empirical potentials ranging from molecular mechanics and the 1,6,12-potential to EPEN, CHARMM, and AMBER is available and can be successfully used for systems with dozens and hundreds of atoms (ref. 2, 9 & 10). It is desirable to add that, even when very carefully parametrized, their transferability is mostly poorer than some users believe (ref. 11).

TABLE 1. Methods suitable for treatment of van der Waals molecules of various size

Group	Number of electrons	atoms	Procedure	Example
1	25	-	H.F.SCF with extended basis set plus BSSE plus correlation energy at the MP4 level or, e.g., CEPA	$\text{CH}_2 \cdots \text{H}_3^+$ , $\text{C}_2\text{H}_4 \cdots \text{CH}_3^+$
2	50	-	H.F.SCF with DZ+P basis set plus BSSE plus correlation energy at MP2 level	$(\text{C}_2\text{H}_4)_2$ , $(\text{HCN})_2$ , $(\text{H.COOH})_2$
3	200	-	H.F.SCF with Huzinaga's minimal basis set plus BSSE; the interaction correlation energy is approximated by London dispersion energy	Purine-pyrimidine complexes, (naphthalene) <sub>2</sub> , anthracene $\cdots$ Kr
4	-	400	$\Delta E^{\text{SCF}}$ is approximated by electrostatic energy corresponding to accurate charge densities, $\Delta E^{\text{COR}}$ , see 3; position of vdW minimum must be determined empirically, using e.g., vdW atomic radii	Segments of nucleic acids interacting with molecules; interactions between large peptides

## Intermolecular complexes

**Charge-transfer complexes.** These complexes have played an important role in organic chemistry for years. They are used for identification (e.g., complexes of organic bases with picric acid) and for quantitative analysis because of their characteristic colour; for analytical purpose frequently a specific, longest-wavelength absorption band, a charge-transfer band is used. It is possible, by inspection of frontier orbitals of the donor and the acceptor, to make a qualitative estimate of the structure of the complex. For quantitative purposes (geometry and energy calculations) good quality SCF calculation and inclusion of the correlation energy are unavoidable (ref. 2).

**Transannular interaction and stacking complexes.** Both these interactions are essentially no more than interaction through space between parallel or nearly parallel conjugated systems. These systems are held together directly (e.g., paracyclophanes) or indirectly (e.g., nucleic acids). The term transannular interaction is used in connection with an extensive set of paracyclophane-like compounds. In a majority of instances the z-axes of the  $p_z$ -orbitals are oriented perpendicularly to the planes in which the interacting systems are located. Attraction between identical subunits is mostly rather weak and essentially a result of dispersion forces. From this point of view, the term "non-bonding" interactions is understandable and adequate. If the conjugated systems are close enough, the interaction is manifested in the electronic (ref. 12) and photoelectron (ref. 13) spectra. For 1-thiacyclooctanone(5), the electronic spectrum remains that of thio-carbonate.

The situation with stacking interactions familiar for nucleic acids is different because, when properly mutually oriented, nucleic acid bases can exert a significant coulombic attraction.

A proper theoretical description of these interactions is difficult because extensive basis sets augmented by a diffuse function must be used in order to obtain a sufficiently high yield for the correlation energy (ref. 14). A theoretical study involving pairs of, e.g., ethylene, formaldehyde and hydrogen cyanide was facilitated because the symmetry was utilized to simplify the calculations. The results can be summarized as follows (ref. 14): The SCF interaction energies are only slightly basis-set-dependent, in contrast to the MP2 interaction energies, which are strongly basis-set-dependent. A modified 6-31G\* basis set (diffuse polarization functions) provides satisfactory values of the SCF, correlation and total interaction energies of stacking complexes.

**Inclusion complexes.** These systems have represented a broad and important part of chemistry over the last twenty years (ref. 15 & 16). The systems range from crown-ethers to cryptates, and include systems like cyclodextrins. Selective binding, a remarkable influence on the reactivity, and potential catalytic and preparative importance make these systems very attractive. These systems form mono- or polycyclic complexes and mimic some features of biologically active systems.

Strong electric fields act inside of cycles and cavities. Interactions with complexes of this type are usually entropically very convenient. There is a great deal of evidence for the unusual and powerful effects of these systems. The formation of sodium anions (ref. 17) and iodide cations (ref. 18) are among the most convincing examples. Some recent works (ref. 19, 20 & 21) illustrate the great versatility of these systems.

Theoretical treatments are mostly based either on molecular mechanics or on the 1,6,12-potential (ref. 22). A gradual transition to more sophisticated procedures is desirable (ref. 13). There is sometimes a tendency to theoretically describe these interactions in a rather complicated way.

Remarkable complexes between viologenes and benzenoid hydrocarbons have been described (ref. 24). In this connection, it is worth mentioning that radical cations or anions ("semiquinones") in the viologene series tend to dimerize reversibly; the dionic dimers formed are diamagnetic. Obviously not a biradical but a singlet ground state is formed (ref. 24).

**Hydrogen-bonded systems.** Without a doubt, H-bonded complexes have been the most intensively investigated (ref. 25) intermolecular complexes. Therefore, just three remarks will be made in this connection. With respect to computational problems, it should be noted that the dominant attractive

contribution comes from the SCF energy. Nevertheless, it is also true (ref. 26) that about 20% of  $\Delta E$  is due to the correlation energy term,  $\Delta E^{\text{COR}}$ . With more extensive complexes this portion is even larger. MP2 stabilization energies are only slightly dependent on the basis set for a basis of DZ+P or better quality. The BSSE at both the SCF and MP2 levels remains almost unchanged when passing from the 6-31G\* to the 6-311G (2d,2p) basis set. For reliable description of H-bonded complexes, MP2/6-31G\* calculations with inclusion of both BSSE's can be recommended. This was carefully investigated for small H-bonded complexes (ref. 26) but it is very probably also true for more extensive systems.

The second comment concerns a topical and intensively studied, double-minimum, proton or hydrogen transfer. There are significant differences between transfer taking place in an electronic ground-state either in the gas phase or in condensed media (ref. 27) and that in an electronically excited state (ref. 28). A double cooperative proton transfer in, e.g., 2,2'-bipyridyl-3,3'-diol can also be interpreted on the basis of symmetry arguments (ref. 29). The lowest excited states of primary and tautomeric structures are represented by nearly pure HOMO-LUMO configurations.

The third point deals with solute-solvent interactions in microhydrate clusters. Carbazole...( $\text{H}_2\text{O}$ ,  $\text{D}_2\text{O}$  or  $\text{NH}_3$ ) $_n$  ( $n = 1, 2, 3$ ) complexes have been studied spectroscopically (ref. 30). Excited state proton transfer was detected in  $\alpha$ -naphthol...( $\text{NH}_3$ ) $_n$  ( $n = 1, 2, 3$ ) clusters by laser spectroscopic techniques (ref. 31).

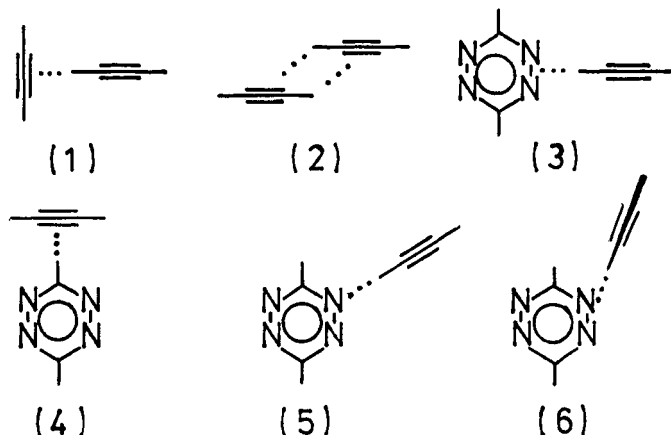
*Chiral discrimination.* Chiral discrimination is the energy difference between the complexes of two identical and different optical antipodes. Its importance for the interactions between chiral biomolecules is still uncertain simply because these energy differences are small. The discriminative nature of some terms of the perturbation expansion was studied in detail by Craig (ref. 32) and theoretical aspects have been considered in general by Mason (ref. 33). As the effect under study is small, two requirements must be satisfied when studying it by quantum chemical methods. First, the method used must be sophisticated enough and, second, all the stationary points on the respective potential energy surface must be very carefully localized. Two cases can be distinguished: intermolecular and intramolecular chiral discrimination, the latter usually being more powerful.

1,2-Difluorohydrazine can be used as a model for studying short-range discriminative interactions between two chiral forms of the NHF radical (ref. 34). The combination of these forms can yield a meso form and chiral active forms, which are mirror images. Four minima and six saddle points were found on the 3-21G and FOGO (ref. 35) hypersurfaces. The thermodynamic properties of the most stable configuration were calculated.

*Real van der Waals molecules.* Extensive attention has been paid to attractive vdW systems consisting of an aromatic molecule (e.g., benzenoid hydrocarbon) and a small number of rare gas atoms. These are good models for interactions between a large "solute" and a "solvent" (ref. 36 & 37). Spectroscopic and thermochemical aspects were investigated. It seems that a mere 6,12-potential is of considerable help. It was, e.g., used in connection with analysis of the interaction of perylene (P) with rare gas atoms (R).  $\text{PR}_n$  complexes ( $n = 1-4$ ) were prepared in seeded supersonic free jet expansion and analyzed by means of laser-induced fluorescence spectroscopy. Two isomers of  $\text{PR}_2$  complexes were identified. In one of them, both R atoms are bound to the same side of the hydrocarbon; in the other one, they are attached to the opposite sides. The three-body terms were also considered in the theoretical analysis. Another good example of real vdW molecules are selfassociates of various hydrocarbons, like acetylene, ethylene (ref. 14), or benzene (ref. 38).

In the dimer of acetylene and a complex between tetrazine and acetylene (ref. 39), the deepest energy minima are associated with structures 1, 2 and 3 - 6 for obvious reasons: the weak acidity of acetylene and weak basicity of acetylene and tetrazine are important here. There is no energy stabilization in the rectangular ( $\text{C}_2\text{H}_2$ ) $_2$  complex but this structure is enforced in 1,5-cyclooctadiyne (ref. 40).

*Multi-molecular clusters.* Extensive sets of charged clusters were studied in the laboratories of Kebarle (ref. 41) and Castleman (ref. 42). The fact that eleven stationary points were found on the PES of the methane dimer radical cation (ref. 43) indicates that it would be hopeless to investigate



the PES of larger clusters along classical lines. The only chance is based on using Monte-Carlo-type computer experiments (ref. 44). It is also worth mentioning that stable conformations of the studied radical cation possess structural features which are unexpected if not impossible in the field of classical molecules, e.g., the deepest minimum corresponds to a linear structure with a central H-H bond. The situation is mostly even more complicated with neutral clusters (ref. 45). Minimum energy configuration of thirteen-molecule clusters of  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{C}_6\text{H}_6$ , cyclohexane, and naphthalene were studied by means of the 12-6-1 potential (many-body terms were disregarded). The configurations are related to the ground-state structures of clusters of rare-gas atoms. In this connection, the application of IR photodissociation spectroscopy of ethylene clusters for structure and energetics analysis should also be cited (ref. 46).

## CHEMICAL TRANSFORMATIONS

### Bimolecular reactions

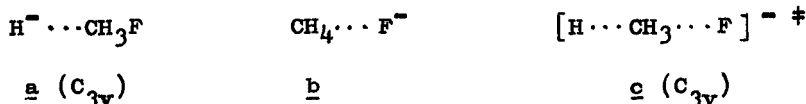
For years there has been a tendency to visualize the course of bimolecular reactions in terms of a three-level scheme (reactants, activated complex, products). It is obvious, however, that, in general, a five-level scheme is valid. The species separating the reactants as well as the products from the activated complex are vdW species (ref. 2). Two cases should be distinguished: reactions between molecules and ion-molecular reactions. In the former case (see Eq. 3, and Eq. 4 in the direction from the left to the right-hand side) true vdW species are formed, i.e., they dissociate readily.



Therefore, the overall reaction course is affected only very slightly by these species. In the latter case, the ionic vdW species can significantly influence the reaction course because they are energetically much more stable than their free components. The mechanism of  $\text{S}_{\text{N}}2$  ionic-molecular reactions was investigated by several groups (e.g., ref. 47 & 48). Perhaps the most extensive calculations were performed in a recent work (ref. 49). The geometry of the both vdW species and the activated complex for reaction 5



are represented by formulae a, b, and c; note that system b does not possess

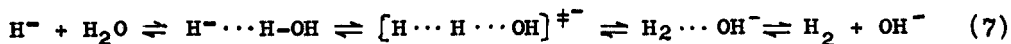


a  $\text{C}_3$  symmetry axis. Let us add that a and b are stabilized with respect to the free components by about 100 and 120 kJ/mol, respectively.

In connection with studies of  $\text{H}^-(\text{H}_2\text{O})$  and  $\text{H}^-(\text{H}_2\text{O})_2$  vdW ions, the energy profile of the proton abstraction process 6 was also investigated (ref. 50).



Similarly as in the above-mentioned instances, also here the transition state of process 7 is neighboring with two vdW systems.



#### Catalytic ability of vdW species

Van der Waals species can act as very mild but efficient catalysts in both orbitally- and spin-forbidden processes (ref. 2). In the former, in pericyclic reactions involving two partners, one of them is replaced by its vdW dimer. Specifically, instead of a forbidden process involving two single or double bonds, an orbitally allowed process with three bonds takes place.

Well-known termolecular reactions including nitric oxide belong to this type of process. The same is true for ClBr formation from  $(\text{Cl})_2$  (vdW dimer) and  $\text{Br}_2$  in molecular beams (ref. 51). Additions of water to cumulenes and to  $\text{CO}_2$  take place along a reaction path including two water molecules (ref. 52 & 53). A similar mechanism could participate in the hydrolysis of isothiocyanates and ketones.

Formation of a vdW complex with an inert system containing a heavy atom or with a paramagnetic species (e.g., NO,  $\text{O}_2$ ) leads to breakdown of spin quantization. This fact has been used for years in analyzing spin-forbidden transitions in electronic spectra (ref. 54 & 55) but can also be utilized to make spin-forbidden chemical reactions feasible.

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