Papers

Intermolecular Potential of Ethylene Dimer — A Modified Semiempirical Method

K BHANUPRAKASH, D SRIKANTAN & A K CHANDRA*

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012

The intermolecular potential of the ethylene dimer in the ground state has been computed semiempirically. It is found that the principal terms of interaction energy are the repulsive exchange and the attractive dispersion. Both these terms are absent in the INDO method. So the realistic potentials are obtained when these two terms are added to the INDO energies. Three different structures, viz. sandwich, T-shaped and shifted parallel of the ethylene dimer have been considered and the most stable one has the slightly shifted parallel structure as found in the ethylene crystal.

In a previous publication[1] we reported the interaction potential of ethylene dimer obtained by exchange perturbation method and observed that T-shaped structure is the preferred geometry of the neutral dimer. Ab initio calculations[2,3] within the framework of a supermolecule also revealed that T-shaped structure of ethylene dimer is more stable than the perfect sandwich structure, in contrast to the CNDO calculations[4], which showed that the more stable ethylene dimer had the perfect sandwich structure. The refinement[5] of Bunn's crystal structure of ethylene[6] at low temperature shows that it has $P2_1/n$ space group and the two molecules could be parallel as in the sandwich geometry. Based on molecular beam experiments[7], the ethylene dimer has been reported to be nonpolar. It, therefore, ruled out the possibility of T-shaped structure being most stable for the ethylene dimer. Recent semiempirical calculations by Fraga[3] on benzene dimer have shown that the minima that were observed for various probable structures of dimer on two-dimensional potential curves did not exist on the multidimensional potential energy surface and probably collapsed to the perpendicular dimer. If one has to deal with the two-dimensional potential energy curves, all the probable structures have to be examined in order to find the most stable one.

In this paper we shall consider the three probable structures of ethylene dimer (Fig. 1) according to a semiempirical treatment, the order probable structures are not presented as they give almost repulsive potential. In the usual CNDO or INDO treatment of supermolecule[9,10] the exchange repulsion is absent, in addition to the dispersion energy, in view of the neglect of the diatomic intermolecular overlap. As a result, the previous CNDO and INDO[9,10] treatments of supermolecule lead to a very large binding energy and small equilibrium interaction bond length. In this study we shall give a semiempirical method of

calculating the exchange repulsion term. We then use the atom-pair potential method[11] to estimate the dispersive interactions and then add these two terms to the INDO potential to obtain physically reasonable potential curves of the neutral dimer. This method can be applied to larger composite systems and the present example may serve as suitable bench mark.

Model for Calculation

The neutral dimer is treated as supermolecule. The orbitals and energies are obtained by the usual single-configuration INDO method[12]. We deal with the three different structures of the dimer and call them sandwich (Fig. 1a), T-shaped (Fig. 1b) and shifted parallel (Fig. 1c), where R denotes the distance between the two
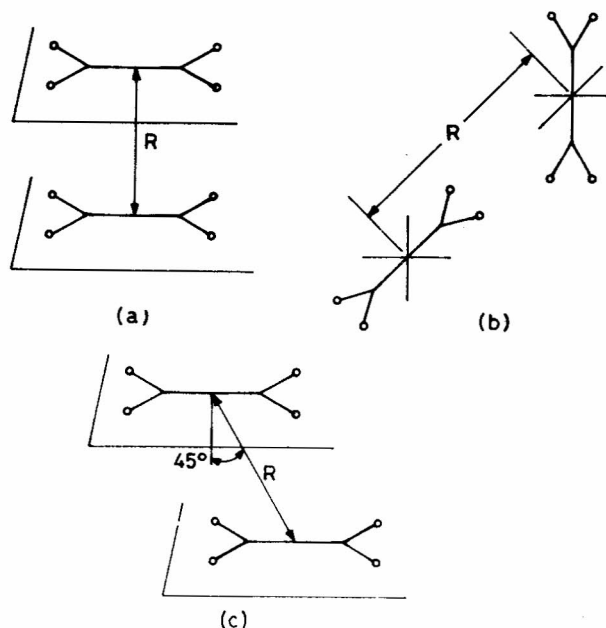

Fig. 1 —(a) Perfect sandwich structure, (b) T-shaped structure, (c) shifted parallel structure [In all cases R denotes the distance between the two centres of masses]

3

centres of masses. The geometry of ethylene monomer $(r_{C-C} = 1.337\ \text{Å}, \quad r_{C-H} = 1.086\ \text{Å}, \quad < HCH = 117°22')$ obtained from experiment is assumed invariant in the dimer.

Since simple Slater orbitals give incorrect results at large distance from the atomic centre, we use the orbital exponent of 1.4 for the carbon $2s$ and $2p$ functions as this gives a reasonable fit to the Hartree-Fock-Roothan orbitals[13] of carbon for $R \geqslant 3.0\ \text{Å}$. For the description of intramolecular bond the usual exponent of 1.60 is used for the carbon $2s$- and $2p$-orbitals. For the hydrogen $1s$-orbital the usual exponent of 1.2 is used for all R.

Calculation of exchange energy

The exchange energy or the closed shell repulsion arises from the first-order exchange of electrons between the two molecules in a perturbation treatment of a composite system. Let the INDO molecular orbitals of one molecule, say A, be denoted by i, j etc., and the corresponding MOs of the other, say B, by i',j' etc. The first-order exchange energy is given as[14,15]

$$E_{\text{exch}} = - \sum_{j}^{occ} \sum_{i}^{occ} n_i n_{j'} <i|V|j'> S_{ij'} \qquad \ldots (1)$$

where n_i, $n_{j'}$ are the occupation numbers of the MOs i and j' respectively, $S_{ij'}$ is the overlap and V is the interaction perturbation. We ignore the matrix elements of V over MOs that are localised on the same molecule as is usually followed in the earlier treatments[15]. Since the MOs are in the LCAO form, the integral $<i|V|j'>$ can be expressed as a linear combination of integrals over the atomic orbitals (AOs).

We consider two one-electron atoms μ and ν' with AOs $\chi_\mu(2)$ and $\chi_\nu(1)$ respectively and assume that each electron experiences one positive unit of nuclear charge at each centre. This means that other electrons present in each neutral atom screen its remaining nuclear charge. The first-order exchange energy is given by[16]

$$I_{\mu\nu'} = - \langle \chi_{\nu'}(1)\chi_\mu(2) \left[\frac{1}{r_{12}} + \frac{1}{R_{\nu'\mu}} - \frac{1}{r_{\nu'2}} - \frac{1}{r\mu 1} \right]$$
$$\times \chi_\mu(1)\chi_\nu(2) \rangle + S^2_{\nu'\mu} \langle \chi_{\nu'}(1)\chi_\mu(2)$$
$$\times \left| \frac{1}{r_{12}} + \frac{1}{R_{\nu'\mu}} - \frac{1}{r_{\nu'2}} - \frac{1}{r_{\mu1}} \right| \chi_{\nu'}(1)\chi_\mu(2) \rangle$$
$$= - \left[\langle \chi_{\nu'}\chi_\mu | \chi_{\nu'}\chi_\mu \rangle + \frac{S^2\nu'\mu}{R\nu'\mu} \right.$$
$$- \langle \chi_{\nu'} \left| \frac{1}{r_{\mu1}} \right| \chi_\mu \rangle S_{\nu'\mu} - \langle \chi_\mu \left| \frac{1}{r_{\nu'2}} \right| \chi_{\nu'} \rangle$$
$$\times S_{\nu'\mu} \right] + S^2_{\nu'\mu} \left[\langle \chi_{\nu'}\chi_{\nu'} | \chi_\mu\chi_\mu \rangle + \frac{1}{R_{\nu'\mu}} \right.$$
$$\left. - \langle \chi_{\nu'} \left| \frac{1}{r_{\mu1}} \right| \chi_{\nu'} \rangle - \langle \chi_\mu \left| \frac{1}{r_{\nu'2}} \right| \chi_\mu \rangle \qquad \ldots (2)$$

where

$$\langle \chi_{\nu'}\chi_\mu | \chi_{\nu'}\chi_\mu \rangle =$$
$$\iint \chi_{\nu'}(1)\chi_\mu(2) \frac{1}{r_{12}} \chi_\mu(1)\chi_{\nu'}(2)\,dV_1 dV_2 \qquad \ldots (3)$$

We employ Mulliken approximation for the electron-repulsion integral and obtain

$$\langle \chi_{\nu'}\chi_\mu | \chi_{\nu'}\chi_\mu \rangle = \frac{S^2\nu'\mu}{4} [\gamma_{\nu'\nu'} + \gamma_{\mu\mu} + 2\gamma_{\nu'\mu}] \qquad \ldots (4)$$

where

$$\gamma_{\nu'\mu} = \langle \chi_{\nu'}\chi_{\nu'} | \chi_\mu\chi_\mu \rangle \qquad \ldots (5)$$

We then employ Ohno's approximation[17] for the two-centre electron-nuclear attraction term and obtain

$$\langle \chi_{\nu'} \left| \frac{1}{r_{\mu1}} \right| \chi_\mu \rangle = \frac{2S_{\nu'\mu}}{R_{\nu'\mu}} \qquad \ldots (6)$$

This approximation is valid for the $2s$-$2p$ and $2s$-$2s$ overlaps also for large R. Substituting Eqs (4) and (6) in Eq. (2), we get

$$I_{\nu'\mu} = - S^2_{\nu'\mu} \left[\frac{1}{4}(\gamma_{\mu\mu} + \gamma_{\nu'\nu'}) - \frac{\gamma_{\mu\nu'}}{2} - \frac{2}{R\nu'\mu} \right] \qquad \ldots (7)$$

If we consider V as an effective one-electron operator, one may write the exchange energy between two one-electron atoms as

$$I_{\nu'\mu} = - \langle \chi_\mu|V|\chi_{\nu'} \rangle S_{\nu'\mu} \qquad \ldots (8)$$

Comparing Eq. (7) with Eq. (8) we have

$$\langle \chi_{\nu'}|V|\chi_\mu \rangle = K_{\nu'\mu} S_{\nu'\mu} \qquad \ldots (9)$$

where

$$K_{\nu'\mu} = \left[\frac{1}{4}(\gamma_{\mu\nu'} + \gamma_{\nu'\nu'}) - \frac{\gamma_{\mu\nu'}}{2} - \frac{2}{R_{\nu'\mu}} \right] \qquad \ldots (10)$$

We use the standard semiempirical values of the one-centre integrals[18], i.e. for carbon $\gamma_{\mu\mu} = 10.33\ \text{eV}$ and for hydrogen $\gamma_{\nu'\nu'} = 12.85\ \text{eV}$. The two-centre integral $\gamma_{\mu\nu'}$ is determined by Mataga-Nishimoto approximation[19] so that characteristics of atoms are reflected in $K_{\nu'\mu}$ via the electron repulsion integrals. We have found that various approximations for evaluating two-centre integrals converge to the theoretically calculated values when $R_{\nu'\mu} \geqslant 3.0\ \text{Å}$, similar to that observed by Murrell and Harget[20]. Since the range of intermolecular separation of interest to us is larger than 3.0 Å, our results are not sensitive to the approximations used in the evaluation of two-centre integrals. We calculate the atomic integrals $\langle \chi_\mu|V|\chi_{\nu'} \rangle$ from Eqs (9) and (10) as a function of R and then insert in Eq. (1) to obtain exchange repulsion energy.

It should be noted that the core charge of carbon in the INDO/CNDO method is 4.0. Equation (2) gives the exchange repulsion term for two one-electron atoms. When this is multiplied by the number of valence electrons on each atom the actual core charges of the interacting atoms are properly accounted for. This is taken into account in Eq. (1) through n_i and n_j.

Calculation of dispersion energy

The ability of the atom-pair potential results to predict experimental dispersive intermolecular interactions is now well established. The first term of the multiple expansion of dispersion energy is given by[11]

$$E_{\text{Disp.}} = -\sum_{\mu \varepsilon B}\sum_{\nu \varepsilon A} A_{\nu'\mu}/R^6_{\nu'\mu} \qquad \ldots (11)$$

where A is the atom-atom parameter derived by Mulder and Huiszoon[11]. They are $A_{C-C} = 0.826$ au, $A_{C-H} = 0.23$ au and $A_{H-H} = 0.0636$ au[11]. While the pairwise A-parameters are isotropic, $E_{\text{Disp.}}$ depends on the intermolecular orientation via $R_{\nu'\mu}$

Calculation of total interaction energy

The total interaction energy of a composite system AB is given by

$$\Delta E = \Delta E_{\text{INDO}}(R) + E_{\text{exch}}(R) + E_{\text{disp}}(R) \qquad \ldots (12)$$

and

$$\Delta E_{\text{INDO}}(R) = E_{\text{INDO}}(R) - E_{\text{INDO}}(\infty) \qquad \ldots (13)$$

where $E_{\text{INDO}}(R)$ is the total energy of the composite system for a given R calculated by the usual INDO method, and $E_{\text{INDO}}(\infty)$ is the sum of the INDO energies of the component molecules. Since ΔE is very small we have ensured that ΔE is significant to 10^{-5} au/mol or 10^{-3} kcal/mol using double precision numbers throughout the computation.

Results and Discussion

The results for the three different dimer structures of the ethylene dimer are graphically shown in Figs 2-4 for the range of R where the potential minima in the total interaction curves are observed. It should be noted that these minima occur at values of $R > 3.0$ Å. The curves (a) in Figs 2-4 reveal that the exchange repulsion at any given R decreases for the three structures in the sequence:

T-shaped > perfect sandwich > shifted parallel

This is in agreement with the results obtained by Suzuki and Iguchi[21] employing the ab initio wavefunctions and exchange perturbation theory. Our results show that the weak bonding in dimer is primarily due to dispersive forces at large R and the minima occur because of the large increase of the exchange repulsion with decreasing R. Neither of these two terms is present in ΔE_{INDO} and, therefore, a straight forward CNDO and INDO calculations of the dimer as a supermolecule can lead to an unreliable picture of bonding.

The present calculations show that, of the three structures of dimer (Fig. 1), the shifted parallel structure (Fig. 1c) is most stable with the binding energy of 0.41 kcal/mol. In the actual ethylene crystal, molecules make a nearly shifted parallel structure[22].
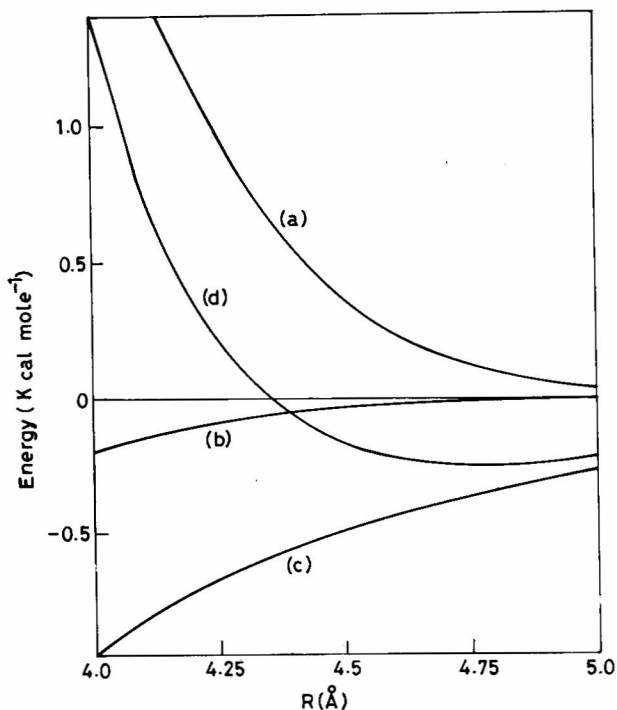

Fig. 2—Variation with R of (a) exchange repulsion, (b) ΔE_{INDO}, (c) attractive dispersion and (d) total interaction energy [ΔE, for the perfect sandwich structure of the dimer]

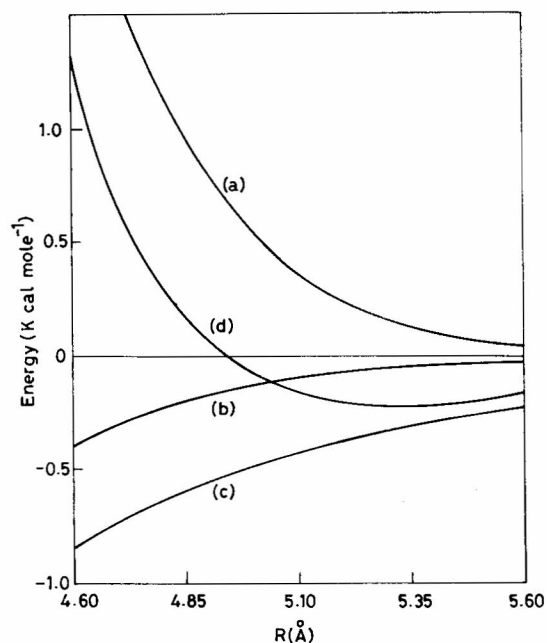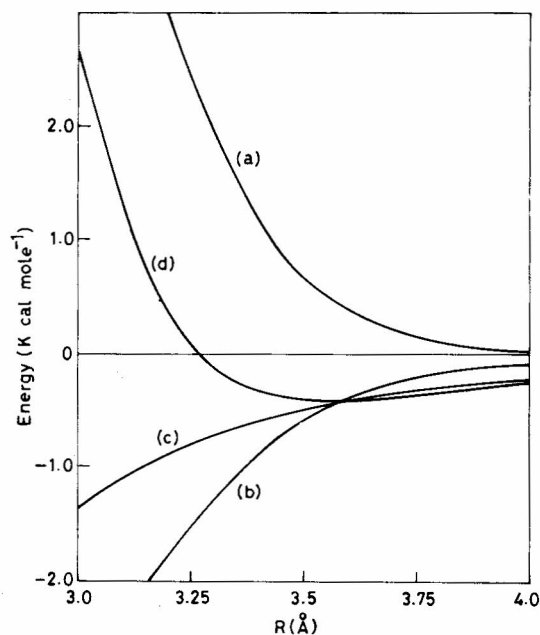Fig. 3—Variation with R of (a) exchange repulsion, (b) ΔE_{INDO}, (c) attractive dispersion and (d) total interaction energy [ΔE, for the T-shaped structure]

Earlier ab initio and other calculations predict the T-shaped structure (Fig. 1b) for the dimer. In the earlier calculations[1-4], the shifted parallel structure was not considered. The results of the recent ab initio

5

Table 1—Calculated Values of ΔE and R_e for Three Different Structures of Ethylene Dimer

Structure	$-\Delta E$ (kcal/mol) (present method)	R_e (Å) (present method)	$-\Delta E$ (kcal/mol)* (STO-3G)	R_e (Å)* (STO-3G)	$-\Delta E$ (kcal/mol)* (4-31G)	R_e (Å)* (4-31G)
Sandwich	0.25	4.8	0.14	3.28	0.09	3.59
T-shaped	0.22	5.4	0.10	4.49	0.61	4.23
Shifted parallel	0.41	3.5	0.13	4.23	0.67	4.23

*Ref. 21.

Fig. 4—Variation with R of (a) exchange repulsion, (b) ΔE_{INDO}, (c) attractive dispersion and (d) total interaction energy [ΔE, for the shifted parallel structure]

calculations of Suzuki and Iguchi[21] by the exchange perturbation method are compared with our results in Table 1, where ΔE is the interaction energy for the bottom of the potential well and R_e, the equilibrium interaction bond length.

The experimental value of the interaction energy in ethylene dimer is obtained from viscosity or second virial coefficient[23] data. The estimated value of the binding energy is 0.41 kcal/mol. The exact agreement between the experimental and the calculated binding energies here may be fortuitous. The main point that has emerged from the present work is that the results of the present semiempirical method are comparable with the results of the ab initio method where the basis set superposition error is eliminated by the perturbative calculation. The present method can, therefore, be used for obtaining qualitatively meaningful in-termolecular potentials in large composite systems. Further work with other composite systems is in progress.

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