

SEMIEMPIRICAL VARIATION CALCULATIONS ON THE INTERACTION ENERGY OF TWO IDENTICAL NONPOLAR SYSTEMS*

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Interaction energies of two identical nonpolar molecules were studied by means of variational CNDO/2 and MINDO/2 methods. The systems studied were dimers X_2 , X being H_2 , N_2 , F_2 and ethylene. MINDO/2 has been demonstrated to be unsuitable for this type of application. At the potential minimum the interaction energy was separated into ΔE_1 (Coulomb + exchange-repulsion energy) and E_2 (induction + charge-transfer energy) components. The dispersion energy at the potential minimum was estimated by a perturbation calculation. In absolute value, the dispersion energy is comparable to or even higher than the interaction energy given by CNDO/2.

CNDO/2 proved useful in estimations of the interaction energy for a pair of polar systems¹. Considerably less attention has been paid to studies of interaction energies for dimerizations of nonpolar systems. Recently two papers were published^{2,3} which were devoted to the study of pair interaction energies in $(N_2)_2$, $(F_2)_2$, $(C_2H_2)_2$, $(C_2H_4)_2$, $(CO)_2$, $(N_2O)_2$, $(CO_2)_2$, and $(HCN)_2$ by making use of CNDO/2 and INDO methods. The interaction energy calculated there was compared with the experimental one in the form of the lattice energy by assuming a pairwise additivity of intermolecular forces. Agreement between theory and experiment was rather good but it was achieved by making assumptions which might be criticized *viz.*:

a) the experimental geometries of the crystals studied were assumed. A theoretically justifiable approach should however be based on optimized crystal geometries,

b) Clementi AOs were used instead of Slater AOs; one- and two-centre electron repulsion integrals were calculated by using the Slater AOs, however. As the authors say "there is no clear rationale for this". Hence, the achieved agreement with the experimental lattice energy must be taken with caution. Moreover, the dispersion energy in the dimers studied should be estimated because it may constitute in nonpolar systems the prevailing contribution to the interaction energy. There is no reason to believe that the dispersion energy is inherently accounted for by the CNDO/2-Clementi method used^{2,3}.

The aim of this paper is to study the interaction energies of various configurations of pairs of nonpolar systems of the types $(C_2H_4)_2$ and $(X_2)_2$, X being H, N, and F.

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CALCULATIONS

Semiempirical CNDO/2 and MINDO/2 method with standard parameter sets were used^{4,5}. Interaction energy was determined as a difference of the dimer energy (E_d) for a particular configuration and the sum of monomer energies (E_m)

$$E = E_d - 2E_m \quad (1)$$

The monomer energy was obtained by a full optimization of all atomic coordinates⁶. The dimer energies were computed in two ways. On the one hand, a standard way was used in which intermolecular distances optimal for monomers were maintained fixed and intermolecular distance assumed variable, and on the other hand, the full optimization⁶ was performed. The dispersion energy was estimated through Eq. (6) of ref.⁷ by means of MO characteristics of isolated monomers given by a particular method. Thus, if the interaction energy was calculated by CNDO/2, the dispersion energy was evaluated from wave functions and orbital energies of optimized monomers that were given by CNDO/2 too. The excitation energies were computed by means of Eq. (6) given in ref.⁸.

RESULTS AND DISCUSSION

MINDO/2 was found to be entirely unsuitable for the calculation of interaction energies of arbitrary systems. It does not give an energy minimum for any molecule containing hydrogen. This applies not only to the studied nonpolar systems H_2 and C_2H_4 but also to strongly polar systems NH_3 and H_2O . Hereafter we therefore discuss only the CNDO/2 results.

Table I presents the interaction energies for various configurations (Fig. 1) of $(H_2)_2$, $(N_2)_2$, $(F_2)_2$, and $(C_2H_4)_2$ given by both the full geometry optimization and the standard treatment. As expected, the former gives energies higher in absolute value than the latter.

With dimers $(X_2)_2$ ($X = H, N, F$) the most stable structure is linear. With linear $(N_2)_2$ the interaction energy is extraordinarily negative. In order to provide an explanation for this overestimation, we separated the interaction energy into ΔE^1 (Coulomb + exchange-repulsion energies) and E^2 (induction + charge-transfer energies) components⁹⁻¹¹. By making use of the ZDO approximation, which is consistent with the use of the CNDO/2 method, we found that ΔE^1 is equal to the perturbation Coulomb interaction energy of two monomers and that it is repulsive. Being proportional to overlap, the exchange-repulsion term vanishes because of the neglect of overlap by CNDO/2. Estimated E^2 energies are reasonable for configurations I-III but too negative for configuration IV.

Owing to the neglect of overlap (and therefore of the exchange-repulsion energy, too) CNDO/2 underestimates the minimum energy X-Y separations, which brings about too negative an E^2 . In contrast, ΔE^1 is of a high positive value because it is represented in CNDO/2 merely by Coulomb energy. In the case with the interaction of strongly polar systems Kollman and Allen⁹ showed that CNDO/2 gives reasonable

dimerization energies by greatly overestimating the E^2 energy part. Obviously, the compensation of underestimated ΔE^1 and overestimated E^2 takes place. With non-polar systems of the X_2 type no such balance is present. This proved to be the case

TABLE I

Interaction Energy (ΔE), Its Components (ΔE^1 , E^2) and Dispersion Energy (E^D) for Various Configurations of $(H_2)_2$, $(N_2)_2$, $(F_2)_2$, and $(C_2H_4)_2$ Dimers (distances R in Å and energies in eV)

Species	Con-figuration ^a	Mode of calculation ^b	R	ΔE^1	E^2	ΔE	E^D
$(H_2)_2$	III	N	2.65	0.0190	— 0.0244	—0.0054	0.0
		O				—0.0076	
	IV	N	2.50	0.0912	— 0.1179	—0.0267	—0.0094
		O				—0.0269	
$(N_2)_2$	II	N	2.45	0.0711	— 0.0761	—0.0050	—0.0698
		O				—0.0058	
	II	N	1.95	0.6950	— 0.7506	—0.0556	0.0
		O				—0.0592	
	III	N	2.65	0.2657	— 0.3223	—0.0566	0.0
		O				—0.0582	
	IV	N	2.4	11.2592	—11.5798	—0.3206	—0.5408
		O				—1.5173	
$(F_2)_2$	III	N	2.3	0.1579	— 0.1952	—0.0373	0.0
		O				—0.0378	
	IV	N	2.6	0.9089	— 1.2954	—0.3865	—0.022
		O				—0.3943	
$(C_2H_4)_2$	I	N	2.8	0.0822	— 0.0913	—0.0091	—0.3361
		O				—0.2466	
	II	N	3.0	0.0358	— 0.0360	—0.0002	—0.0851
		O				—0.2387	
	III	N	4.1	0.1638	— 0.1759	—0.0121	—0.1362
		O				—0.2483	
	IV	N				—	
		O				—0.2392	

^a See Fig. 1; only configurations leading to energy minimum were considered. ^b N without optimization, O geometry optimization involved.

most markedly with a linear structure, where E^2 is considerably more negative than with the other three configurations under study.

Various configurations of the $(C_2H_4)_2$ dimer were found to be very close in energy, in particular if the geometry optimization was performed. The standard treatment gives no minimum for the "linear" structure (IV in Fig. 1). This prevents a direct comparison of E^2 energies for different configurations but it is evident that ΔE^1 is more repulsive for III and IV than for the other configurations. Comparable

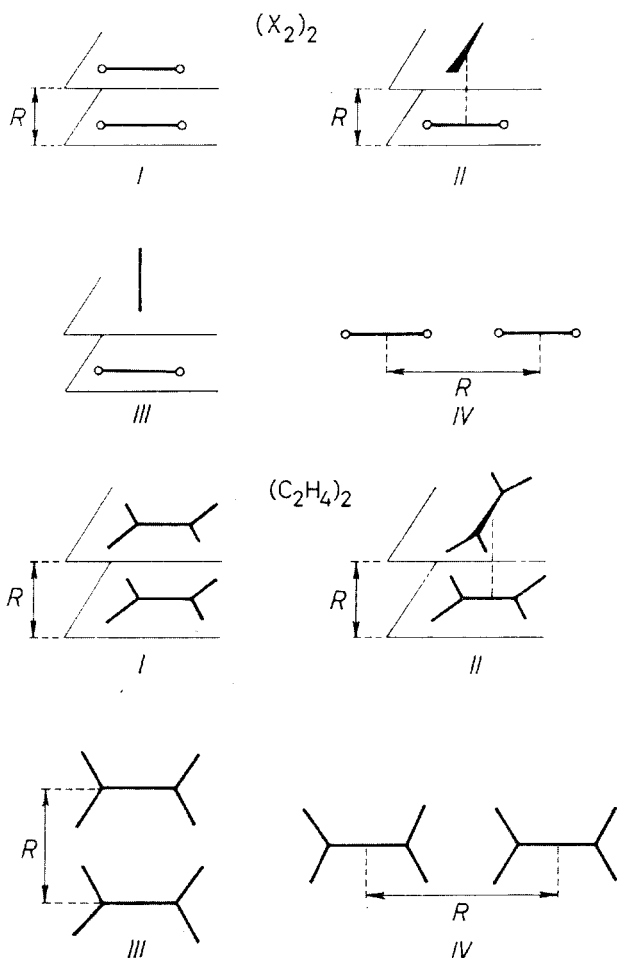


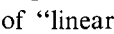
FIG. 1

Configurations of $(X_2)_2$ and $(C_2H_4)_2$ Dimers

values of interaction energies for different configurations imply that E^2 must be more attractive in *III* and *IV* than it is in the other configurations. Nevertheless, the balance between ΔE^1 and E^2 brings about, as with polar systems⁹, that reasonable values of interaction energies are obtained for all configurations.

It is well-known that the SCF interaction energy between two arbitrary systems consists of several contributions (in the terminology of perturbation theory): *a*) Coulomb, *b*) exchange-repulsion, *c*) induction, *d*) charge-transfer and *e*) dispersion (due to electronic correlations). The nonempirical SCF MO energy includes all these contributions, except for dispersion energy¹². With semiempirical methods the situation is less clear-cut.

The CNDO/2, INDO, and MINDO/2 type methods were parametrized in such a way to reproduce experimentally determined quantities. This implies that the total SCF energy includes the correlation energy through the semiempirical parameters. Accurate calculations demonstrated¹³ that the intermolecular correlation energy for large distances can be identified with the London dispersion energy. The CNDO/2 interaction energy, however, lacks this typical feature. It involves no term inversely proportional to the sixth power of the intersystem separation. Apparently, the neglect of the dispersion energy is compensated by overestimating another attractive component of the interaction energy. The latter, however, may be differently dependent on the dimer geometry than the dispersion energy.

In light of the above mentioned facts let us comment on the calculated dimerization energy between arbitrary systems. It is known that CNDO/2 gives a good account of the dimerization energy of polar systems. Kollman and Allen¹ reported the dimerization energy of 6.6–6.9 kcal/mol for the linear structure of $(\text{HF})_2$ for $R(\text{F}-\text{F})$ of 2.45 Å. Our calculation predicts the dispersion energy at that distance to be -0.6 kcal/mol. The energy of dimerization of "linear" $(\text{H}_2\text{O})_2$ () is 5.9 kcal/mol for $R(\text{O}-\text{O})$ of 2.53 Å and the dispersion energy is -1.3 kcal/mol. Thus, in both cases the dispersion energy does not exceed 20% of the interaction energy. Recently¹⁴, a second order perturbation theory has been used to introduce electronic correlation effect on CNDO/2 interaction energy between molecules HCHO and H₂O. The second order perturbation energy introduce changes in the potential minima which amount to 14% of the CNDO/2 value. This is in good agreement with the above noted 20% dispersion energy contributions in $(\text{HF})_2$ and $(\text{H}_2\text{O})_2$ dimers.

In contrast to the dispersion energies of polar systems dealt with, the dispersion energies (Table I) of nonpolar systems studied (except for F_2)* are comparable to or even higher than the CNDO/2 interaction energies. The highest dispersion energies were found with linear structures (*IV* in Fig. 1) of $(\text{X}_2)_2$ dimers. Hence, adding dispersion energy to the CNDO/2 interaction energy means further stabiliza-

* For a more detailed discussion of the underestimation of the dispersion energy in $(\text{F}_2)_2$ see ref.⁸

tion of the linear structure. The interaction energies in $(C_2H_4)_2$ predicted by CNDO/2 are almost the same for all configurations, though the respective separations between monomers are much different. This fact affects the estimated dispersion energies. Though the dispersion energies of $(C_2H_4)_2$ configurations were found¹⁵ to decrease in the series *IV, III, I, II*, the configuration *I* was predicted to have the lowest equilibrium distance which implies that *I* is stabilized by dispersion energy most appreciably. The dispersion energy of the "linear structure" (*IV*, cf. Fig. 1) was computed at $R = 5.2 \text{ \AA}^*$ to be -0.0828 eV . This value is very close to the dispersion energy of configuration *II* obtained at the energy minimum (Table I). Since the respective CNDO/2 interaction energies are also close in value, a surprising conclusion emerges that configurations *II* and *IV* of $(C_2H_4)_2$ are of almost the same stability.

Finally, let us emphasize that the inclusion of dispersion energy leads to deeper energy minima with all dimers studied and that it may change the order of configuration stabilities.

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* This distance resulted from the geometry optimization of the "linear" $(C_2H_4)_2$.