

NATURE OF STATIONARY POINTS ON CNDO/2 ENERGY HYPERSURFACES OF VAN DER WAALS MOLECULES FORMED BY POLAR MOLECULES

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An attempt was made to find a complete set of stationary points on CNDO/2 energy hypersurface for five molecular complexes. Diagonalization of Hessian matrices served for analysis of the nature of stationary points which permits to distinguish between relative minima and saddle points. The total number of stationary points and real minima of the individual complexes is indicated in parentheses: (HF)₂ (8, 1); (H₂O)₂ (7, 3); (LiF)₂ (2, 1); (CH₃OH)₂ (6, 4) and CH₃OH...HF (2, 1). CNDO/2 structural characteristics are compared with experimental values and with results of nonempirical calculations.

The CNDO/2 method has been frequently used for the study of electronic structure of molecular complexes¹⁻⁴. The method offers qualitatively and semiquantitatively correct results with hydrogen bonded complexes and with complexes between polar (or charged) subsystems. It fails badly with other types of molecular complexes, *e.g.*, true van der Waals molecules, because it has not been parametrized for systems of this sort⁵.

Meaningful exploitation of any type of quantum chemical methods for structure determination of molecular complexes requires, first, to patiently search on the energy hypersurface for as many stationary points as possible and, second, to make a decision about the nature of the stationary points found. Using *ab initio* methods for these purposes is very tedious even with relatively small complexes and at present hardly feasible with larger complexes, *e.g.*, the ethanol dimer.

In order to get reliable information on the geometry of the van der Waals molecules we have to base it on nonempirical calculations including, if possible, correlation energy. Nevertheless semiempirical calculations may still be of value. Namely, in order to make nonempirical structure determination more economic, it is useful in the first step to semiempirically locate and characterize stationary points of the parts of the hypersurface under study. The established characteristics of important stationary points are then used as a starting geometry for nonempirical calculation. Clearly, such an approach is adequate only if CNDO/2 is capable of qualitatively describing complexes under study. It is the purpose of this paper to show that this condition is partly satisfied with a few representatives of strong van der Waals molecules.

To our knowledge only two papers concerning van der Waals molecules exist in which an empirical potential and the CNDO/2 method were applied for characterizing the nature of the found stationary points. Scheraga and coworkers⁶ using an empirical potential fitted for water, have

shown that the quasilinear structure of the $(\text{H}_2\text{O})_2$ dimer represents a real minimum. This conclusion was confirmed later on the basis of an *ab initio* SCF study⁷. Seven stationary points have been found on the CNDO/2 energy hypersurface for the $\text{CH}_2\text{O}\cdots\text{H}_2\text{O}$ complex, from which only one satisfies the criterion valid for real minima, and three of them represent saddle points^{8,9}. For the sake of completeness let us mention the nonempirical SCF studies in which the structure of real minima was established: $\text{H}_2\text{O}\cdots\text{H}_2\text{O}$ (ref.⁷), $\text{HF}\cdots\text{HF}$ (ref.⁹), $\text{H}_2\text{O}\cdots\text{HF}$ (ref.¹⁰), $\text{HCN}\cdots\text{HF}$ (ref.¹¹), $\text{HCl}\cdots\text{HCl}$ (ref.¹²), $\text{LiH}\cdots\text{LiH}$ (ref.¹³), $\text{HCl}\cdots\text{HF}$, $\text{HCl}\cdots\text{FCl}$ (ref.¹⁴) and $(\text{H}_2)_3$ (ref.¹⁵). In ref.¹² structures of saddle point of $(\text{HCl})_2$ and $(\text{HF})_2$ dimers were investigated, too. Cyclic and bifurcated structures of various H-bonded complexes were investigated by Kerns and Allen¹⁶; in the paper no complete vibrational analysis was performed, however.

In the present paper we have studied the following complexes: $(\text{HF})_2$, $(\text{H}_2\text{O})_2$, $(\text{LiF})_2$, $(\text{CH}_3\text{OH})_2$ and $\text{CH}_3\text{OH}\cdots\text{HF}$. Former studies on the systems are cited in due connection in the Discussion.

CALCULATIONS

Stationary points on energy hypersurface are the points for which first derivatives of total energy with respect to all coordinates vanish. The nature of the stationary point can be determined if second derivatives of total energy with respect to all coordinates are known. When diagonalizing the matrix of the second derivatives (Hessian matrix), we obtain eigenvalues and the respective eigenvectors. If all eigenvalues are non-negative, the stationary point is a real minimum. If just one eigenvalue is negative (and all other are positive or equal to zero) the stationary point corresponds to a saddle point. If two or more eigenvalues are negative, the stationary point corresponds neither to a stable system nor to an activated complex for any reaction; it is a saddle point of higher order.

Let us mention that the "step by step" method or the more efficient gradient method can be used for locating minima. Activated complexes can be found, however, only by using the Hessian matrix. The gradient method can be applied for this purpose only then, if the stabilization leads to a symmetry breakdown. This appears to be the case of systems under study. We have used the quadratically convergent variable metric method which was applied within the frame of NDO type of calculations in ref.¹⁷. Second derivatives of energy with respect to all coordinates (force and interaction constants) were calculated in Cartesian coordinates.

Throughout the paper the original version of the CNDO/2 method² was used. Interaction energies were determined by means of the following equation

$$E = E_D^{\text{OPT}} - (E_{M1}^{\text{OPT}} + E_{M2}^{\text{OPT}}), \quad (1)$$

where E_D^{OPT} and E_{M1}^{OPT} (E_{M2}^{OPT}) are energies of optimized complex and of optimized subsystem monomers.

RESULTS AND DISCUSSION

$(\text{HF})_2$. We have found eight stationary points (Fig. 1) on the respective energy hypersurface from which only structure *I* corresponds to the real minimum ($\Delta E = -39.1$ kJ/mol). Structures *III* and *V* were found to be saddle points ($\Delta E = -21.2$ and -4.7 kJ/mol). Shifts of atoms in *III* and *V* corresponding to the eigenvectors

which belong to the negative eigenvalues tend in both cases, as it is schematically indicated in Fig. 1, to the real minimum *I*.

With the $(\text{HF})_2$ dimer we can compare the CNDO/2 structure predictions with that of *ab initio* SCF (ref.⁹) and of molecular beam spectroscopy¹⁸. In both studies the quasilinear structure (*I* in Fig. 1) of the dimer was found to be a real minimum. The cyclic structure *III* was proved to be a saddle point in refs^{9,12,16}.

$(\text{LiF})_2$. Two stationary points have been found on the energy hypersurface of the dimer (Fig. 2). The cyclic structure represents a real minimum ($\Delta E = -784 \text{ kJ/mol}$); linear structure is neither minimum, nor saddle point. On the basis of an *ab initio* SCF calculation Kollman¹⁹ predicted the cyclic structure be more stable than the

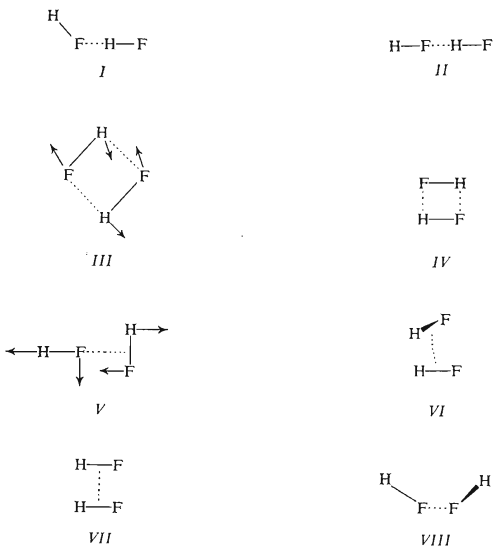


FIG. 1

CNDO/2 Stationary Point for $(\text{HF})_2$

Shifts of atoms given by the eigenvector belonging to the negative eigenvalue are indicated for the saddle points *III* and *V*.

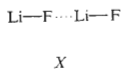


FIG. 2
CNDO/2 Stationary Points for $(\text{LiF})_2$

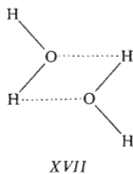
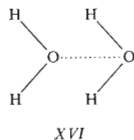
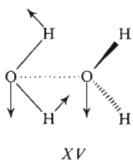
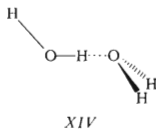
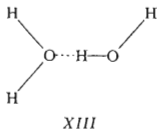
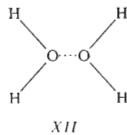
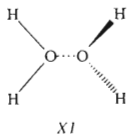


FIG. 3
CNDO/2 Stationary Points for $(\text{H}_2\text{O})_2$

Shifts of atoms given by the eigenvector belonging to the negative eigenvalue are indicated for the saddle point XV.

linear one but the nature of the found structures were not investigated. The dimer was studied experimentally²⁰ and a cyclic structure with stabilization energy of 246 kJ/mol was assigned to it.

(H₂O)₂. Stationary points found on the (H₂O)₂ energy hypersurface are depicted in Fig. 3. Structures *XIII* (*XIV*), *XV* (*XVI*) and *XVII*, called linear, bifurcated and cyclic, were believed for long time to be real minima. Chemically unrealistic structures *XI* (*XII*), firstly described in ref.²¹, are apparently an artifact of the CNDO/2 method, as pointed out recently in ref.²². The stabilization energies of structures *XI*–*XVII* are the following: –60.2, –51.2, –35.8, –35.1, –15.3, –5.09 and 1.93 kJ/mol. Using the eigenvalues of the Hessian matrix we have confirmed conclusions of the study by Scheraga and coworkers⁶ based on a sophisticated empirical potential, as well as of the *ab initio* study of Curtiss and Pople⁷, namely that the structure *XIV* represents a real minimum. The criterion valid for a minimum is also satisfied by structures *XIII* and *XI*. With the structure *XV* we have found just one negative eigenvalue, hence it represents, in agreement with refs 6. and 16, a saddle point. Displacement of atoms as suggested by the eigenvector corresponding to the negative eigenvalue, tend to the quasilinear structure (Fig. 3). Structures *XII*, *XVI*, *XVII* possess two or more negative eigenvalues, hence, they represent saddle points of higher order.

(CH₃OH)₂. Two stationary points, corresponding to linear and cyclic structures (Fig. 4), were found. The stabilization energy (in kJ/mol) of these structures is –31.5 and –8.44. The linear structure *XVIII* corresponds to a minimum, while the cyclic one to a saddle point. The transition of the saddle point into the minimum

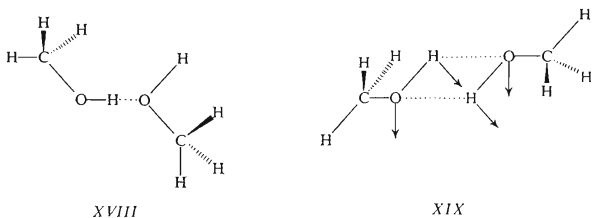


FIG. 4

CNDO/2 Stationary Points for (CH₃OH)₂

Shifts of atoms given by the eigenvector belonging to the negative eigenvalue are indicated for the saddle point *XIX*.

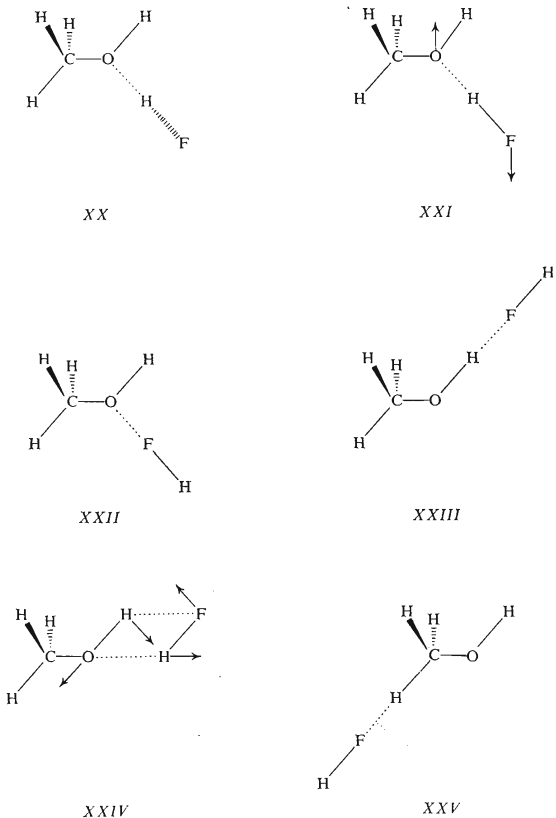


FIG. 5

CNDO/2 Stationary Points for $\text{CH}_3\text{OH}\cdots\text{HF}$

Shifts of atoms given by the eigenvector belonging to the negative eigenvalue are indicated for the saddle points *XXI* and *XXIV*.

(estimated by means of the eigenvector belonging to the negative eigenvalue) is indicated in Fig. 4.

The methanol dimer was investigated nonempirically by Del Bene²³ who showed that the linear structure was the most stable.

$\text{CH}_3\text{OH}\cdots\text{HF}$. Stationary points found are indicated in Fig. 5. The stabilization energies (in kJ/mol) are -60.3 , -59.6 , -56.6 , -21.7 , -14.4 and -2.33 .

Investigating the eigenvalues of Hessian matrices we have found structures *XX*, *XXII*, *XXIII* and *XXV* to be real minima, while *XXI* and *XXIV* correspond to saddle points. Similarly as with the $\text{O}\cdots\text{O}$ structure of the $(\text{H}_2\text{O})_2$ dimer, the $\text{O}\cdots\text{F}$ structure *XXII* is evidently an artifact of CNDO/2 (*vide supra*).

CONCLUSION

The results suggest that CNDO/2 being so economic might be a useful tool for rough location of stationary points on energy hypersurfaces of some "strong" van der Waals molecules and for determination of their nature. But one has to be aware of the following possibilities of failures: *a*) a certain stationary point might be missing on a CNDO/2 hypersurface, *b*) in some situations CNDO/2 fails qualitatively leading to a chemically unacceptable structure (*e.g.*, $(\text{H}_2\text{O})_2$ dimer possessing an $\text{O}\cdots\text{O}$ bond or $\text{CH}_3\text{OH}\cdots\text{HF}$ with an $\text{O}\cdots\text{F}$ bond). In this case both chemical experience and simple *ab initio* calculation reveal immediately a CNDO/2 failure.

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