Theoret. chim. Acta (Berl.) 11, 178—181 (1968)

# A Molecular Orbital Study of the Difluorodiazine ($N_2F_2$) System

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Received June 27, 1968

A semiempirical MO method (CNDO/2) with empirical constants adjusted to give agreement with ground state geometries has been used to study isomerization mechanism in the $N_2F_2$ system. Calculated transition states do not correspond to the simple postulated transition states.

## Introduction

Difluorodiazine exists as two stable isomers, 1,2-*cis* and *trans* forms, and structural parameters are well-established [1, 2]. The existence of a third isomer, 1,1-difluorodiazine, has been discounted in recent years [1–8]. Relative heats of formation of the two isomers have been experimentally determined, *cis* 3.0 kcal/mole more stable than *trans* [5], and the energy barrier to isomerization (*trans* → *cis*) has been measured kinetically, $k = 10^{14} \exp(-32.2 \text{ kcal/RT}) \text{sec}^{-1}$ [9].

The large amount of structural and thermochemical information, and the small number of atoms, makes the difluorodiazine system an attractive one for all valence electron molecular orbital calculations of the extended Hückel type (EHT) as formulated by Hoffmann [10], or the approximate SCF method (CNDO/2) of Pople and Segal [11].

We have carried out several CNDO/2 calculations on the difluorodiazine system, our particular interest being the structure and relative energy of the transition state for the *cis-trans* isomerization. Two recent papers have also appeared which consider this problem in some detail: the first by Ray and Narasimhan uses the EHT method [12], the second by Gordin and Fischer [13] using one of the approximate SCF methods (INDO) devised by Pople and his coworkers [11, 14]. An earlier paper by Kaufman *et al.* [15] is also interesting in this regard.

Because of the evident interest of several other groups, we have terminated our research in this system. However, our calculations do differ from the previous work in several ways, and our results are somewhat different. Accordingly we wish to briefly summarize the present status of our studies.

## Method of Calculation

All calculations were carried out on the IBM 7040 computer using the CNDO/2 Fortran-4 program written by G. A. Segal[1] [16]. Three empirical parameters

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[1] Available from the Quantum Chemistry Program Exchange, Indiana University, Bloomington, Indiana, USA.

are used in the CNDO/2 calculation, the Slater exponents, the average ionization potential for each type of atomic orbital in the basis, and the exchange integral proportionality constant (called $\beta$-proportionality constant). Values of the $\beta$-proportionality constant are established for each second row atom by requiring that the calculated energy for the homonuclear diatomic molecules be a minimum at the experimentally known bond distance.

In the calculations reported here the bond lengths and bond angles of all species were varied until the most stable configuration was found. Using the original CNDO/2 program this gave geometries for $N_2F_2$ species in which the N–F bond distance (1.26 Å for both *cis*- and *trans*-difluorodiazine) was much shorter than the experimental length (*cis* 1.41 Å, *trans* 1.40 Å) [2], although the right order of relative energies was found, *cis* 4.5 kcal/mole more stable than *trans*. The correct planar configuration was confirmed and the FNN angle was calculated to be 112° for the *cis* compound and 109° for the *trans* compound. The experimental angles are 114° and 106° respectively [2].

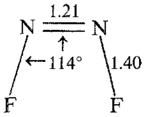
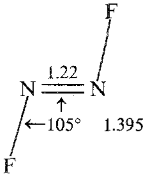
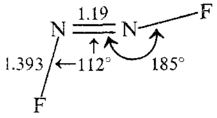
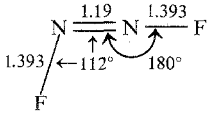
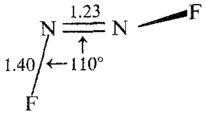
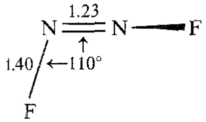
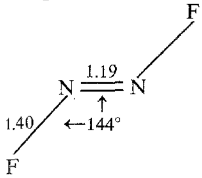
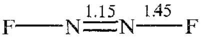
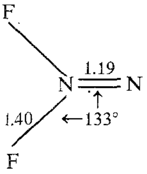
The results are in almost precise agreement with those found by Gordon and Fischer using the INDO method [13]. However, at this point we felt that it would be desirable to adjust the empirical parameters in the CNDO/2 treatment to obtain agreement of calculated and experimental ground state geometries, before proceeding to calculate the energy surfaces for isomerization. Wiberg has shown for hydrocarbons [17], and we corroborate this point, that the $\beta$-proportionality largely determines the bond length between two atoms. Since the N–N bond length was satisfactory in our results, we only varied the fluorine proportionality constant and we found a linear dependence of N–F bond length on fluorine $\beta$-proportionality constant, $d(\text{N–F}) = 1.495 - 0.0071\,\beta$. The value of $\beta_F$ which gave the correct N–F bond length for *trans*-difluorodiazine was 14.07 and this value was used in all of the subsequent calculations. It is interesting to note that the calculated N–N bond distance was affected negligibly by the variation in fluorine $\beta$-constant.

## Results and Discussion

Refer to the Table for the calculated geometries and energies of difluorodiazine species. The first two entries for the ground state *cis* and *trans* molecules show almost perfect agreement with the experimental geometries and relative energy difference. This was quite encouraging so we proceeded to estimate the energies for various reaction pathways of isomerization. Gordon and Fischer [13] pointed out that the two most probable mechanisms for isomerization either involve twisting around the nitrogen-nitrogen bond or an inversion of one nitrogen atom. A third possible isomerization pathway might have a completely linear state, symmetry $D_{\infty h}$. Our calculated energy for the twisted, $C_2$ point group symmetry, transition state is 85.7 kcal/mole, in good agreement with the Gordon and Fischer value. 85.0 kcal/mole. We also confirm their finding that the transition state is not found at a dihedral angle of 90°.

For the nitrogen inversion mechanism our results differ. As one proceeds from *trans*-difluorodiazine to *cis*-difluorodiazine, maintaining $C_s$ symmetry, the energy maximum occurs before one fluorine atom and two nitrogen atoms are colinear. The energy maximum 81.1 kcal/mole is not sufficiently different from

Table. *Geometries and energies of difluorodiazine species*

| Bond lengths and bond angles | Dihedral angle and symmetry | Relative energy (kcal/mole) |
|---|---|---|
|  | 0°, $C_{2v}$ | 0.00 (minimum) |
|  | 180°, $C_{2h}$ | 3.14 (minimum) |
|  | 180°, $C_s$ | 81.10 (maximum) |
|  | $C_s$ | 75.40 |
|  | 95°, $C_2$ | 85.70 (maximum) |
|  | 90°, $C_2$ | 79.65 |
|  | 180°, $C_{2h}$ | 155.2 (maximum |
|  $\mathrm{F{-}N\overset{1.15}{=}N\overset{1.45}{-}F}$ | $D_{\infty h}$ | 106.8 |
|  | $C_{2v}$ | 39.0 (minimum) |

that of the twisted state to allow any choice to be made. The transition state for an all-colinear pathway is not linear ($C_{2h}$-symmetry) and is much higher in energy than either of the other two possible transition states.

One further result, the calculated energy of 1,1-difluorodiazine, is higher than either of the known isomers by approximately 39.0 kcal/mole. The non-existence of 1,1-difluorodiazine is probably indicated by this result.

In a recent paper [18] we showed that semiempirical molecular orbital methods are not suitable for the calculation of energy barriers to rotation around single bonds, the number and relative heights of energy extrema being incorrectly calculated for some simple molecules. We believe our present results strengthen this conclusion, and that clear-cut decisions about particular reaction pathways will be very difficult to obtain from molecular orbital calculations of this type. The present work also shows how very difficult it is to make an inteligent guess as to the structure of a transition state for the purpose of making molecular orbital calculations. In the $N_2F_2$ case, none of the three pathways for isomerization has the transition state postulated by previous workers.

*Acknowledgment.* We thank the staff of the computer center of Texas Technological College for assistance and generous allotments of computer time. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work (PRF No. 3069-A4). J. Feuer is the recipient of a National Science Foundation traineeship.

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