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Relationes

Study of the Transition State in the Isomerization of *trans*-N_2F_2 to *cis*-N_2F_2 by Extended Hückel Theory

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Introduction

The transition state in the isomerization of *trans*-N_2F_2 to *cis*-N_2F_2 has been studied theoretically by using extended Hückel theory. It has been shown that in this isomerization process a twisted transition state is more likely than a linear one.

Recently the isomerization of N_2F_2 (difluorodiazine) from *trans* form to *cis* form has been studied experimentally by Binenboym et al. [1]. They have found that *trans*-N_2F_2 isomerizes to the *cis* form and the barrier to isomerization is about 32 kcals/mole. They have also suggested that the isomerization takes place through a linear transition state rather than through twisting about the N–N bond. Precise structural data being available [2] for both the isomers of N_2F_2 it was thought worthwhile to study the isomerization process theoretically, particularly to see which one of the two alternative transition states is more feasible. To our knowledge, though a study for both the isomers of N_2F_2 has been made [3] by extended Hückel theory (E.H.T.) [4] to explain the relative stabilities between the isomers and bond length differences, no study has as yet been made for deciding the geometry of the transition state and barrier height in the isomerization of *trans*-N_2F_2 to *cis*-N_2F_2. In addition to numerous other earlier applications, recently E.H.T. has also been applied [5] quite successfully for predicting the rotational barriers in B_2Cl_4, B_2F_4 and N_2O_4. It is also interesting to note that Kato et al. [6] employed this theory for studying the transition state in the nucleophilic substitution reactions in methyl chloride. In view of all these facts an E.H.T. study of the isomerization process of N_2F_2 has been made. The results of our calculations are presented here.

Results and Discussion

Extended Hückel calculation procedure of Hoffmann [4] was employed. 1*s* orbitals of nitrogen and fluorine were not considered and hence the N_2F_2 system was treated as a 24-electron case. Valence state ionization potentials needed for the present computations were taken from the work of Basch et al. [7]. Off-diagonal matrix elements were calculated by using Wolfsberg-Helmholz relation [8]. Overlap integrals were obtained by using Mulliken's relations [9] and employing Slater atomic orbitals. The constant K in the Wolfsberg-Helmholz relation was taken to be 1.75 as has been suggested by Hoffmann [4].

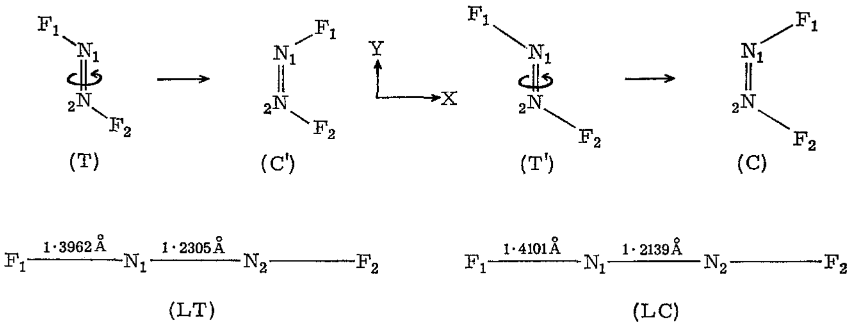


Fig. 1. Various configurations of the N_2F_2 system. θ is the angle of twist around Y axis and is measured starting from *trans* configuration. Bond lengths and angles for T and C were taken from Ref. 2

Calculations have been made for various configurations of N_2F_2. In one set of calculations the total energy ($E = \sum_i \varepsilon_i$, ε_i = orbital energy) variation with the angle (θ) of twist around the N–N bond was studied. Starting from *trans* configuration, various other configurations were obtained by rotating the N_1–F_1 bond about the N_1–N_2 bond by an angle θ. Two types of trans configurations were assumed namely T and T'. T corresponds to the molecular structure with the experimentally observed bond lengths and angles of *trans*-N_2F_2 while T' is the hypothetical *trans*-N_2F_2 with the bond lengths and angles corresponding to *cis*-N_2F_2 (C). C' is the hypothetical *cis*-N_2F_2 in which the bond lengths and angles are those of *trans*-N_2F_2 (T). In another set of calculations the total energy values for the linear configurations were examined. These linear configurations are labelled LT and LC. LT is the linear structure in which N–N and N–F bond lengths are those of *trans*-N_2F_2 (T). LC is the linear structure in which the N–N and N–F bond lengths are

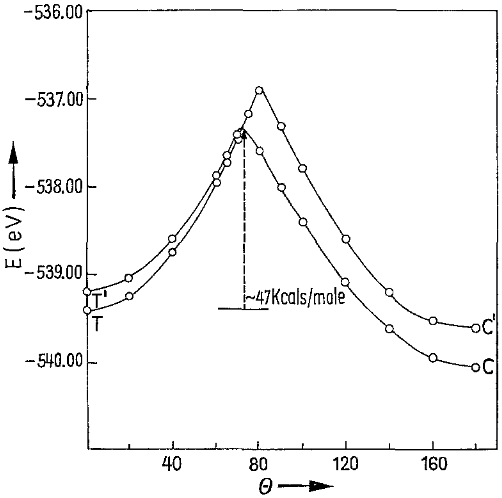


Fig. 2. Total energy (E) *vs* θ curve for N_2F_2 system. Wolfsberg-Helmholz relation with $K = 1.75$ has been employed for evaluating the off-diagonal matrix elements. (See Fig. 1 and text for the meaning of T, T', C and C')

Table 1. *Calculated Energy Values for Different Configurations of* N_2F_2 *and* C_2H_4

System[a]	Calculated Total Energy (eV)		Binding Energy (kcals/mole)		
			Calculated		Observed[b]
	$K = 1.75$	$K = 2.00$	$K = 1.75$	$K = 2.00$	
T	−539.4168	−547.1660	255.41	434.42	244.3
C	−540.0626	−548.0556	270.33	455.07	247.3
T'	−539.1941	−547.1719			
C'	−539.6203	−547.4053			
LT	−531.7076	−540.2164			
LC	−531.8146	−540.2554			
Rotational barrier in ethylene	78.45 kcals	101.70 kcals			∼65 kcals

[a] See text and Fig. 1 for these symbols.
[b] Obtained from Ref. [10, 11].

those of *cis*-N_2F_2 (C) (see Fig. 1 for the structures). The results of the calculations on the dependence of total energy (E) on the angle of twist θ are shown graphically in Fig. 2, while the total energy values for T, T', C, C', LT and LC are given in Tab. 1. It can be seen from Tab. 1 that the calculated binding energy for *trans*-N_2F_2 is 255.4 kcals/mole and this is in good agreement with the experimental value of 244.3 kcals/mole [10]. It is also seen from Tab. 1 that *cis*-N_2F_2 (C) is more stable than *trans*-N_2F_2 (T). This indeed is the case experimentally, though the calculated value (about 15 kcals/mole) for this extra stabilization is much higher than that observed experimentally which is about 3 kcals/mole [10]. It can also be seen from Tab. 1 that T' and C' have higher energy than T and C respectively as is expected and hence the two energy curves (see Fig. 2) cross each other. Under these circumstances the barrier height for the isomerization of *trans*-N_2F_2 to *cis*-N_2F_2, if it proceeds through a twisting of the N–N bond, would be given by the energy difference as shown in Fig. 2. This difference is about 47 kcals/mole. It is also seen that, if a linear transition state is to be considered for the isomerization process, the barrier height would be very much higher. If LT is considered the barrier height would be about 178.1 kcals/mole and if LC is considered the barrier height would be 175.6 kcals/mole. Experimental barrier height being as low as 32 kcals/mole [1] it is felt that in the isomerization of *trans*-N_2F_2 to *cis*-N_2F_2 a twisted transition state is more likely than a linear one.

Calculations were also made with a value of $K = 2.00$ in the Wolfsberg-Helmholz relation [8] and the total energy values obtained for various configurations are plotted against the angle θ (see Fig. 3). This choice of K is probably not a good one since the energy value calculated for T' comes to be lower than that of T contrary to observation. Total energy values of T, T', C, C', LT and LC calculated with $K = 2.00$, are also given in Tab. 1. The fact that this choice of K is not good is further confirmed by the high value of the extra stabilization energy (∼21 kcals/mole) of the *cis* isomer over the *trans*. Binding energy of *trans*-N_2F_2 in this calculation is also overestimated. Nevertheless, the barrier heights predicted with $K = 2$ for the linear transition state and twisted transition state are very widely different and an examination of Tab. 1 along with Fig. 3, would show that a twisted transition state is still preferred to a linear one in the isomerization of *trans*-N_2F_2 to *cis*-N_2F_2.

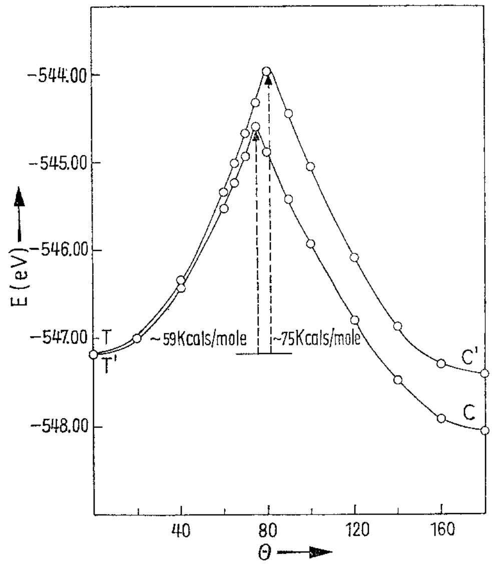


Fig. 3. Total energy (E) *vs* θ curve for N_2F_2 system. Wolfsberg-Helmholz relation with $K = 2.00$ has been employed for evaluating the off-diagonal matrix elements. (See Fig. 1 and and text for the meaning of T, T', C and C')

Following Kaufman et al. [3] we employed the Cusachs relation

$$H_{rs} = 0.5\,(H_{rr} + H_{ss})\cdot S_{rs}(2 - |\,S_{rs}\,|)$$

for calculating the off-diagonal matrix elements where H_{rr} and H_{ss} are the valence state ionization potentials for the r-th and s-th atomic orbitals and S_{rs} is the overlap integral between atomic orbitals r and s. The energy values calculated for different configurations are shown in Fig. 4. The barrier heights in these calculations again show the same trend as in the previous calculations, in that the twisted rather than the linear transition state is preferred. However, it is noticed from the E *vs* θ curves (see Fig. 4) that the minimum energy values are now obtained at θ values slightly different from 0° and 180°, thereby suggesting the equilibrium

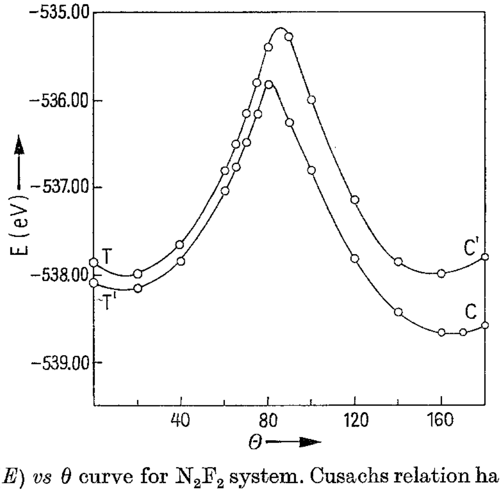


Fig. 4. Total energy (E) *vs* θ curve for N_2F_2 system. Cusachs relation has been employed. (See Fig. 1 and text for the meaning of T, T', C and C')

configurations to be slightly non-planar. Since the experimental observations do not confirm this behaviour it is felt that the results obtained from calculations using Cusachs relation are open to question. On account of this the total energy values obtained with Cusachs relation for the various configurations are not reproduced in Tab. 1.

As a check on our present approach calculations were made using our program for planar ethylene (D_{2h}) and non planar ethylene (D_{2d}) and the results are also given in Tab. 1. A study of Tab. 1 shows that when a value of $K = 2.00$ is employed in the Wolfsberg-Helmholz relation the barrier height is over-estimated (calculated value is 101.7 kcals/mole, while experimental value is 65 kcals/mole [11] for ethylene) in case of both ethylene and N_2F_2 (see Fig. 3 and Tab. 1). When a value of $K = 1.75$ is employed a much better value for the barrier height is obtained in both the cases though these are still higher than the experimental values (see Fig. 2 and Tab. 1). Our present calculations give barrier heights, which show some dependence on the approximation made for evaluating the off-diagonal matrix elements. Nevertheless, all the calculations unambiguously indicate that a twisted transition state is much more favourable than a linear one in the isomerization of *trans*-N_2F_2 to *cis*-N_2F_2 and probably with a judicious choice of K in Wolfsberg-Helmholz relation for the evaluation of off-diagonal matrix elements, the barrier heights in case of ethylene and N_2F_2 may be fairly well predicted. No attempt has been made here to obtain this type of agreement.

BINENBOYM et al. [1] have ruled out a triplet transition state from a consideration of the very high preexponential factor in the rate equation. The linear transition state (*LT* or *LC*) belongs to $D_{\infty h}$ group and application of group theory would show that for N_2F_2 molecule (in linear configuration) with the basis set of orbitals employed there would would be four doubly degenerate m.o. levels. The orbital energies of the first thirteen M.O.'s along with their symmetries, calculated using different procedures, are given in Tab. 2. It can be seen from Tab. 2 that M.O.'s 12 and 13 are degenerate. The system under consideration being a 24-electron case a linear transition state (*LT* or *LC*) would be a triplet state and hence can be ruled out as a possibility in the isomerization of *trans*-N_2F_2 to *cis*-N_2F_2. In

Table 2. *Energy Levels in the Two Linear Configurations (LT and LC) of* N_2F_2 *(Point Group Symmetry* $D_{\infty h}$*)*

M.O.	Symmetry	Oibital Energy Values in Electron Volts					
		LT[a]			*LC*[a]		
		$K = 1.75$	$K = 2.00$	Cusachs Relation	$K = 1.75$	$K = 2.00$	Cusachs Relation
1	A_{1g}	−41.0247	−42.1224	−41.1533	−40.9875	−42.0532	−41.1256
2	A_{1u}	−40.7486	−41.5179	−40.8682	−40.7144	−41.4494	−40.8452
3	A_{1g}	−29.4029	−30.7645	−28.3593	−29.5496	−30.9396	−28.4242
4	A_{1u}	−21.0780	−21.4373	−21.2335	−21.0458	−21.4152	−21.2119
5	A_{1g}	−19.1080	−19.6195	−18.9632	−19.1075	−19.6131	−18.9685
6, 7	E_{1u}	−18.7977	−18.9815	−18.8898	−18.7891	−18.9652	−18.8772
8, 9	E_{1g}	−18.7474	−18.8275	−18.8036	−18.7400	−18.8138	−18.7938
10, 11	E_{1u}	−14.6327	−14.9790	−14.5883	−14.7031	−15.0777	−14.6490
12, 13	E_{1g}	−10.1360	− 9.0704	− 9.9006	−10.0382	− 8.9438	− 9.8301

[a] See Fig. 1 and text for the configurations. For these configurations the Y-axis was taken as the molecular axis.

the case of ethylene in D_{2d} configuration the two highest occupied orbitals are also degenerate [5] and consequently a triplet transition state would be expected; but the transition state being non-linear can undergo Jahn-Teller distortion to lift this degeneracy [12] and hence a triplet transition state should not be expected in the isomerization process of ethylene. The experimentally observed high preexponential factor [11] in the rate equation in the case of ethylene supports the above argument. On the other hand this type of Jahn-Teller distortion is not possible for the linear transition state (*LT* or *LC*) in N_2F_2 and hence, judging from the magnitude of the preexponential factor, the linear transition state, which is a triplet, can be definitely excluded as a possibility in the isomerization of *trans*-N_2F_2 to *cis*-N_2F_2. In the case of isomerization of *trans*-N_2F_2 to *cis*-N_2F_2 through a twisted transition state one does not expect orbital degeneracy due to symmetry considerations and is hence favoured.

BINENBOYM et al. [1] have estimated the activation energy for rotation about carbon-carbon double bond to be ~60 kcal/mole from a consideration of the difference in heat of reaction of the following two steps.

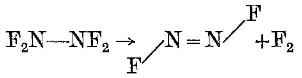
$$H_3C\text{—}CH_3 \rightarrow H_2C{=}CH_2 + H_2 \tag{1}$$

$$\Delta H = \Delta H_f(C_2H_4) - \Delta H_f(C_2H_6) = 33 \text{ kcals}$$

$$H_3C\text{—}CH_3 \rightarrow H_2\dot{C}\text{—}\dot{C}H_2 + H_2$$

$$\Delta H = 2\,D(C_2H_5\text{—}H) - D(H\text{—}H) = 93 \text{ kcals}\,. \tag{2}$$

Truly, this difference can be attributed to the activation energy for rotation about carbon-carbon bond since the difference in the heat of reactions in the above two equations is essentially the energy difference between ethylene and the structure in which π-bond overlap has been decoupled, say by rotation, since a linear configuration is not possible in this case. However, if one would consider the following two reactions,



$$F_2N\text{—}NF_2 \rightarrow {}_{F}\!\!\diagup N{=}N\diagup^{F} + F_2 \tag{3}$$

$$\Delta H = \Delta H_f(\textit{trans}\text{-}N_2F_2) - \Delta H_f(N_2F_4) = 19.6 \text{ kcals}$$

$$F_2N\text{—}NF_2 \rightarrow F\dot{N}\text{—}\dot{N}F + F_2 \tag{4}$$

$$\Delta H = 2\,D(N_2F_3\text{—}F) - D(F\text{—}F) = \sim 104 \text{ kcals}$$

the difference in their heat of reaction is not necessarily the energy difference between *trans*-N_2F_2 and a structure in which π-bond overlap has been decoupled by rotation only since the π-decoupled system (4) can have a linear configuration also. So the difference of ~84 kcals cannot be unambiguously taken as an estimate of the activation energy for *rotation* about a nitrogen-nitrogen double bond. Hence, the arguments of BINENBOYM et al. [1] to exclude isomerization through twisting about the nitrogen-nitrogen double bond is not unambiguous.

Conclusion

The quantitative agreement with experimental barrier height and the extra stabilization energy of *cis*-N_2F_2 over *trans*-N_2F_2 may not be considered to be very good, but this is only to be expected as small differences between large quantities are being calculated. It appears from our present calculations that the use of Cusachs relation for evaluating the off-diagonal matrix elements in this system is open to question since the experimentally observed planarity of N_2F_2 is not correctly predicted by the use of this relation. We therefore prefer the use of the Wolfsberg-Helmholz relation in this system. A value of $K = 1.75$ appears to be preferable. The results of all the E.H.T. calculations made here for difluorodiazine clearly show that a twisted transition state is more probable than a linear one (*LT* or *LC*) in the isomerization of *trans*-N_2F_2 to *cis*-N_2F_2. This conclusion also receives further support from a consideration of the high preexponential factor in the rate equation [1] and the multiplicity of the transition state.

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