

## Some Theoretical Considerations about the Conformers for the Diacetamide Molecule

ALBERTO L. CAPPARELLI, JULIO MARAÑÓN and OSCAR M. SORARRAIN  
*Departamentos de Físico-Química y Física, Facultad de Ciencias Exactas,\* ia Plata*

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The structure and possible conformers for the molecule of diacetamide are theoretically analysed using the CNDO/2 and INDO methods. The results are compared with the available experimental data.

Analisam-se teoricamente as estruturas e configurações possíveis da molécula de diacetamida, fazendo-se uso dos métodos de CNDO/2 e INDO. Comparam-se os resultados obtidos com os dados experimentais disponíveis.

### 1. INTRODUCTION

The conformational analysis of imides is useful for biological applications. The molecule of diacetamide is an acyclic imide with three possible planar conformers: cis-trans, cis-cis and trans-trans.

Lee<sup>1</sup> has studied the free imide group using UV and IR spectroscopies and dipolar measurements. He concluded that only three planar conformers are present: cis-trans, cis-cis and trans-trans; moreover the values for the dipolar moments of imides are given in the following way: cis-cis < cis-trans < trans-trans; the cis-cis conformer is the most stable one for cyclic imides. The same author, in a later paper<sup>2</sup>, reported having

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\* Postal address: Calle 49 y 115, La Plata, Republica Argentina.

measured the dipolar moments of N-methyl diacetamide and diacetamide. His conclusion was that, for both molecules, the cis-trans conformers are the most stable ones.

The experimental results obtained with UV, IR and NMR techniques, for solutions, also show that the cis-trans conformer is the most stable one.

Uno<sup>3,4</sup> has analysed the IR spectra of diacetamide and N-deuterated compounds. His conclusion has been that only two conformers are possible for the crystalline state, and the cis-trans conformer is the dominant one. He also attributed a dimeric structure to the molecule of diacetamide in the solid state.

Gentile<sup>5</sup>, analysing a group of complexes of diacetamide in divalent transition salts, detected only the cis-trans and trans-trans conformers.

Uno and Kuroda<sup>6,7,8</sup> studied the cis-trans conformer for the C- and N-deuterated compounds, using IR spectroscopy, and found that the energy for the trans-trans conformer is 27 kcal/mol, that means 3 kcal/mol above the cis-trans one.

Noe<sup>9</sup> used the FMR technique for the analysis of diacetamide and N-methyl diacetamide. The cis-trans conformer is also for this author the dominant one; moreover, the spectra for the cis-cis and trans-trans conformers were not found.

Steinmetz<sup>10</sup> concluded, from microwave spectroscopy, that there were three possible conformers for the molecules of formimide and N-deuterioformimide: cis-trans, cis-cis and trans-trans. In a very recent theoretical analysis, we predicted<sup>11</sup> three stable conformers for the molecule of formimide. In this paper we are presenting a similar theoretical analysis for the molecule of diacetamide using the CNDO/2 and INDO methods<sup>12</sup>. The results are compared with the available experimental data.

## 2. THEORETICAL CONFORMATIONAL ANALYSIS

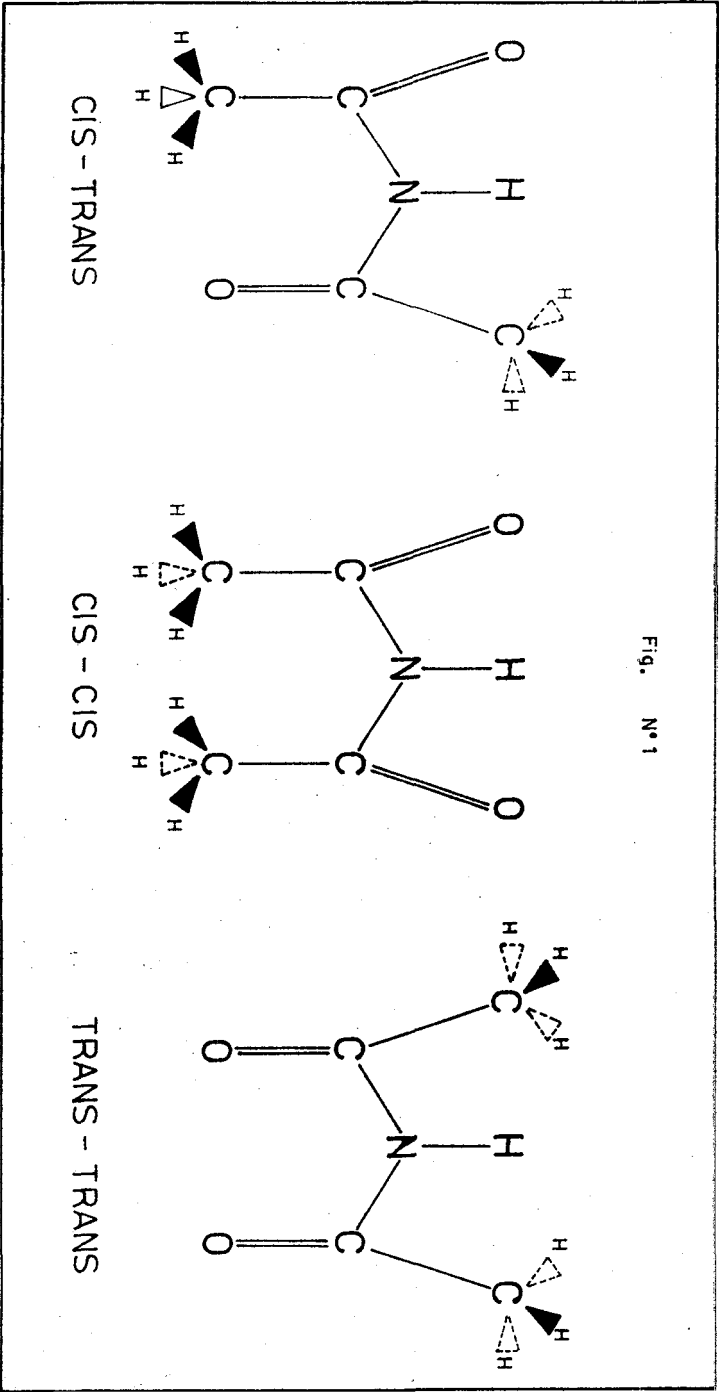
The structural parameters for the molecule of diacetamide were derived from the minimum of the total energy as a function of the bond distances and angles. The variation for the total energy is given for the  $d_1$ ,  $d_2$ ,  $d_3$  and the  $\widehat{\text{CNH}}$  angle (cf. Figs. 2, 3, 4 and 5). From those Figures the geometrical parameters are derived. They are given in Table 1.

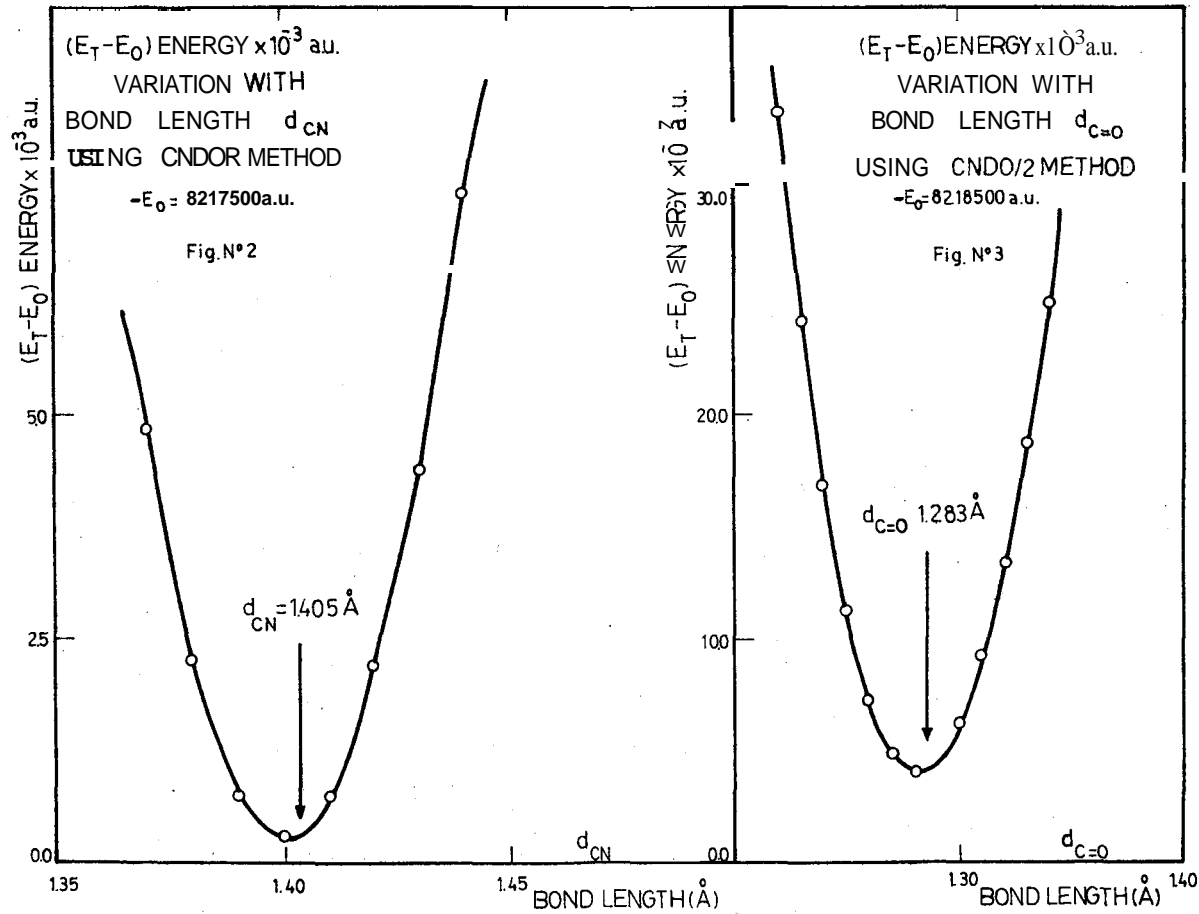
The CNDO/2 and INDO<sup>12</sup> methods were used for the calculations, and the coordinates describing the motions were taken following the rules given by Hilderbrandt<sup>13</sup>. The parameters derived here are in good agreement with the experimental ones given by UNO<sup>6</sup> (cf. Table 1).

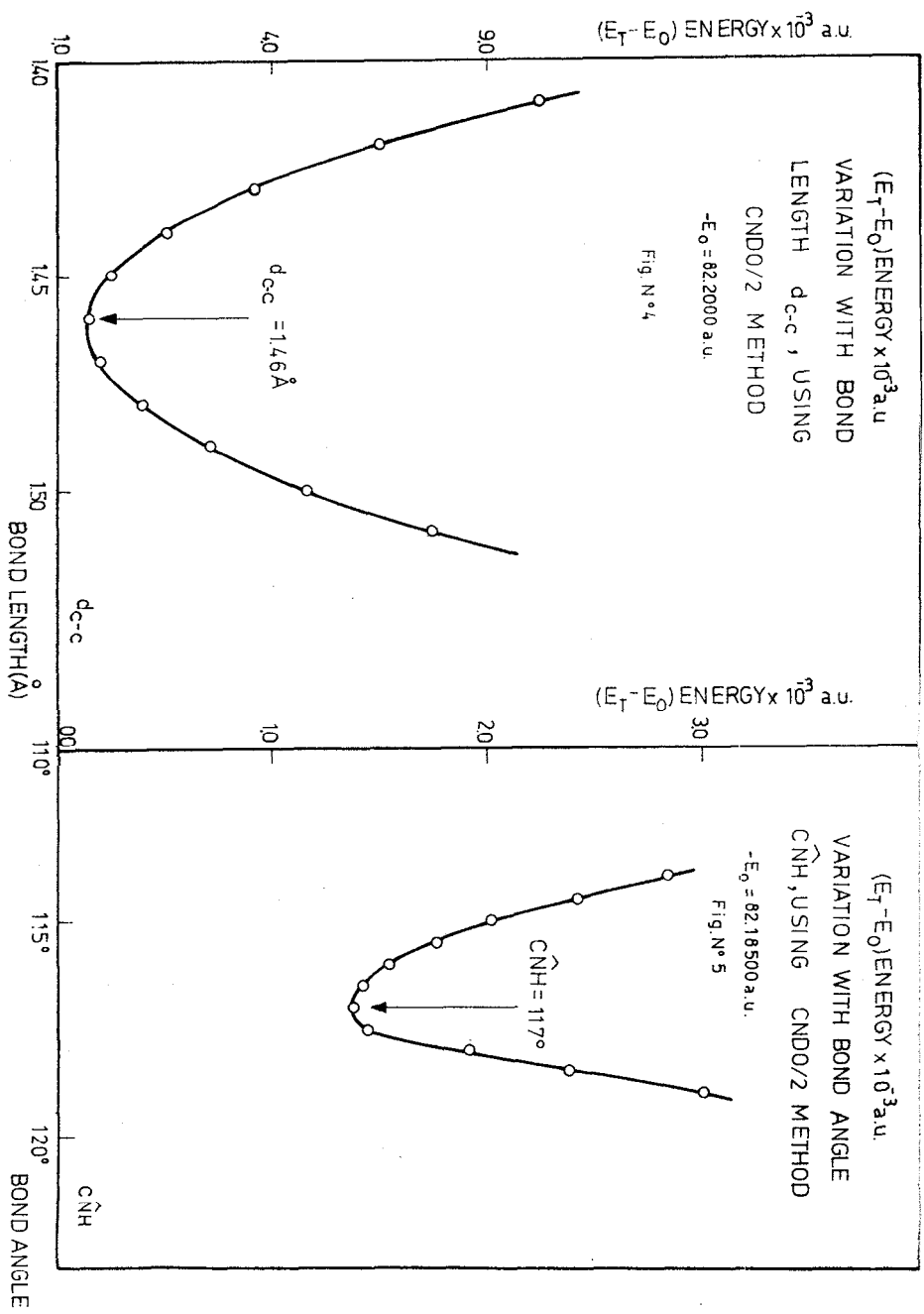
TABLE 1

Geometrical Parameters	Ref. 6	Our Results
$d_{\text{C-N}}$	1.402 A <sup>o</sup>	1.405 A <sup>o</sup>
$d_{\text{C=O}}$	1.240 A <sup>o</sup>	1.283 A <sup>o</sup>
$d_{\text{C-C}}$	1.527 A <sup>o</sup>	1.460 A <sup>o</sup>
$d_{\text{C-H}}$	1.08 A <sup>o</sup>	1.110 A <sup>o</sup>
$d_{\text{N-H}}$	1.00 A <sup>o</sup>	1.050 A <sup>o</sup>
$\widehat{\text{NCO}}$	120.8 <sup>o</sup>	119.5 <sup>o</sup>
$\widehat{\text{CNH}}$	114 <sup>o</sup> 36'	117 <sup>o</sup>
$\widehat{\text{CNC}}$	130 <sup>o</sup> 48'	126 <sup>o</sup>

Structural parameters for the molecule of diacetamide. The parameters shown in the last column were derived using the gradient for the total energy. The CNDO/2 was used for the calculations. Parameters for the minimum of the total energy are reported here.







The internal barrier for the cis-trans  $\rightarrow$  trans-trans transformation, as a function of the rotation angle, is given in Fig.6.

From the results given here, we conclude that the total energy for the trans-trans conformer is 2.97 kcal/mol over the cis-trans one, and the height of the barrier is 11.93 kcal/mol. There is then a very good agreement with the experimental value (3 kcal/mol, Ref.6) for the difference between the two conformers, although the theoretical barrier is clearly lower than the experimental one measured by Uno<sup>6</sup>.

The last named author<sup>14</sup> has analysed the spectra of diacetamide and N-deuterated acetamide, giving 40 kcal/mol for the height of the barrier corresponding to the cis-trans  $\rightarrow$  trans-trans' transformation; then, considering the similarity between acetamide and diacetamide, the accuracy of the experimental value gives a possibility of having a smaller difference between the calculated value presented here and the experimental

TABLE 2

Torsion angle (deg.)	Cis-Trans	$\rightarrow$ Trans-Trans $\rightarrow$	Cis-Trans $\rightarrow$	Cis-Cis
	CNDO/2	INDO	CNDO/2	INDO
-30	3.77	3.71	3.63	3.56
0	3.60	3.55	3.60	3.54
20	3.69	3.76	3.59	3.53
40	4.06	4.23	3.61	3.55
60	4.63	4.85	3.65	3.59
80	5.28	5.51	3.67	3.60
100	5.92	6.13	3.66	3.55
120	6.51	6.66	3.64	3.47
140	6.98	7.05	3.70	3.50
160	7.31	7.28	3.75	3.52
180	7.43	7.28	3.64	3.40

Variation of the dipolar moment with the torsional angle of C-N bonds in diacetamide. The CNDO/2 and INDO methods were used (unit: Debye).

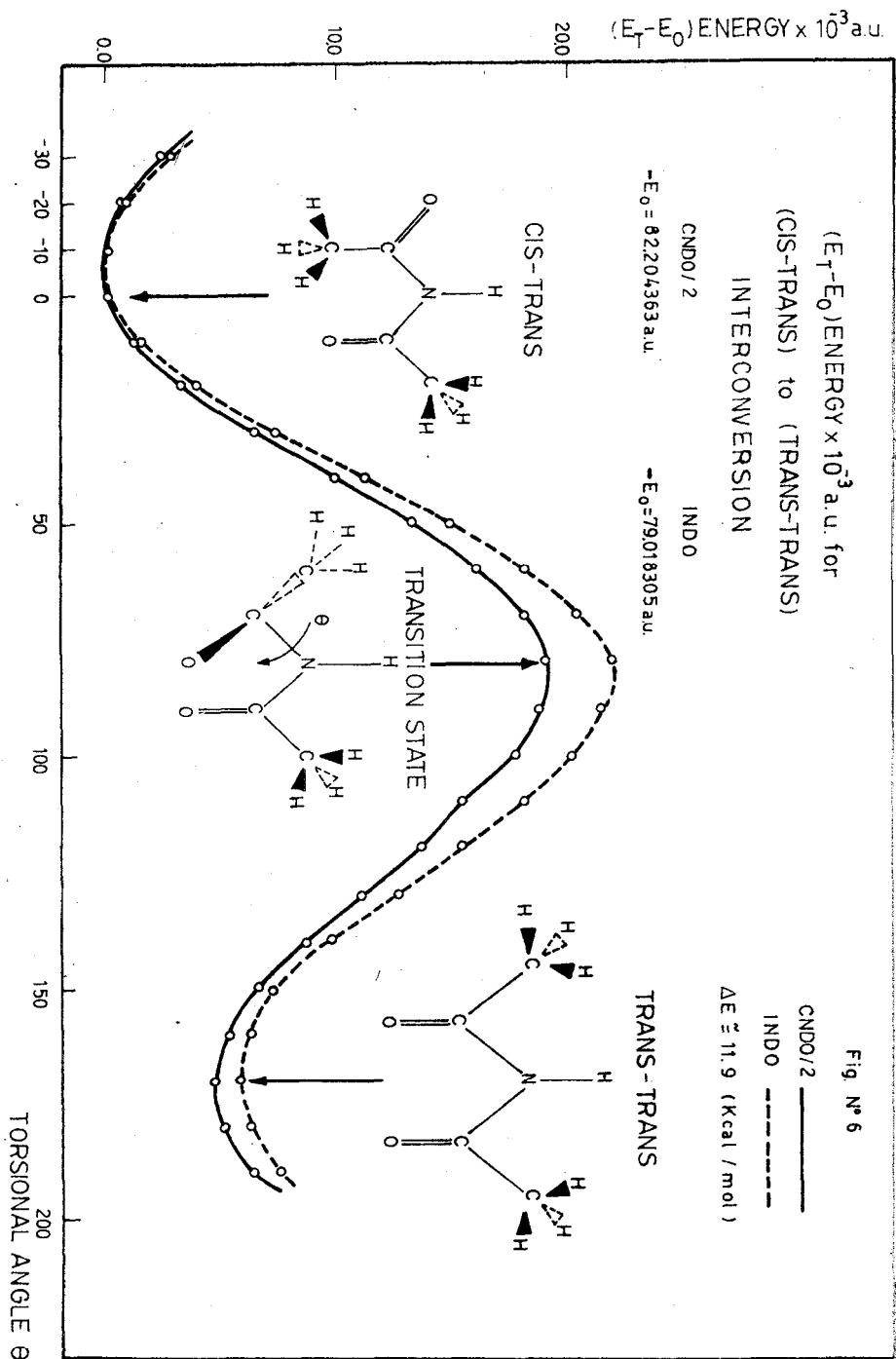




TABLE 3

	Cis-Trans			Trans-Trans			Cis-Cis		
	CNDO/2	INDO	REF.1	CNDO/2	INDO	REF.1	CNDO/2	INDO	REF.1
$\mu_a^*$	0.019	0.031	-	0.0	0.0	-	0.0	0.0	-
$\mu_b^*$	1.765	1.821	-	7.430	7.302	-	-3.645	-3.400	-
$\mu_c^*$	-3.143	-3.042	-	0.0	0.0	-	0.0	0.0	-
$\mu_T$	3.604	3.546	$\approx 2.91$	7.430	7.302	$> 6.0$	3.645	3.400	

The dipolar moment components  $\mu_a^*$ ,  $\mu_b^*$ ,  $\mu_c^*$ , and dipolar moment  $\mu_T$  for the three conformers, cis - trans, cis - cis, and trans-trans, are given for the molecule of diacetamide. The CNDO/2 and INDO were used for the calculations. The structural parameters are taken from Table 1, and the experimental values from Ref.1. (The dipolar components are given in the principal axes system) Units: Debye.

one<sup>6</sup>. It should then be interesting to check the theoretical value for the height of the barrier.

The total energy, as a function of the rotation angle, is shown for the cis-trans  $\rightarrow$  trans-trans transformation in Fig.7. The dipolar moment, as a function of the rotation angle, for the cis-trans  $\rightarrow$  trans-trans, and trans-trans  $\rightarrow$  cis-cis, is given in Table 2. The total dipolar moments are given in Table 3; the values are given in the principal axis system (they are also compared with the experimental ones given by Lee<sup>1</sup>).

The values for the dipolar moment, for the cis-trans and trans-trans conformers, agree with the experimental relation given in Ref.1. On the other hand, the dipolar moment for the cis-cis conformer is higher than that for the cis-trans, in disagreement with Lee's inequalities. Incidentally, the relation we mentioned is also theoretically predicted for the molecule of formimide<sup>11</sup>:

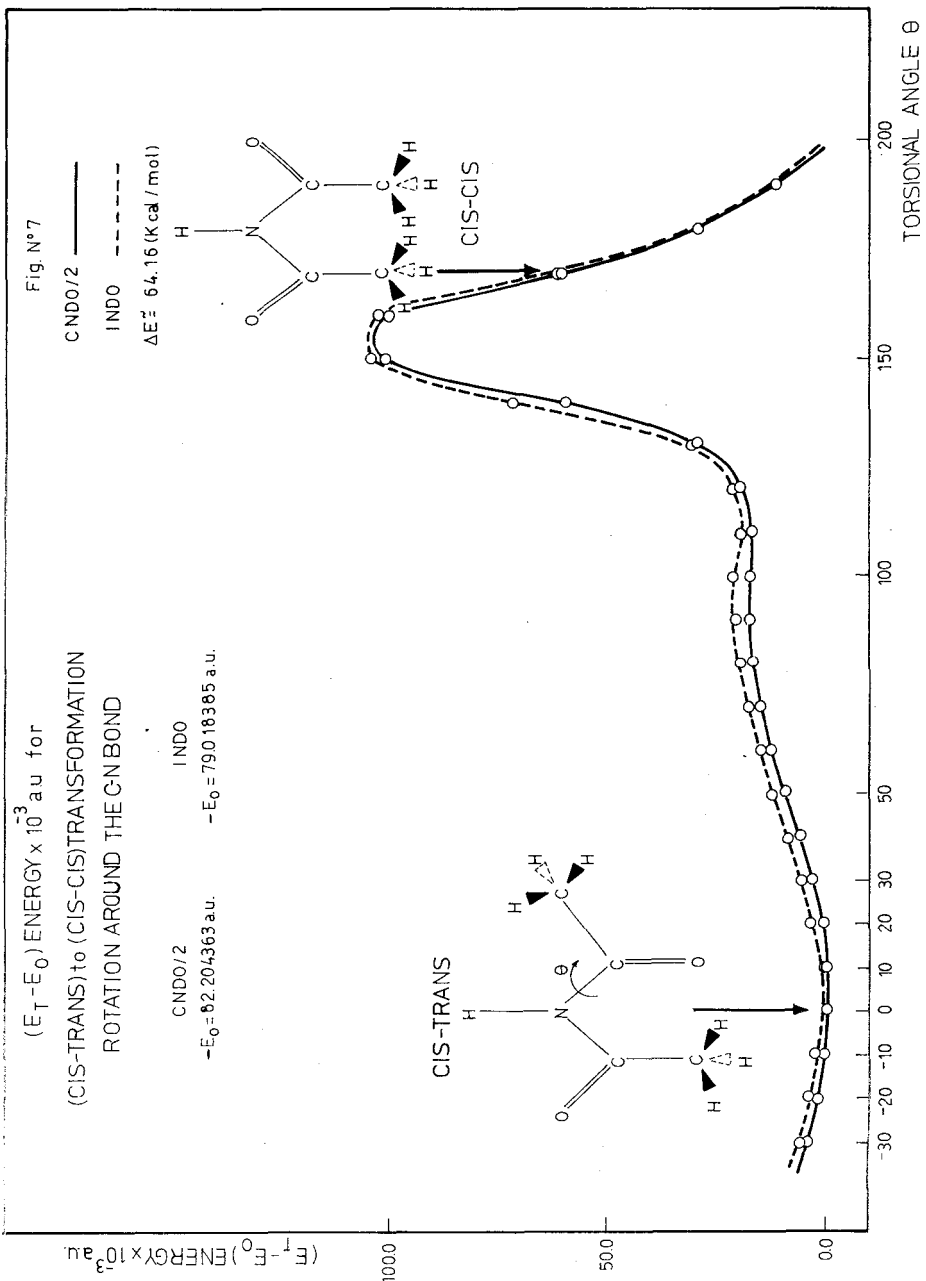
cis-cis		cis-trans		trans-trans	Debye
1.73	<	3.39	<	6.44	CNDO/2
1.53	<	3.42	<	6.47	INDO

The dipolar moments, in the principal axis system, are given for both stable conformers in Figs.8 and 9.

From the geometries given above for both stable conformers, we have calculated the  $K$  parameter used in microwave spectroscopy, although there is no available experimental data; then, it would be interesting to check the values obtained in a future microwave analysis (cf. Table 4)<sup>15</sup>.

### 3. CONCLUSIONS

Experimentally, only results for the cis-trans and trans-trans conformers are available. The cis-trans conformer is also theoretically the most stable one. The theoretical conformational analysis we have made clearly agrees with the experimental fact that the cis-cis conformer must



DIPOLAR MOMENT OF  
 CIS-TRANS CONFORMER  
 IN DIACETAMIDE IN THE  
 PRINCIPAL INERTIAL SYSTEM

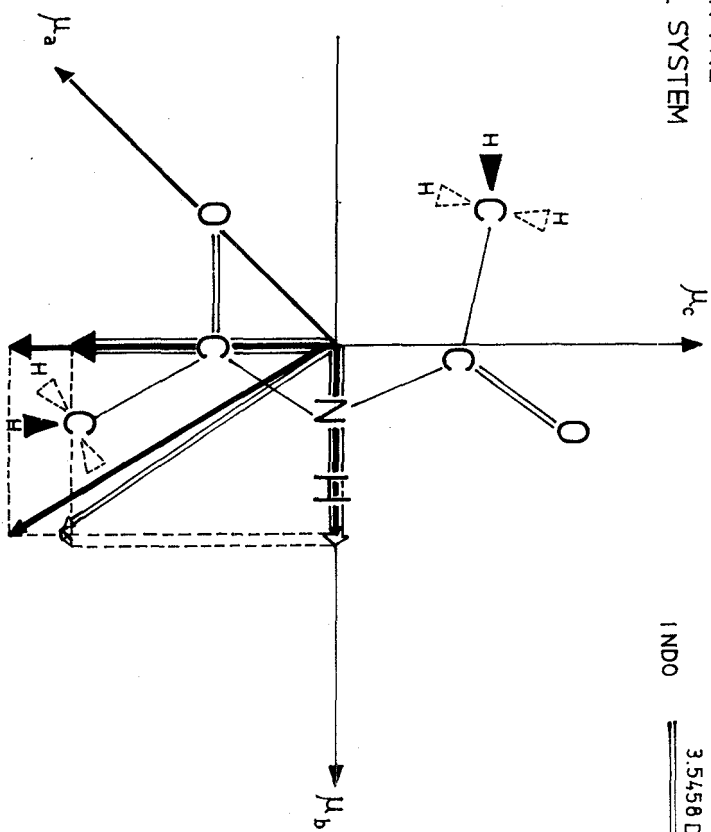


Fig. N° 6

CNDO/2  $\frac{3.6045 D_y}{3.5458 D_y}$   
 INDO  $\frac{3.5458 D_y}{3.5458 D_y}$

DIPOLAR MOMENT OF  
DIACETAMIDE TRANS-TRANS  
CONFORMER IN PRINCIPAL  
INERTIAL SYSTEM

Fig. N°9

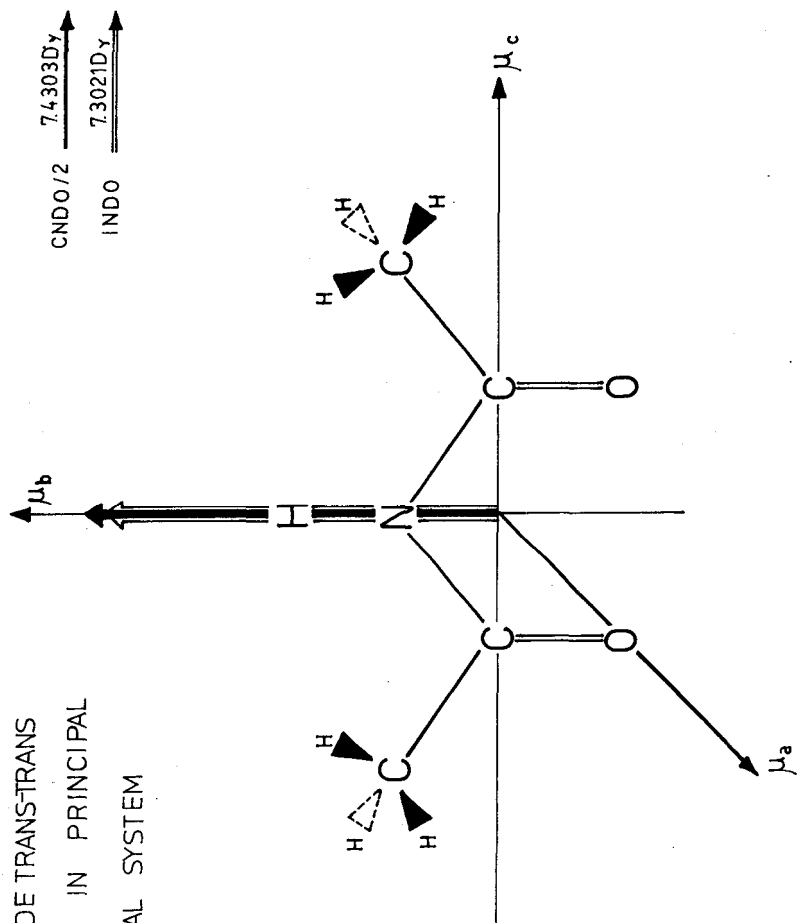


TABLE 4

	Cis-Trans	Trans-Trans	Cis - Cis
<i>A</i>	5454.77	5179.40	6004.82
<i>B</i>	1792.11	1869.57	1726.22
<i>C</i>	1370.89	1396.49	1362.48
<i>K</i>	-0.79	-0.75	-0.84
<i>I<sub>a</sub></i>	92.67	97.60	84.18
<i>I<sub>b</sub></i>	282.09	270.39	292.86
<i>I<sub>c</sub></i>	368.76	361.99	371.03

Rotational constants *A*, *B*, *C* and *K*, used in microwave spectroscopy. The structural parameters were derived from the gradient for the total energy method. The CNDO/2 was used in the calculations.

be unstable. The shape of the barrier and the differences for the total energies in the stable conformers are also in reasonable agreement with experiment. The dipolar moments for the cis-trans and trans-trans conformers agree with the relation predicted by Lee<sup>1</sup>.

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15. The program used to evaluate the constants on Table 4 was written by Dr. Luis M Boggia of the microwave laboratory, *Universidad Nacional de La Plata*.