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A Theoretical Description of the *trans-cis* Conversion in the Lowest Excited States of Diimide

A Comparison of Different Methods for the Calculation of Excited State Wave Functions

Renzo Cimiraglia
Istituto di Chimica Fisica dell'Università di Pisa, Via Risorgimento 35, I-56100 Pisa, Italy

Josep M. Riera
Instituto Quìmico de Sarrià, Barcelona-17, Spain

Jacopo Tomasi
Laboratorio di Chimica Quantistica ed Energetica Molecolare del C.N.R., Via Risorgimento 35, I-56100 Pisa, Italy

The lowest excited states of the diimide molecule have been calculated by three different SCF-type methods, the performances of which are analyzed in regard to the prediction of geometries and energies.

The calculations have been performed with two basis sets (STO-3G and 4-31G) both supplemented with more diffuse functions on the N atoms.

Lowest energy pathways for the *trans-cis* interconversion in the various states are presented for the three calculation methods and for the two basis sets.

Key words: Diimide – Excited state calculations – Photoisomerization

1. Introduction

We will compare in the present paper the performances of some methods of calculating excited states molecular wave functions. The methods we have selected for this comparison give descriptions of the excited states which are intermediate between the results of sophisticated methodologies applicable only to small molecular systems and the results of semiempirical procedures which are of low reliability or overspecialized for a limited class of compounds.

The first method is the Electron-Hole Potential (EHP) method, proposed by Morokuma and Iwata [1], the second a version of the generalized open-shell SCF formalism, proposed by Carbò *et al.* [2] which relies on coupling operator projections (COP), the third and last method adopts an effective Hamiltonian based on the "half-electron" approximation (HEA) [3, 4]. We do not give here the details of the various methods, which are all well known, and we limit ourselves to recalling their main features.

The EHP method, starting from the SCF wave function for the ground state, carries out a unitary transformation in the manifold of the virtual SCF orbitals and another one in the manifold of the occupied SCF orbitals so as to arrive at the variationally "best" excited state energy at a single excitation level.

The COP method is based on a general restricted open-shell rigorous Hartree Fock procedure which can be summarized in the following points: a) The state that one wishes to calculate is represented by a monoconfigurational wave function. b) The wave function energy is minimized by diagonalizing a unique operator which allows for the necessary coupling between occupied orbitals pertaining to different shells.

In the HEA method all states are expressed in terms of molecular orbitals obtained via a unique effective Hamiltonian which involves, in addition to the "sea" of doubly occupied orbitals, two orbitals j and k with occupation intermediate between 0 and 1. The triplet state wave function is built by the appropriate filling of the molecular orbitals thus obtained, while the singlet states are best obtained by diagonalization of a 3×3 CI matrix involving the configurations j^2, j^1k^1 and k^2.

All three methods employ a unique Fock-type operator and share the gratifying feature of dispensing with the transformation of the two-electron integral supermatrix, which constitutes a substantial bottleneck for calculation on large molecules.

The comparisons will be performed on the diimide[1] molecule (Fig. 1) because the problems presented by this molecular system are sufficiently representative of some features shared by a large number of compounds of photochemical interest and because there are several theoretical studies [5–18] which can be used as a partial test of our results.

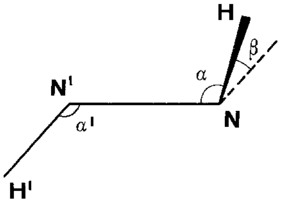

Fig. 1. The diimide molecule with the indication of the angular coordinates

In fact one of the most interesting features of this molecule is the presence in the ground state potential surface of two minima (corresponding to the *trans* and *cis* conformations) separated by large barriers. There are two possible ways of connecting the minima on the potential surface.[2] The first requires a rotation around the N–N bond, leading to a twisted conformation (I) at the top of the

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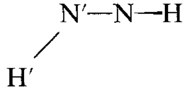
[1] This molecule is now referred to as "diazene" by Chemical Abstracts. The term "diimine" has been employed, among others, by F. A. Cotton and G. Wilkinson in the book "Advanced Inorganic Chemistry", 3rd Ed., New York: Interscience Publishers 1972.

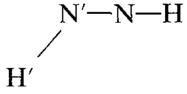
[2] A third possible mechanism of isomerization involves as transition state a full linear conformation ($D_{\infty h}$) which turns out to have a much higher energy than I and II.

barrier. It is well known [19] that during this process orbital symmetry is not conserved because a crossing occurs between the highest occupied molecular orbital (HOMO) and the lowest unoccupied one (LUMO).

The second pathway requires a planar inversion through the bent semilinear intermediate II.



I



II

The shape of the potential surfaces corresponding to the lowest excited states T_1 and S_1 ($n \rightarrow \pi^*$ states in the planar geometries) is, as expected, decidedly different from that of the ground state. The occurrence of a minimum in the T_1 surface in correspondence with the barrier in S_0 for the rotational isomerization (I) and the absence of intermediate maxima on the S_1 surface sheet corresponding to the same motion, are well ascertained features for which satisfactory explanations have already been given.

Our present aim does not consist in an attempt to reproduce the general qualitative features of these surfaces but rather in quantitative checks on the prediction of energies and geometries provided by the methods and the basis sets we have selected. The experience gained in such a way will be, hopefully, applied to larger molecular systems at present less known and for which more elaborated methods are not applicable.

2. Results

We shall consider three main points in the description of the excited states given by the methods under investigation: a) vertical transition energies, b) energy curves for the *trans-cis* isomerization via the rotation around the N–N bond along a path retaining a C_2 axis as symmetry element, c) energy curves for the *trans-cis* isomerization via the inversion at the N atom along a path retaining a plane as symmetry element.

We shall make use of the usual STO-3G and 4-31G basis sets, both supplemented with a set of diffuse p Gaussian orbitals on the N atoms (orbital exponent $= 0.1$[3]) with a view to ameliorating the description of the excited states.

Some attention will also be devoted to the ground state results, in order to check whether the addition of such diffuse orbitals should produce changes in the prediction of ground state geometries and barriers.

2.1. Vertical Excitations

We report in Table 1 the vertical transitions to the two lowest excited states T_1 and S_1 (of ($n \rightarrow \pi^*$) type). They refer to the optimized ground state geometries.

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[3] This value was found to minimize the lowest triplet energy in the EHP scheme.

Table 1. Vertical transition energies (in eV) from the ground state in its *trans* and *cis* conformations

		trans		*cis*	
Reference	Method	^3B_g	^1B_g	$^3B_1$	$^1B_1$
This work	EHP STO-3G+p	1.47	2.81	2.13	3.56
„	COP „	1.38	2.73	2.05	3.51
„	HEA „	1.61	2.80	2.29	3.56
„	EHP 4-31G+p	1.91	3.21	2.07	3.53
„	COP „	1.81	3.11	1.95	3.45
„	HEA „	1.96	3.14	2.17	3.49
C.D.P.P. [8]	open-shell	1.84	–	1.93	–
W.F.A. [9]	„ „	3.21	3.84	–	–
W. [14]	„ „	1.76	3.08	2.20	3.72
W.P. [15]	„ „	1.8	3.1	–	–
V.P.B.K.H. [16]	„ „	1.74	3.02	–	–
R.H.K. [5]	CI	3.01	3.92	2.07	3.36
C.D.P.P. [8]	„	2.58	–	2.71	–
D.D.P. [11]	„	–	3.37	–	4.37
V.P.B.K.H. [16]	„	2.07	2.97	–	–

Trans diimide is more sensitive to changes in the basis set: passing from the 4-31G+p basis to the STO-3G+p one the transition energies decrease of about 0.4 eV. The open-shell procedure (COP), enjoying a fuller orbital optimization with respect to the EHP method, consistently gives lower values of the transition energies. As to the HEA results, it should be noted that we have used a three configuration ground state description.

The 4-31G+p results for the $n \rightarrow \pi^*$ singlet transition are in passably good accordance with the scant experimental data (Trombetti [20] detected a transition centered at about 3.5 eV).

The calculations we have found in the literature can be divided into two broad classes: a) those which use an open-shell procedure to calculate the energy of the excited states (Refs. [8, 9] and [13–16]), b) those which rely on CI procedures (Refs. [5, 8, 11, 16]). The reader is referred to the original papers for more information about the details concerning procedure and basis set employed by the different authors. Of particular interest in the present context are the calculations of Vasudevan *et al.* [16] which give for a fairly extended basis parallel results obtained with open-shell and CI methods (the latter referred to a mixing of a large number of configurations); also in this case the open-shell procedure gives a lower value for the vertical transition energies. The results of Ref. [15] only concern the *trans* state, but it can be inferred by examining the results of Cadioli *et al.* [8] that the same considerations should be valid also for the *cis* geometry. For the *trans* geometry (the results for the *cis* case are less abundant) most of the reported values are in the range 1.8–2.1 eV for S_0–T_1 and in the range 3.0–3.2 for the S_0–S_1 transition energy, the exceptions being probably amenable either to the use of unoptimized geometries or to deficiencies in the basis sets.

We report in Table 2 the minimum energy geometries for the S_0, T_1 and S_1 states in the *trans* and *cis* forms in the two basis sets. We also compare in the same table our results with the analogous ones obtained in the STO-3G basis; a further set of comparisons is made in the S_0 state also for the 4-31G basis.

Table 2. Geometries and energies for the *trans* and *cis* conformations[a]

		trans				*cis*				
Reference	Method	R_{NN}	R_{NH}	α	E	R_{NN}	R_{NH}	α	E	ΔE
					State S_0					
B.S. [13]	SCF STO-3G	1.21	*1.01*	109	−108.5678	1.21	*1.01*	115	−108.5598	5.0
This work	SCF STO-3G+*p*	1.31	1.06	108	−108.6460	1.31	1.06	115	−108.6388	4.5
,,	HEA ,,	1.31	1.06	108	−108.6414	1.31	1.06	115	−108.6345	4.3
H.K. [18]	SCF 4-31G	1.23	1.01	111	−109.8127	1.22	1.02	116	−109.7988	8.7
This work	SCF 4-31G+*p*	1.23	1.01	110	−109.8165	1.23	1.02	116	−109.8034	8.2
,,	HEA ,,	*1.23*	*1.01*	*110*	−109.8104	*1.23*	*1.02*	*116*	−109.7977	7.9
W.P. [15]	SCF double ζ	1.24	1.02	110	−109.9531	1.24	1.03	116	−109.9401	8.2
A.S. [17]	SCF extended	1.21	1.02	109	−110.0262	1.21	1.03	114	−110.0152	6.9
					State T_1					
B.S. [13]	SCF STO-3G	1.26	*1.01*	120	−108.4508	1.22	*1.01*	132	−108.4314	12.2
This work	EHP STO-3G+*p*	1.37	1.05	118	−108.6019	1.30	1.06	133	−108.5769	15.7
,,	COP ,,	1.34	1.05	119	−108.6065	1.29	1.04	134	−108.5803	16.4
,,	HEA ,,	1.37	1.05	118	−108.5935	1.30	1.06	133	−108.5658	17.4
,,	EHP 4-31G+*p*	1.26	1.00	122	−109.7614	1.23	1.00	134	−109.7443	10.7
,,	COP ,,	1.26	*1.00*	122	−109.7656	1.23	*1.00*	134	−109.7490	10.4
,,	HEA ,,	1.26	*1.00*	122	−109.7538	1.23	*1.00*	134	−109.7347	12.0
					State S_1					
B.S. [13]	SCF STO-3G	1.26	*1.01*	121	−108.3932	1.22	*1.01*	133	−108.3641	18.2
This work	EHP STO-3G+*p*	1.34	1.05	120	−108.5560	1.29	1.05	135	−108.5252	19.3
,,	HEA ,,	1.34	*1.05*	120	−108.5521	1.29	*1.05*	135	−108.5203	20.0
,,	EHP 4-31G+*p*	1.25	*1.00*	125	−109.7165	1.22	*1.00*	137	−109.6932	14.7
,,	HEA ,,	1.26	*1.00*	125	−109.7126	1.23	*1.00*	137	−109.6884	15.2

[a] Distances in Å, angles in degrees, energies in hartrees, $\Delta E = E_{cis} - E_{trans}$ in kcal/mol. Unoptimized values are reported in italics.

For the ground state Ahlrichs and Staemmler's accurate calculations [17] can be considered as a good standard for the comparison of the other results.

It appears that the inclusion of the diffuse *p* functions in the STO-3G basis, although beneficial as to the excited state energies, seriously fails in predicting the correct geometries; particularly, the R_{NN} bond length turns out to be excessively large. This anomaly definitely seems to depend on the basis, because fairly large (unpublished) CI calculations in the STO-3G+*p* basis set lead to a R_{NN} value of the same order. The STO-3G prediction of the R_{NN} distance [13], as is often the case for minimal basis set calculations, is fairly good.[4]

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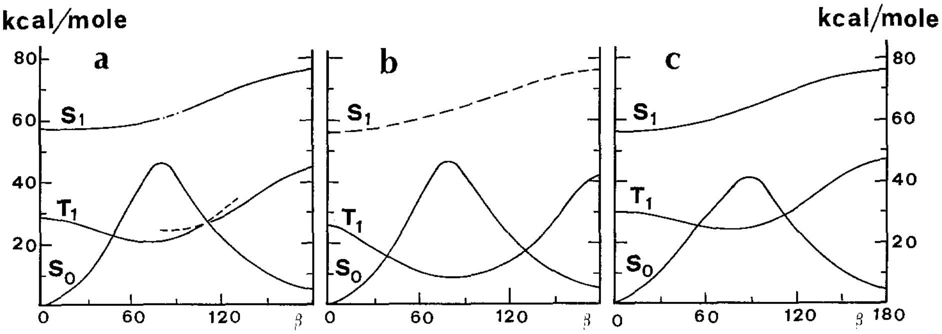
[4] It should be noted that the STO-3G results of Ref. [18] are at variance with those of Ref. [13], probably because of an incorrect geometry optimization strategy in [18].

The 4-31G+p results compare well with all the extended basis set calculations.

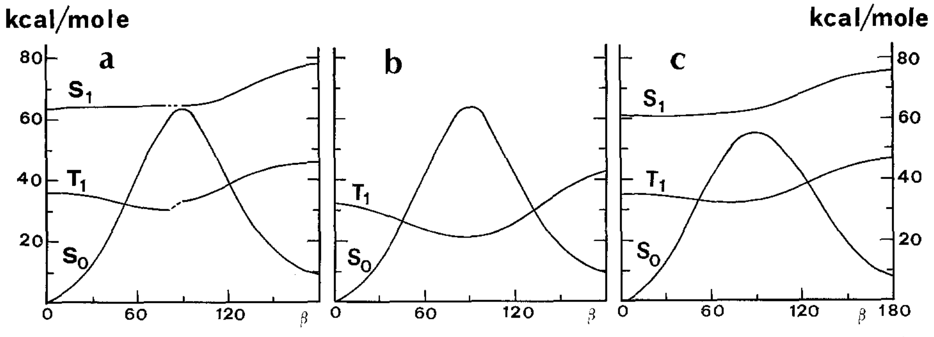
In the T_1 and S_1 states the only comparisons that can be made are those with Baird and Swenson's STO-3G calculations [13]; again our STO-3G+p results overestimate the R_{NN} distance, a characteristic which will manifest itself throughout the potential energy surfaces.

2.2. *The Rotational Mechanism of Isomerization*

The three lowest potential energy curves (S_0, T_1 and S_1) for the rotational conversion from the *trans* to the *cis* form, obtained with the three methods in question, are reported in Figs. 2a, b, c for the basis STO-3G+p and in Figs. 3a, b, c for the basis 4-31G+p. An optimization of the geometrical parameters has been performed for each state and each method independently at a fairly large number of β values and therefore the curves displayed in the figures may be considered the lowest energy pathways along the whole rotational transformation.



Figs. 2a, b, c. (a = EHP, b = COP, c = HEA) Energy trend for the *trans-cis* conversion by rotation around the N–N bond in the STO-3G +p basis set. In the abscissae is reported the β angle (see Fig. 1). The S_0 curve of a and b has been calculated with a two-configuration wave function. The S_0 curve of c has been calculated with a two-configuration wave function built on HEA orbitals. In all cases the S_0 *trans* energy is taken as the origin of the energy scale



Figs. 3a, b, c. (a = EHP, b = COP, c = HEA) Energy trend for the *trans-cis* conversion by rotation around the N–N bond in the 4-31G+p basis set. Same remarks as in Fig. 2

According to the philosophy of the EHP method the ground state surface should be described by a closed-shell SCF formalism. The crossing of the HOMO and LUMO orbitals remarked in the introduction produces a crossing of two configurations

$$\ldots 3a^2 3b^2 4a^2 5a^2 \tag{1}$$

$$\ldots 3a^2 4a^2 3b^2 4b^2 \tag{2}$$

the first predominant at transoid geometries, the second at cisoid geometries.[5] The broken lines of Figs. 2a and 3a report the energy trend of (1) and (2). The full line S_0 curve refers to a CI mixing of these two configurations.

As to the T_1 and S_1 states, formally one arrives at the same single excitation configuration

$$\ldots 3a^2 3b^2 4a^2 4b^1 5a^1 \tag{3}$$

either if one starts from configuration (1) or from configuration (2). In the first case however 5a is determined on the manifold of the occupied orbitals while in the second case it is determined on the manifold of the virtual ones (the converse holds for orbital 4b). The two versions are not identical and the difference is emphasized particularly in the STO-3G+p case by the limitation of the basis set. Consequently if one makes EHP calculations for the T_1 state starting from SCF calculations constrained to have configuration (1) or (2), one obtains two curves which cross at $\beta = 110°$ (the crossing for S_0 is at $\beta = 84°$). Such defect is shared by all the methods which describe excited states by means of single excitations with respect to a one determinant ground state. We report in Fig. 4 the results of a CI calculation, for the STO-3G+p basis, including all the single excitation configurations (CSECI method). Such results are hardly distinguishable from those obtained by direct application of the EHP method, which needs a far lower computational effort.

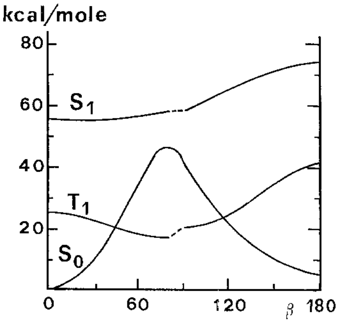


Fig. 4. Energy trend for the *trans-cis* conversion by rotation around the N–N bond. CSECI calculation in the STO-SG +p basis set. The S_0 curve is the same as in Fig. 2a

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[5] In configurations (1) and (2) the labelling of the orbitals is given according to the C_2 symmetry group notation, because in this type of motion only a C_2 axis is conserved. It has been ascertained that the best energy pathway actually requires the retention of the C_2 symmetry.

It should be noted, in passing, that the EHP orbitals have a greater efficacy with respect to the SCF canonical ones in improving the excited state wave function in a limited CI calculation; so, for instance, the energy gap between the two T_1 curves at $\beta=80°$, which is of 4 kcal/mol reduces to less than 0.001 kcal/mol by allowing for a mixing with five doubly excited and one singly excited configurations.

The bad description of the ground state produces in the EHP representation of the S_1 curves shortcomings which are not clearly recognizable at the scale adopted in drawing Fig. 2a. Larger are these defects in the CSECI curve of Fig. 4.

The description of T_1 given by the COP method does not suffer from this drawback because this method treats each state separately. On the other hand COP has some difficulties in describing the S_1 surface because the convergency process has turned out in some cases to be hardly achievable. On the whole, however, the S_1 curve (reported only for the STO-3G+p basis set) has a trend similar to that found by Baird and Swenson [13] with simple substitution of rigid canonical SCF orbitals ("virtual excitation") and to that found with the EHP method.

Table 3. Geometries and energies for the twisted conformation[a]

Reference	Method	R_{NN}	R_{NH}	α	β	E	ΔE[b]
			State S_0				
B.S. [13]	SCF STO-3G	1.24	*1.01*	124	82	−108.4860	84.0
This work	SCF[c] STO-3G+p	1.45	1.06	106	80	−108.5737	46.2
,,	HEA ,,	1.45	*1.06*	109	90	−107.5758	41.2
,,	SCF[c] 4-31G+p	1.29	*1.01*	118	*90*	−109.7158	64.0
,,	HEA ,,	*1.29*	*1.01*	*118*	*90*	−109.7215	55.8
W.P. [15]	SCF double ζ	1.25	1.02	127	*90*	−109.8465	66.9[d]
			State T_1				
B.S. [13]	SCF STO-3G	1.26	*1.01*	117	77	−108.4619	−7
This work	EHP STO-3G+p	1.41	*1.06*	110	80	−108.6149	−8.2
,,	COP ,,	1.44	*1.06*	110	82	−108.6333	−17.3
,,	HEA ,,	1.41	*1.06*	111	80	−108.6029	−5.8
,,	EHP 4-31G+p	1.28	1.01	116	*90*	−109.7649	−2.2
,,	COP ,,	1.32	*1.01*	113	*90*	−109.7828	−10.8
,,	HEA ,,	1.29	*1.01*	116	*90*	−109.7576	−2.4
			State S_1				
B.S. [13]	SCF STO-3G	1.22	*1.01*	127	*90*	−108.3903	18
This work	EHP STO-3G+p	1.31	1.05	122	*90*	−108.5353	13
,,	HEA ,,	1.28	*1.05*	128	*90*	−108.5395	7.9
,,	EHP 4-31G+p	1.23	*1.01*	127	*90*	−109.7149	1.0
,,	HEA ,,	1.22	*1.01*	129	*90*	−109.7087	2.4

[a] Distances in Å, angles in degrees, energies in hartrees, ΔE in kcal/mol.

[b] $\Delta E=E_{\text{twist}}-E_{trans}$.

[c] SCF values corrected with a 2×2 CI, as explained in the text. The energies for the *trans* form calculated in the same approximation are respectively: −108.6474 (STO-3G+p) and −109.8178 a.u. (4-31G+p).

[d] A MCSCF calculation with this geometry gives $\Delta E=60.43$ kcal/mol.

The half-electron approximation has a structure suitable for dealing with the electronic states involved in this portion of the potential surface. The ground state wave function is given by a mixing of two configurations involving the 5a and 4b orbitals and consequently the S_0 curve in the region of the barrier has a correct shape. The T_1 curve runs smoothly with a minimum in the expected region and the S_1 surface has a trend in line with the preceding calculations.

The qualitative trend of the 4-31G+p curves displayed in Fig. 3 is quite similar to that found for the smaller basis. The defects of the EHP method are here less evident (the energy gap at $\beta=90°$ is 1 kcal/mol).

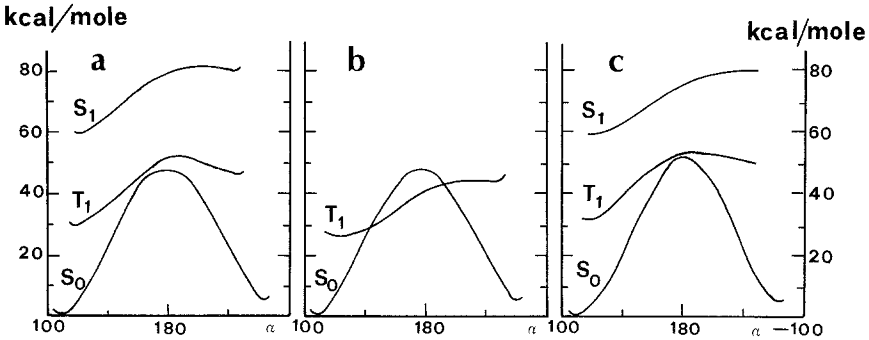
A better appreciation of the difference among the results given by the different methods can be obtained by examining some numerical values. In Table 3 we report geometries and energies for the twisted conformation, with reference to a few previous works. It may be noticed that the ground state barrier is underestimated by the STO-3G+p basis set.

For the excited states comparisons can be performed only with the values of Baird and Swenson [13]. The geometry optimization they give for T_1 at $\beta=90°$ has been obtained by excitation to SCF canonical virtual orbitals; their calculations are then refined by using an open-shell procedure at the same geometry.

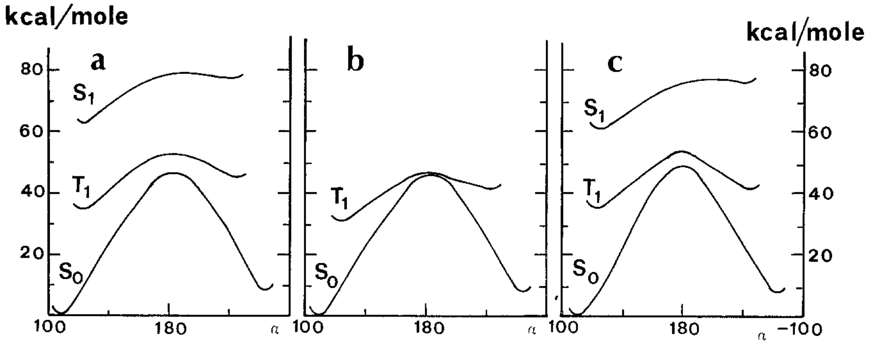
Kosower [21] gives for the 0–0 band of the S_0–T_1 transition a rough estimate in the range 14–18 kcal/mol: the value of BS [13] of 36 kcal/mol can be compared with our predictions: EHP 19.6 kcal/mol, COP 8.0 kcal/mol, HEA 24.2 kcal/mol for the STO-3G+p basis and EHP 32.4 kcal/mol, COP 21.1 kcal/mol, HEA 33.1 kcal/mol for the 4-31G+p basis.

2.3. *The Inversional Mechanism of Isomerization*

The energy curves for the isomerization process via the inversion at one N atom, obtained with the methods under examination, are reported in Figs. 5a, b, c for the STO-3G+p basis set and in Figs. 6a, b, c for the 4-31G+p one. The curves



Figs. 5a, b, c. (a=EHP, b=COP, c=HEA) Energy trend for the *trans-cis* conversion by inversion in plane in the STO-3G+p basis set. In the abscissae is reported the α angle with the constraint of keeping $\beta=0$ (see Fig. 1). For the energy scale the same convention holds as in Fig. 2



Figs. 6a, b, c. (a = EHP, b = COP, c = HEA) Energy trend for the *trans-cis* conversion by inversion in plane in the 4-31G+p basis set. Same remarks as in Fig. 5

Table 4. Geometries and energies for the bent conformation[a]

Reference	Method	$R_{NH'}$	α'	R_{NN}	R_{NH}	α	E	ΔE[b]
			State S_0					
B.S. [13]	SCF STO-3G	*1.01*	110	1.20	*1.01*	*180*	−108.472	60.0
This work	SCF STO-3G+p	1.07	108	1.30	1.03	*180*	−108.5742	45.1
,,	HEA ,,	1.07	111	1.27	1.03	*180*	−108.5630	49.2
H.K. [18]	SCF 4-31G	1.03	112	1.22	0.98	*180*	−109.7358	48.3
This work	SCF 4-31G+p	1.03	112	1.22	0.98	*180*	−109.7428	46.3
,,	HEA ,,	*1.03*	*112*	*1.22*	*0.98*	*180*	−109.7323	49.0
W.P. [15]	SCF double ζ	1.03	110	1.23	0.99	*180*	−109.8783	46.9
A.S. [17]	SCF extended	1.03	110	1.21	1.00	*180*	−109.9370	56.0
			State T_1					
B.S. [13]	SCF STO-3G	*1.01*	118	1.24	*1.01*	*180*	−108.411	25.0
This work	EHP STO-3G+p	1.06	114	1.34	1.03	*180*	−108.5678	21.4
,,	COP ,,	*1.06*	108	1.36	1.03	*180*	−108.5850	13.5
,,	HEA ,,	1.07	109	1.35	*1.03*	*180*	−108.5619	19.8
,,	EHP 4-31G+p	1.01	121	1.24	0.98	*180*	−109.7329	17.9
,,	COP ,,	*1.01*	115	1.26	*0.98*	*180*	−109.7424	14.5
,,	HEA ,,	*1.01*	118	1.24	*0.98*	*180*	−109.7251	18.0
			State S_1					
B.S. [13]	SCF STO-3G	*1.01*	116	1.24	*1.01*	*180*	−108.357	23.0
This work	EHP STO-3G+p	1.06	114	1.34	1.03	*180*	−108.5264	18.6
,,	HEA ,,	*1.07*	108	1.35	*1.03*	*180*	−108.5274	15.5
,,	EHP 4-31G+p	*1.01*	124	1.23	*0.98*	*180*	−109.6915	15.7
,,	HEA ,,	*1.01*	118	1.24	*0.98*	*180*	−109.6879	15.6

[a] Distances in Å, angles in degrees, energies in hartrees, ΔE in kcal/mol.

[b] $\Delta E = E_{\text{bent}} - E_{\textit{trans}}$.

refer also in this case to geometries optimized in some points along the reaction coordinate.

The calculation of the potential energy curves for this type of isomerization is simpler than for the preceding one because there is no crossing of configurations. The inclusion of doubly excited configurations concerns in this case mainly the introduction of electronic correlation into the description of the states, a subject which goes beyond the scope of this paper.

In Table 4 we report the geometries found for the bent conformation ($\alpha = 180°$) together with other results obtained by other authors.

The predictions for the T_1 barrier given by the EHP and HEA methods are in close agreement between themselves and not too far from the values of BS [13] who adopt a wave function obtained by promotion of an electron to a rigid virtual canonical orbital.

The COP barrier is, as expected, consistently lower in both basis sets.

A characteristic shared by all the results in the S_0 and T_1 states is the prediction of a shortening of the NH distance while the length of the N′H′ bond, which does not undergo inversion, remains essentially the same as in the *trans* conformation. The remaining geometrical parameters are less changed (with respect to the *trans* geometry) than in the twisting mechanism of inversion.

3. Conclusions

The systematic comparison of the representations of the potential energy surfaces given by the three methods, permits us to state that the half-electron method gives acceptable results for the lowest excited states. For the ground state one has reasonable results as well, if one further refines the wave function by allowing for a small (3×3) configuration interaction.

The COP method offers, among the three, the best upper bound to the excited state energy as a consequence of the fuller optimization of the molecular orbitals in the single determinant scheme. The main drawbacks of the rigorous open-shell method are: 1) the orbitals of the excited state wave functions are not orthogonal to those of the ground state, 2) the way such a method treats the correlation energy presumably yields too low excitation energies, 3) the equations to be solved require a rather large amount of computation time[6] and sometimes have bad convergency properties.

The reader can be referred to Baird and Barr's interesting paper [22] for a systematic comparison between the Roothaan restricted open-shell method and the half-electron technique. One of the main conclusions of that paper is that, whereas appreciable differences appear in the energy results, optimum geometries predicted by the two methods do not differ significantly.

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[6] We can give the ratios of the times involved in a single cycle for SCF, HEA, EHP and COP. SCF:HEA:EHP:COP=1:1:1.25:4.20.

The EHP method, lastly, hinges on a safer variational procedure than HEA, doing without the intuitive considerations which underlie the half-electron effective Hamiltonian. In addition the EHP method treats the excited state correlation energy not very differently, we think, from the way it is treated in the SCF ground state, and enjoys the benefits of some extensions of Brillouin's theorem, which make themselves felt in a possible subsequent CI calculation. In the particular case of diimide, however, it was *a priori* evident that the EHP method would not have worked in the twisting mechanism of isomerization, on account of the symmetry jump we discussed about previously.

The 4-31G$+p$ basis set can be considered a sufficiently reliable set: the addition of some more diffuse functions aids in the description of the excited states (such effect is even more evident in the π–π^* states, not included in this paper) and the results seem comparable with those obtainable with larger basis sets.

The addition of diffuse p functions to the STO-3G basis gives rise to some spurious effects which are particularly evident in the geometry optimizations. A search of geometries of stable conformations, as well as of saddle points with such a basis, does not seem advisable. In this case again the enrichment of the basis set can lead to better evaluations of the vertical transition energies; the reader is referred to Refs. [23, 24] for further comparisons on related systems ($H_2C{=}O$ and $H_2C{=}NH$).

We would conclude by adding that the data of the present paper as well as those of the literature do not seem sufficient for a complete description of the isomerization via rotation in the diimide molecule; such important details as the exact determination of the crossing points between the S_0 and T_1 states, have not been given a rigorous answer. More precise calculations, drawing both on a more flexible basis set and on more sophisticated computational techniques, are required.

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