

*Original Investigations***Fragment Interaction Analysis of Structural Problems in the Framework of *Ab initio* SCF-MO Computations**

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We describe here a procedure which allows to extend the application of the quantitative orbital interaction analysis at the *ab initio* SCF-MO level to any kind of orbital interaction. In this new procedure a localization scheme is applied to the fragment MOs obtained with the procedure suggested by Wolfe et al. (JACS **99**, 1296 (1977)): in this way also the resulting σ -type fragment localized MOs have correct orbital occupancies and can be used for a PMO analysis. In addition the availability of quantitative expressions for the fragment localized MOs allows also to compute the total energy of the system in the absence of the orbital interactions under examination. For illustrative purposes the procedure is applied to the analysis of the factors which determine the preferential stability of *trans* over *cis* diimide.

Key words: Fragment interaction analysis – Structural problems – Diimide.

1. Introduction

Procedures based on the analyses of the energy effects associated with the orbital interactions occurring between the component fragments seem to be very useful for analyzing structural problems [1]. These procedures usually involve the following steps: (i) sequential dissection of the molecule under consideration into component fragments; (ii) construction of the group MOs of each fragment; (iii) evaluation of the interaction energy obtained in the course of combining the component fragments to yield the composite system in a specified geometry.

On the other hand *ab initio* SCF-MO theory with a clearly defined set of basis functions associated with each atom seems to provide a complete model for molecular structure [2]. Therefore procedures which perform orbital interaction

analyses at the *ab initio* SCF-MO level should be very useful for elucidating structural problems. Preliminary results, in fact, obtained with procedures of this type recently suggested [3, 4] seem to be very promising. However the applicability of the procedures suggested so far is limited to problems involving only π -type MOs.

It is the purpose of this paper to describe a general procedure which allows to evaluate in the framework of an *ab initio* SCF-MO computation, the energy effects associated with the orbital interactions occurring between any type of fragment MOs. This procedure can therefore be applied not only to the analysis of the orbital interactions between π MOs, as performed by the procedure suggested by Wolfe et al. [3], but also to the analysis of orbital interactions involving σ bond MOs and σ -type lone pairs. Furthermore the energy effects associated with the orbital interactions are estimated with two different treatments, one based on a Perturbational Molecular Orbital approach (PMO approach) and the other based on SCF-MO total energy values computed in the absence of the interactions under examination (total energy approach). It is suggested that the combined use of these two types of quantitative information provides a better understanding of the role played by the various factors which control a structural problem.

For illustrative purposes we describe here the application of such a computational procedure to the analysis of the factors which determine the relative stability of the *cis* and *trans* isomers of the N_2H_2 molecule.

2. Computational Procedure

The present computational procedure involves the following steps.

2.1. Computation of the Fragment MOs

The procedure used here for obtaining the eigenvectors of the fragment MOs is derived from that recently suggested by Wolfe et al. [3], which will be denoted hereafter as the WSW procedure. In the WSW procedure the energies and the eigenvectors of the fragment MOs are obtained from the solution of the following eigenvalue problem

$$\mathbf{F}^0 \mathbf{C}^0 = \mathbf{S}^0 \mathbf{C}^0 \epsilon^0 \quad (1)$$

where \mathbf{F}^0 and \mathbf{S}^0 are the Fock matrix and the overlap matrix for the composite system with all the non-diagonal matrix elements between atomic orbitals belonging to the different interacting fragments set equal to zero. The availability of quantitative expressions for the fragment MOs allows also to obtain estimates of the matrix elements and overlap integrals between the interacting MOs over the fragment molecular basis. The energy effects associated with the orbital interactions are then estimated in terms of the following second order perturbation equations:

$$\Delta E_{ij}^2 = 2(H_{ij} - \epsilon_i S_{ij})^2 / (\epsilon_i - \epsilon_j) \quad (2)$$

$$\Delta E_{ij}^4 = 4S_{ij}(S_{ij}\epsilon_0 - H_{ij}) / (1 - S_{ij}^2) \quad (3)$$

where ΔE_{ij}^2 denotes the stabilization energy arising from the interaction of a doubly occupied MO, ϕ_i , with a vacant MO, ϕ_j , while ΔE_{ij}^4 denotes the destabilization energy arising from the interaction of two doubly occupied MOs, ϕ_i and ϕ_j . The symbols ε_i and ε_j denote the orbital energies of ϕ_i and ϕ_j , respectively, ε_0 the mean of these energies, H_{ij} the interaction matrix element and S_{ij} the overlap integral.

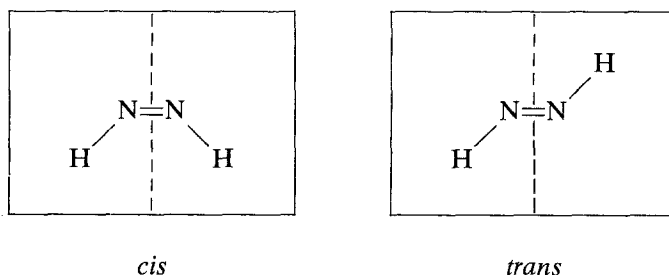
As already pointed out by Wolfe et al. [5], this procedure provides useful information only for the analysis of the energy effects associated with π MOs, but can not be used for a quantitative analysis of the effects of σ orbital interactions. In fact, the correct application of Eqs. (2) and (3) requires that the interacting orbitals have correct orbital occupancies, while the orbital occupancies of the formally doubly occupied σ MOs obtained with the WSW procedure differ significantly from the value of 2.

Wolfe et al. [6] have recently suggested a modification to their procedure for analyzing the interactions associated with the fragment orbitals which contribute to the HOMO of the composite molecule, when the HOMO contains a significant contribution from a hybrid lone pair orbital, as in the case of amines and their congeners.

Here we suggest a more general procedure which completes the WSW quantitative analysis and allows to extend its application to all kinds of orbital interactions. Our suggestion consists in applying a localization procedure to the set of fragment MOs obtained from the solution of the eigenvalue problem (1). The localization procedure is applied separately to the set of the occupied and to the set of the vacant fragment MOs. In our applications we have used the Boys' method of localization [7]. This new procedure, i.e. the WSW procedure followed by localization, provides for each fragment a new set of MOs which are still orthogonal and have now correct orbital occupancies. We shall denote this new set of MOs as fragment localized MOs.

We have applied this procedure to the two stable isomers of diimide, using the dissection illustrated in Scheme 1.

Scheme 1



We have applied the localization treatment only to the σ fragment MOs.

The orbital occupancies of the various MOs associated with an HN-fragment computed with the WSW procedure and with the present procedure are shown in Table 1. It can be seen that, while none of the occupied σ fragment MOs obtained with the WSW procedure has an electron occupancy close to 1 or 2, the occupied MOs obtained after the application of the localization procedure have electron occupancies close to 2, except one whose electron occupancy is close to 1. Fig. 1 illustrates the valence localized MOs of an HN-fragment. The first MO (σ_N) is the singly occupied orbital localized along the N—N axis and pointing toward the other nitrogen atom, the second MO (σ_{NH}) is a doubly occupied σ MO associated with the N—H bond, the third MO (n_σ) is a doubly occupied in plane nitrogen lone pair, the fourth MO (π) is a singly occupied p_π -type nitrogen atomic orbital and the fifth MO (σ_{NH}^*) is a vacant orbital associated with the N—H bond.

2.2. PMO Approach

Following the procedure outlined by Wolfe et al. [3], the availability of quantitative expressions for the fragment localized MOs allows to obtain estimates, in the framework of the SCF computations, of the matrix elements and overlap integrals between the fragment localized MOs according to the following

Table 1. Energies^a (ϵ_i) and gross populations (Q_i) of the fragment orbitals of *cis* and *trans* diimide computed with the WSW procedure and with the present procedure

MOs	<i>cis</i>				<i>trans</i>			
	Rigid model ^b		Optimized model ^c		Rigid model ^d		Optimized model ^c	
	ϵ_i	Q_i	ϵ_i	Q_i	ϵ_i	Q_i	ϵ_i	Q_i
WSW procedure								
σ_1	-15.4215	2.0008	-15.4187	2.0008	-15.4038	2.0085	-15.4096	2.0008
σ_2	-1.1669	1.6164	-1.1560	1.6094	-1.1401	1.6012	-1.1512	1.6063
σ_3	-0.5857	1.5969	-0.5985	1.5758	-0.5969	1.5821	-0.5869	1.6192
σ_4	-0.4409	1.7739	-0.4285	1.7957	-0.4214	1.7995	-0.4315	1.7597
π	-0.1734	1.0000	-0.1707	1.0000	-0.1626	1.0000	-0.1669	1.0000
σ_5	0.5684	0.0120	0.5674	0.0184	0.5822	0.0163	0.5847	0.0140
Present procedure								
$1s_N$	-15.3004	2.0005	-15.2979	2.0004	-15.2833	2.0004	-15.2889	2.0005
σ_N	-0.9483	1.0108	-0.9505	1.0035	-0.9414	1.0006	-0.9427	1.0114
σ_{NH}	-0.7912	2.0101	-0.7825	2.0050	-0.7664	1.9990	-0.7730	2.0044
n_σ	-0.5751	1.9667	-0.5708	1.9727	-0.5711	1.9837	-0.5745	1.9697
π	-0.1734	1.0000	-0.1707	1.0000	-0.1626	1.0000	-0.1669	1.0000
σ_{NH}^*	0.5684	0.0120	0.5674	0.0184	0.5822	0.0163	0.5847	0.0140

^a Values in a.u.

^b Geometry obtained with rigid rotation of the *trans* geometry.

^c Optimized geometries. See Ref. [2].

^d Geometry obtained with rigid rotation of the *cis* geometry.

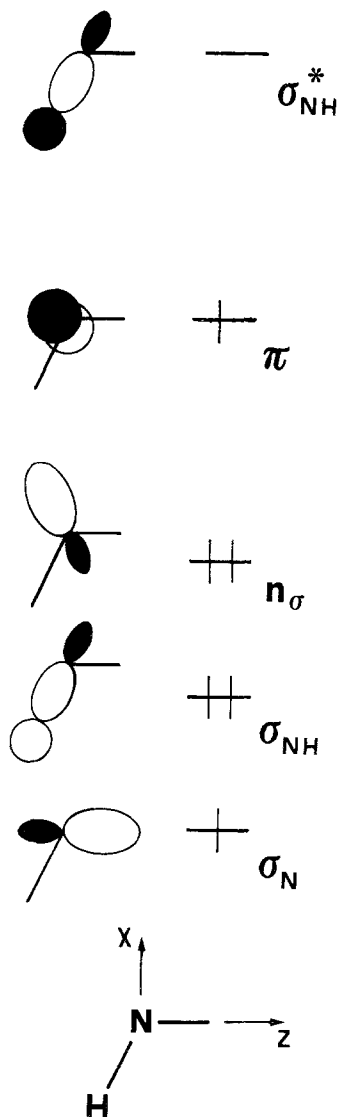


Fig. 1. The valence localized MOs of a HN-fragment

relations:

$$\mathbf{H} = (\mathbf{C}_L^0)^\dagger \mathbf{F} \mathbf{C}_L^0 \quad (4)$$

$$\mathbf{S} = (\mathbf{C}_L^0)^\dagger \mathbf{S}' \mathbf{C}_L^0 \quad (5)$$

where \mathbf{C}_L^0 denotes the coefficient matrix of the fragment localized MOs, \mathbf{F} the Fock matrix and \mathbf{S}' the overlap matrix for the composite system between atomic orbitals. Furthermore, as energies of the fragment localized MOs, we have chosen the expectation values of the Fock operator over the fragment localized basis, i.e. the diagonal elements of \mathbf{H} .

Insertion of the values of the matrix elements, overlap integrals and energies of the fragment localized MOs, computed as described above, in the expressions (2) and (3), makes possible to obtain estimates of the various two-electron stabilization energies ΔE_{ij}^2 and four-electron destabilization energies ΔE_{ij}^4 .

These energy terms are the only ones appearing in the expression of the interaction energy when the PMO treatment is carried out at the Extended Hückel level of MO theory [8]. However, when we operate within the framework of a SCF-MO scheme, other terms appear in the expression of the interaction energy [9, 10], and among these of particular relevance should be the Coulomb Energy (E_c) associated with the interaction of the various fragments.

In the Devaquet expression [9] the term E_c represents the Coulomb interaction between the net charges of the two interacting molecules (electrostatic energy).

Usually, in these approaches, the energy effects associated with the orbital interactions are estimated in terms of Eqs. (2) and (3), which describe just the energy effects associated with the two-orbital mixing. However, also higher order mixing can be significant: in order to evaluate its effect, we can compare the solution of the Hückel type variational problem involving all the orbitals under examination with the solutions obtained in terms of the related 2×2 variational problems. In fact, Eq. (3) is just the solution of a 2×2 variational problem of this type involving two doubly occupied MOs [11], while Eq. (2) is an approximate expression of the solution of a 2×2 variational problem involving a doubly occupied and a vacant MO [11].

2.3. Total Energy Approach

The availability of quantitative expressions for the fragment localized MOs allows also to compute the total energy of the system in the absence of the orbital interactions under examination on the basis of the following expression:

$$E_T^0 = \text{tr}[(\mathbf{h}^0 + \mathbf{H}^0)\mathbf{R}^0]. \quad (6)$$

Here all the matrices are defined over the fragment localized basis. The density matrix \mathbf{R}^0 is defined as $\mathbf{R}^0 = \mathbf{T}\mathbf{T}^\dagger$, where \mathbf{T} is the matrix formed with the doubly occupied MOs referring to the situation in the absence of the interactions under examination, \mathbf{h}^0 is the matrix of the one-electron hamiltonian and \mathbf{H}^0 is the Fock matrix computed from \mathbf{R}^0 with all non diagonal matrix elements between fragment localized MOs belonging to the different interacting fragments set equal to zero.

This approach is a generalization of that described in Ref. 4, which was developed only for π type MOs. Also, the present approach is similar, in principle, to that suggested by Kitaura and Morokuma [12].

The E_T^0 values provide useful information about the effect of the orbital interactions under examinations. In particular they can be used to show the changes of geometrical parameters in the absence of a certain orbital interaction. The difference $E_T - E_T^0$, where E_T denotes the total energy of the system, represents

an estimate of the electronic energy component of the energy effect associated with a given interaction. The exact relationship of this quantity with the corresponding quantity computed in terms of the quantitative PMO analysis is not yet clear. However, the $E_T - E_T^0$ values provide additional information which used together with that obtained in the PMO treatment leads to a better understanding of the effects of the various factors that concur to determine the preferred structure of a molecule.

3. Fragment Interaction Analysis in *cis* and *trans* Diimide

For illustrative purpose we apply the procedure previously described to the analysis of the factors which determine the preferential stability of *trans* versus *cis* diimide. All computations have been carried out at the STO-3G level [13], and the SCF values have been computed with the GAUSSIAN 70 series of programs [14]. The computations have been performed at four different geometries, i.e. at the *trans* STO-3G optimized geometry [2], at a *cis* geometry obtained through a rigid rotation of the *trans* geometry, at a *cis* STO-3G optimized geometry [2] and at a *trans* geometry obtained through a rigid rotation of the *cis* optimized geometry: the *trans* configuration with optimized geometry has been found to be more stable by 2.84 kcal/mol. than the *trans* configuration obtained through rigid rotation, more stable by 10.17 kcal/mol than the *cis* configuration obtained through rigid rotation and more stable by 7.35 kcal/mol than the *cis* configuration with optimized geometry.

In this analysis we dissect the diimide molecule into two HN-fragments as shown in Scheme 1 and we examine the energy effects associated with the non-bonded interactions occurring between these two fragments. These interactions are depicted in Fig. 2, while the results of the quantitative analysis are listed in Table 2 and 3.

We compare first the *trans* configuration with the *cis* at the geometry obtained through rigid rotation. The following points are of interest: (i) The overall energy effect associated with the non-bonded interactions ($\Sigma\Delta E$) is destabilizing and more destabilizing in the *cis* than in the *trans* geometry. The difference between the two destabilizing effects (12.31 kcal/mol) is of the same order of magnitude as the difference between the corresponding total energies and therefore, at this level, non-bonded interactions provide a satisfactory rationalization of the preferential stability of *trans* over *cis* diimide. (ii) The results of the quantitative analysis suggest that the dominant factor is the destabilizing interaction between the two σ_{NH} bond MOs: this interaction is, in fact, much more destabilizing in the *cis* than in the *trans* geometry, and the relative destabilization is much larger than that associated with the destabilizing interaction between the two σ lone pairs, which favors the *cis* geometry. The relative effect of the third destabilizing interaction, $\sigma_{\text{NH}} - n'_\sigma$ is small and favors the *trans* geometry. Also the energy effect associated with the stabilizing interactions is small: in particular that associated with the $\sigma_{\text{NH}} - \sigma_{\text{NH}}^*$ interaction is almost negligible, while that associated with the $n_\sigma - \sigma_{\text{NH}}^*$ interaction is more significant and favors the *cis*

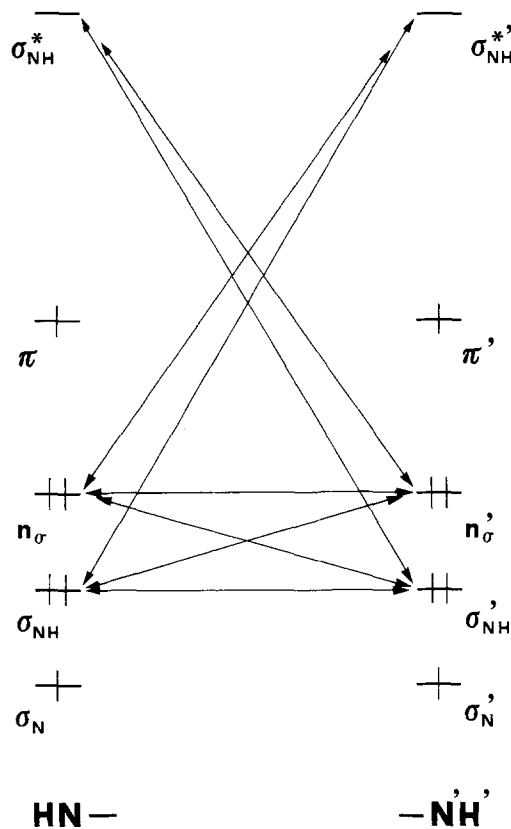


Fig. 2. Non-bonded orbital interactions occurring between two HN-fragments

geometry as previously suggested [1, 15]. However its effect is not large enough to change the trend dictated by the $\sigma_{\text{NH}} - \sigma'_{\text{NH}}$ interaction.

In Table 2 we have reported also the values of the electrostatic energies (E_{el}) associated with the interaction between the two HN-fragments, computed in

Table 2. Total energies^a with (E_{T}) and without (E_{T}^0) non-bonded interactions computed at the STO-3G level for *cis* and *trans* diimide, together with the electrostatic energy^b (E_{el}) between the two HN-fragments

	<i>cis</i>		<i>trans</i>	
	Rigid model	Optimized model	Rigid model	Optimized model
E_{T}	-108.54074	-108.54524	-108.55243	-108.55695
E_{T}^0	-108.65701	-108.64032	-108.65350	-108.69873
E_{el}^b	0.00270	0.00261	0.00154	0.00103

^a Values in a.u.

^b $E_{\text{el}} = \sum_{r < r'} q_r q_{r'} / R_{rr'}$, where q_r denotes the net atomic charge on atom r and $R_{rr'}$ the distance between atoms r and r' .

Table 3. Two-electron stabilization (ΔE_{ij}^2) and four-electron destabilization (ΔE_{ij}^4) energies^a associated with the non-bonded interactions in *cis* and *trans* diimide (see Fig. 2)

	<i>cis</i>		<i>trans</i>	
	Rigid model	Optimized model	Rigid model	Optimized model
$\Delta E_{\sigma_{\text{NH}}, \sigma_{\text{NH}}}^4$	31.95	18.39	7.10	5.71
$\Delta E_{n_{\sigma}, n_{\sigma}'}^4$	0.44	2.78	14.56	14.75
$\Delta E_{\sigma_{\text{NH}}, n_{\sigma}'}^4$	10.30	10.59	8.78	8.75
$\Delta E_{\sigma_{\text{NH}}, \sigma_{\text{NH}}}^2$	-0.45	-0.30	-1.62	-1.41
$\Delta E_{n_{\sigma}, \sigma_{\text{NH}}}^2$	-2.71	-3.75	-0.46	-0.39
$\Sigma \Delta E^b$	46.67	34.25	35.06	34.36
$\sum_i^{\text{occ}} n_i \varepsilon_i^c$	-34.2815	-34.2529	-34.1830	-34.2155

^a Values in kcal/mol.

^b $\Sigma \Delta E = \Delta E_{\sigma_{\text{NH}}, \sigma_{\text{NH}}}^4 + \Delta E_{n_{\sigma}, n_{\sigma}'}^4 + 2\Delta E_{\sigma_{\text{NH}}, n_{\sigma}'}^4 + 2\Delta E_{\sigma_{\text{NH}}, \sigma_{\text{NH}}}^2 + 2\Delta E_{n_{\sigma}, \sigma_{\text{NH}}}^2$.

^c Sum of the energies of the localized MOs of a HN-fragment (Values in a.u.).

terms of the atomic charges of the composite molecule obtained with the Mulliken analysis. The electrostatic energy computed in this way has just an indicative value. In the present case also this term favors the *trans* geometry, however its relative effect is small (~ 1 kcal/mol).

We have also estimated the importance of the energy effects associated with higher order mixings and found that they are negligible.

We proceed now to compare the results previously discussed with those obtained for the *cis* optimized geometry. The comparison shows that in the *cis* configuration the geometry tends to change in order to reduce the large destabilizing effect associated with the $\sigma_{\text{NH}} - \sigma_{\text{NH}}'$ interaction and to increase the stabilizing effect associated with the $n_{\sigma} - \sigma_{\text{NH}}^*$ interaction. This result is obtained mainly through an increase of the HNN angle [2] (from 105.3° to 111.5°) and of the N—H bond length [2] (from 1.061 Å to 1.064 Å). For the *cis* optimized geometry the overall energy effect is much less destabilizing than for the *cis* geometry obtained with rigid rotation of the *trans* geometry and becomes of the same order of magnitude as that obtained for the *trans* geometry. However this reduction of the destabilizing effect has been obtained at the expenses of a destabilization of the various fragment localized MOs, as suggested by the increase of the corresponding orbital energies which accompanies the geometry relaxation in the *cis* configuration (see the values of the term $\sum_i^{\text{occ}} n_i \varepsilon_i$ in Table 3, where ε_i are the energies of the various localized MOs and n_i their formal occupation numbers). Therefore, the variational optimization of the *cis* geometry causes a significant modification of the various energy effects, even if the final gain in total energy is quite small (~ 2.8 kcal/mol).

This interpretation is also supported by the total energy values computed in the absence of the non-bonded interactions listed in Table 2. It can be seen that in the

absence of the non-bonded interactions, the total energy value computed at *cis* geometry obtained with rigid rotation of the *trans* geometry is lower than that computed at *cis* optimized geometry. This trend is clearly indicative of a destabilization of the various fragment localized MOs in the optimized geometry.

We examine now the comparison in the opposite direction, i.e. we compare first the *cis* optimized configuration with the *trans* geometry obtained with rigid rotation of the *cis* geometry and then this *trans* with the *trans* at optimized geometry. The comparison shows that the overall energy effect is almost of the same order of magnitude in the three geometries under comparison. Therefore, in this case, even the trend in the rigid model does not agree well with the total energy behaviour. The comparison of the values of the term $\sum_i^{\text{occ}} n_i \epsilon_i$ shows also that in the *trans* configuration the geometry relaxation is accompanied by a stabilization of the various fragment localized MOs.

The present results show clearly the limitations of a quantitative PMO analysis based only on Eqs. (2) and (3). The discrepancies with the total energy behaviour are certainly due to the fact that a PMO approach of the type used here implies that the intrafragment matrix elements are not varied in the geometries under examination [16]. Therefore, the PMO results agree better with the total energy behaviour only when the latter condition is satisfied.

We have suggested here to improve the analysis using also the information provided by the term $\sum_i^{\text{occ}} n_i \epsilon_i$: the trend of this term should, in principle, provide information about the trend of the first order effects. However, the present results show that this term provides useful indications only when we compare two very similar geometries, such as the two *cis* or the two *trans*, but not the *cis* and the *trans*.

Therefore the quantitative PMO analysis presented here must be used with caution, since it does not seem to be able to rationalize quantitatively the *ab initio* SCF-MO results in all cases. Nevertheless, this type of analysis is certainly a useful instrument for a better understanding of structural problems, since it provides information about the various factors which determine the molecular structure.

The present results suggest that the best procedure is that where the starting point is the less crowded optimized geometry. Using this procedure, the rationalization of the preferential stability of the *trans* over the *cis* configuration of diimide depends on the model used. In a rigid model, where the *cis* geometry has been obtained through a rotation of the *trans* optimized geometry, the *trans-cis* energy difference is caused by second order energy effects associated with the non-bonded interactions. However, in an optimized model, the *trans-cis* energy difference is caused by destabilization of the orbital energies of the fragment localized MOs which accompanies the *cis* geometry relaxation. The two explanations are equivalent: however, the rationalization based on the rigid model is simpler to visualize and therefore seems preferable for a qualitative theory of structural problems.

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