

A Quantitative Analysis of the Importance of π -Non-bonded Interactions in Double Rotors

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The effects of the π interactions upon the methyl rotational barrier in double rotors $\text{CH}_3\text{-X-CH}_3$ is investigated in terms of a procedure which allows rotational barriers to be computed also in the absence of the π interactions under examination. It is found that when X is a π acceptor such as >C=O , the change in the methyl rotational barrier going from the single to the double rotor is controlled by the π non-bonded interactions. On the other hand, when X is a π donor such as >O , both π and σ conjugative interactions combine to give an increase in the rotational barrier.

THE object of this paper is to discuss quantitatively the effect of π -non-bonded interactions upon the methyl rotational barrier in double rotors. For those compounds which have been examined experimentally, it has been found that the dimethyl barriers differ, in some cases significantly, from the values in the corresponding monomethyl compounds. For instance, the dimethyl ether barrier ($2.72 \text{ kcal mol}^{-1}$)¹ is almost three times larger than that for methanol ($1.07 \text{ kcal mol}^{-1}$),² the value for isobutene ($2.21 \text{ kcal mol}^{-1}$)³ is larger than that for propene ($2.00 \text{ kcal mol}^{-1}$)⁴ and acetone has a smaller barrier ($0.78 \text{ kcal mol}^{-1}$)⁵ than acetaldehyde ($1.17 \text{ kcal mol}^{-1}$).⁶

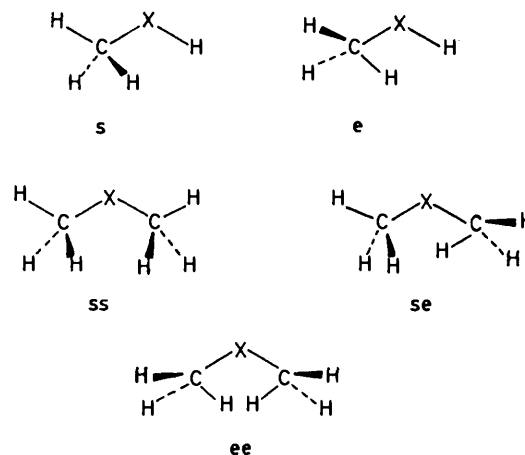
Pople and his co-workers⁷ have already investigated this problem using an *ab initio* SCF-MO approach at the 4-31G level and have found that the experimental results are satisfactorily reproduced. They have also rationalized their results by suggesting that the changes of the rotational barriers going from a single rotor $\text{CH}_3\text{-X-H}$ to the corresponding double rotor $\text{CH}_3\text{-X-CH}_3$ are controlled by π -non-bonded interactions which lead to aromatic stabilization when the central fragment X is a π -donor (as in dimethyl ether) and to an anti-aromatic destabilization when the central atom X is a π -acceptor (as in acetone).

Whangbo and Wolfe⁸ have recently carried out a quantitative molecular orbital analysis of the methyl rotational barriers in $(\text{CH}_3)_2\text{X}$ molecules. In their analysis they have computed the energy effects associated with the π -orbital interactions occurring between the fragments X and $(\text{CH}_3)_2$ or between the fragments CH_3X and CH_3 in terms of second-order perturbation expressions and in both cases they have compared the differences in the total orbital interaction energies of the ss and se conformations with the computed methyl rotational barriers.

We describe here a more reliable computational procedure for assessing the effect of π -non-bonded interactions in these species. We have recently shown that the procedure suggested by Wolfe *et al.*⁹ for carrying out quantitative orbital analyses can become more informative and provide more accurate results when the total energy of the system is computed in the absence of the π -interactions under examination.¹⁰ In the present paper

we show an application of the latter procedure by computing the methyl rotational barriers in double rotors with and without π -non-bonded interactions. The comparison of these values will clearly show the effect of these interactions upon the rotational barriers.

Computations.—The molecular species considered in this study are dimethyl ether, isobutene, and acetone as well as the related methyl derivatives methanol, propene, and acetaldehyde. The methyl derivatives have been considered in the staggered (s) and eclipsed (e) forms



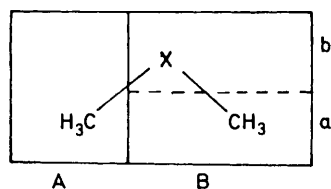
while for the dimethyl derivatives we have examined the three conformations ss, se, and ee.

In order to evaluate fully the effects of the π -orbital interactions, we have first optimized at the STO-3G level the geometries of these molecules in the various conformations, using a recently suggested procedure based on *ab initio* computations of the forces,¹¹ except for methanol where we have used the STO-3G fully optimized geometries computed by Pople *et al.*¹²

The quantitative orbital analyses have been carried out at both STO-3G^{13a} and 4-31G^{13b} levels for the various conformations. In all cases the 4-31G computations have been performed using the STO-3G geometries. For the dimethyl derivatives the orbital analysis will employ the dissection shown in Scheme 1.

The π -orbital interactions occurring in these molecules

have already been discussed in the literature.^{8,14} They are illustrated in Figure 1 for the case where X has just a lone pair of π symmetry and in Figure 2 for the case where X has a doubly occupied and a vacant MO of π -symmetry. It is useful to point out that in the situation of partial decoupling the π -interactions that are allowed



SCHEME 1

to occur in a double rotor are those occurring in the corresponding single rotor.

In order to obtain the various quantitative information required to assess the effects caused by the interactions occurring between the π -group MOs of the interacting fragments we have carried out the following calculations:¹⁵ (a) calculations with the procedure for quantitative analysis, where the π -interactions between the fragments A, B_a, and B_b are decoupled (complete decoupling); (b) calculations with the procedure for quantitative analysis, where only the π -interactions

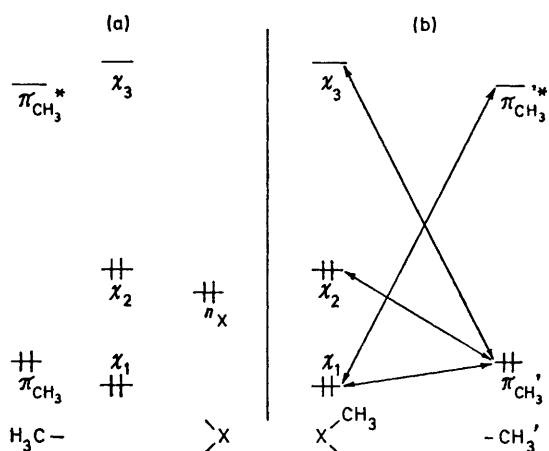


FIGURE 1 π -Orbital interactions occurring in a double rotor $\text{CH}_3\text{-X-CH}_3$, where the central fragment X has a lone pair of π -symmetry

between the fragments A and B are decoupled, but not those between the sub-fragments B_a and B_b (partial decoupling).

The results of the analysis with partial decoupling for the *se* conformation depend on the chosen dissection since the two methyl groups are not equivalent. In such cases we have carried out the analysis for both dissections (I) and (II) in Scheme 2.

In all cases we have computed the rotational barriers in three different situations illustrated in Scheme 3 where ΔE^0 denotes the rotational barrier computed in the absence of π -interactions (situation of complete decoupling), $\Delta E'$ denotes the rotational barrier computed in the presence of the π -interactions occurring between

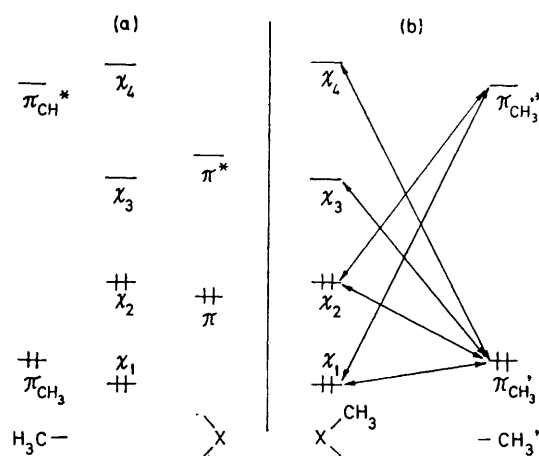
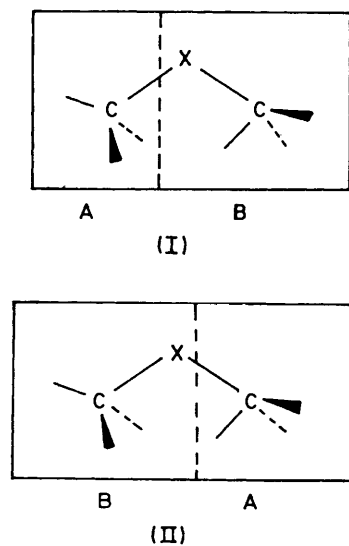


FIGURE 2 π -Orbital interactions occurring in a double rotor $\text{CH}_3\text{-X-CH}_3$, where the central fragment X has a doubly occupied and a vacant MO of π -symmetry

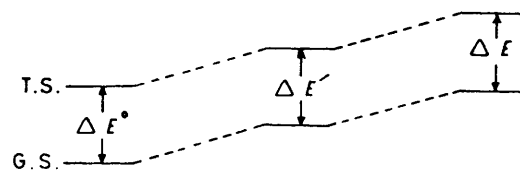
the rotating methyl group and the X fragment (situation of partial decoupling), and ΔE denotes the rotational barrier in the presence of all π -interactions. The experimental rotational barrier refers to the transformation *ss* \rightarrow *se*. However we have reported here also the values referring to the transformation *se* \rightarrow *ee*. The



SCHEME 2

computed rotational barriers are listed in Table 1 while Table 2 reports the overall effects associated with the π -interactions under examination.

The SCF rotational barriers for these molecules have already been discussed in the literature.⁷ The slight geometrical changes due to the full geometry optimiz-



SCHEME 3

ation used here do not alter the previous conclusions, the most important being that both computational levels reproduce satisfactorily the experimental trends, even if the rotational barriers at the 4-31G level seem, on average, more accurate.

The analysis of the computational results shows that (i) in all single rotors the overall π -effect is destabilizing, and less destabilizing in the staggered than in the eclipsed conformation. In all cases the methyl rota-

(except for the $se \rightarrow ee$ barrier in dimethyl ether at the 4-31G level) and larger than the corresponding value in the single rotors. The change is particularly large in the case of the $ss \rightarrow se$ barrier in dimethyl ether. (iv) In isobutene and acetone the effect of the π -interactions occurring between the rotating methyl group and the adjacent X fragment is similar to that in the corresponding single rotors and consequently the methyl rotational barrier in the absence of the π -interactions

TABLE I
Methyl rotational barriers (kcal mol⁻¹) in methyl and dimethyl derivatives with (ΔE) and without (ΔE^0 , complete decoupling and $\Delta E'$, partial decoupling) π -interactions

Compound	Transformation	Experimental	4-31G			STO-3G		
			ΔE	ΔE^0	$\Delta E'$	ΔE	ΔE^0	$\Delta E'$
Propene	s \rightarrow e	2.00	1.820	-0.226		1.537	0.119	
Isobutene	ss \rightarrow se	2.21	2.089	0.439	1.870	1.594	0.364	1.757
	se \rightarrow ee		2.598	0.377	1.989	1.958	0.370	1.876
Acetaldehyde	s \rightarrow e	1.17	1.017	-0.269		1.117	0.326	
Acetone	ss \rightarrow se	0.78	0.853	0.188	1.544	1.098	0.521	1.462
	se \rightarrow ee		1.544	0.289	1.675	1.619	0.690	1.682
Methanol	s \rightarrow e	1.07	1.205	0.094		2.014	1.136	
Dimethyl ether	ss \rightarrow se	2.72	2.297	1.456	1.199	2.874	2.121	2.636
	se \rightarrow ee		1.625	-0.464	0.276	2.679	1.261	2.284

tional barrier in the absence of the π -interactions becomes very small (in propene and acetaldehyde even slightly negative at the 4-31G level). Therefore the present results show that in the single rotors the π -interactions are the dominant factor for determining the magnitude of the methyl rotational barrier. (ii) In the double rotors the overall π -effect is again destabilizing and in all cases this destabilization follows the trend $ss < se < ee$. It is also observed that the overall π -effect is slightly larger than the value obtained by summing the effects of the two component single rotors. The difference

caused by the second methyl group, $\Delta E'$, is larger than the barrier in propene and acetaldehyde. A similar situation is observed also in dimethyl ether for the barrier corresponding to the $se \rightarrow ee$ transformation, while in the case of the $ss \rightarrow se$ transformation the effect of these π -interactions is much smaller. (v) The effect of the additional π -interactions caused by the second methyl group upon the $ss \rightarrow se$ barrier (compare $\Delta E'$ with ΔE) causes an increase of this barrier in isobutene and dimethyl ether, but a decrease in acetone. This effect arises from the fact that in isobutene and dimethyl ether the ss conformation is relatively more stabilized by these additional interactions, while in acetone the opposite trend is observed. The effect upon the $se \rightarrow ee$ barrier shows again the same trend, except for the $se \rightarrow se$ barrier computed at the STO-3G level in isobutene.

TABLE 2

Estimates of the overall π -effect (I_A^a) in single and double rotors

Compound	I_A (4-31G)			I_A (STO-3G)		
	s or ss	se	e or ee	s or ss	se	e or ee
Propene	22.52	24.56	12.18			13.60
Isobutene	47.76	49.41	51.63	24.72	25.95	27.54
Acetaldehyde	11.34		12.63	9.16		9.95
Acetone	24.59	25.26	26.51	18.54	19.11	20.04
Methanol	35.03		36.14	16.82		17.70
Dimethyl ether	71.48	72.02	74.11	33.94	34.69	36.11

^a $I_A = E_T - E_T^0$, where E_T denotes the total energy at the SCF level and E_T^0 the total energy computed with complete decoupling.

between the latter value and the corresponding overall π -effect shows that in all cases investigated here the se conformation is relatively less destabilized by the non-bonded π -interactions occurring between the two methyl groups than the ss and the ee conformations. Consequently in the double rotors the overall contribution of the π -non-bonded interactions to the rotational barrier is smaller than that in the corresponding single rotor in the $ss \rightarrow se$ transformation, and larger in the $se \rightarrow ee$ transformation. (iii) In all double rotors the methyl rotational barrier in the absence of π -interactions, ΔE^0 , is still significant

Conclusions.—The present results show that when the central fragment is a π -donor ($X = \text{>O}$), the π -non-bonded interactions due to the presence of the second methyl group actually cause an increase of the barrier of the related single rotor, and a decrease when the central fragment is a π -acceptor ($X = \text{>C=O}$), in agreement with previous qualitative rationalizations.⁷ The ethylene fragment >C=CH_2 behaves here as a weak π -donor at the 4-31G level, while at the STO-3G level again as a weak π -donor in the $se \rightarrow ee$ transformation and as a weak π -acceptor in the $ss \rightarrow se$ transformation.

The present results also show that the overall contribution of the π -interactions to the $ss \rightarrow se$ rotational barrier is smaller than that in the corresponding single rotor and also that the barrier in the absence of the π -interactions is still significant, particularly in dimethyl ether. These results suggest that the π -interactions are not the only important factor in the double rotors. It has recently been pointed out that in molecules of this

type σ -conjugative interactions can also occur and in the following we present a qualitative discussion of the effect of such interactions in these molecules, based on the ideas suggested in refs. 14 and 16. In the double rotors the key σ -interaction should be that between the doubly occupied in-plane C-H bond MO and the vacant X-C bond MO ($\sigma_{\text{CH}}-\sigma_{\text{XC}}^*$), while in the single rotors that between the double occupied C-H bond MO and the vacant X-H bond MO ($\sigma_{\text{CH}}-\sigma_{\text{XH}}^*$). There are indications that the stabilization energy associated with such interactions is larger when the two orbitals are arranged in an *anti*-periplanar manner compared with a *syn*-periplanar arrangement. It has also been suggested that the σ_{XC}^* MO is a better acceptor than the σ_{XH}^* MO and that the σ_{OC}^* MO is a better acceptor than the σ_{CC}^* MO. Consequently these interactions cause a preferential stabilization of the staggered conformation and the stabilization is larger in the double rotors because the σ_{XC}^* MO is a better acceptor than the σ_{XH}^* MO and because there are two such interactions. Furthermore this effect is small in isobutene and acetaldehyde where the σ_{CC}^* MO is involved but more significant in dimethyl ether where the better acceptor σ_{OC}^* MO is involved.

Therefore, when X = >C=CH_2 or >C=O the change in the methyl rotational barrier going from the single to the double rotor is mainly controlled by the π -non-bonded interactions and the contribution of the σ -conjugative interactions is small. However, when X = >O , both π - and σ -conjugative interactions combine to give an increase in the rotational barrier.

The present results show that the rationalization of structural problems improves significantly through the use of quantitative orbital analysis. In fact, even if the trends dictated by orbital symmetry can be identified at a qualitative level, in the majority of cases the magnitude of the related effects can be assessed with confidence only in terms of a quantitative analysis.

It is also worth pointing out that the information obtained with the present computational procedure at the minimal STO-3G and at the split-valence 4-31G levels agree very well. The results in Table 2 show that the magnitude of the overall effect associated with the π -interactions varies significantly with the basis set. However at the two computational levels the trend of these quantities remains the same and the related energy differences of the same order of magnitude.

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