On the Origin of the Rotational Barrier in Trimethylene

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A quantitative assessment of the barrier of rotation in singlet trimethylene is made by an energy partitioning analysis within the MINDO/2 approximation, including 3X3 configuration interaction between HOMO and LUMO. The dominating factors originate from (a) the non-bonding repulsion between 1,3-positioned atoms and (b) the weak attraction between the 1,5-positioned *cis*-hydrogens in the EE conformation. The energy difference between the EE and EF conformation is lowered by radical stabilizing substituents, such as a CH_3 group (attached to the carbon atom bearing one unpaired electron), because one of the unpaired electrons is stabilized in the EF conformation.

Introduction

An understanding of the mechanism in sigmatropic reactions is hindered by the imperfect knowledge of rotational barriers. Theoretic investigations have been limited thus far to the simplest representative, the trimethylene system. The initial extended Hückel (EH) calculations by Hoffmann [1] have been subjected to more accurate valence bond and *ab initio* studies by Hayes et al. [2], Goddard et al. [3], Salem et al. [4] and others [5]. In addition an *ab initio* study of the tetramethylene singlet biradical was recently reported by Segal [6].

Although all theoretical calculations on the trimethylene biradical confirm the original prediction of Hoffmann that **1** is energetically favoured over **2**, albeit to a lesser extent, the experimental results are diverging. Most experiments indicate a mechanism with competing double rotation and single rotation [7]. Only recently in a fascinating experiment Berson, Pedersen and Carpenter [8] have given strong support for the original Hoffmann prediction.

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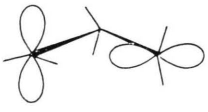

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In the following study factors which determine the rotational barrier in singlet trimethylene will be evaluated. Our analysis relies on the method of energy partitioning, which yields quantities interpretable in Ruedenberg's picture of the chemical bond [9]. In more detail the following points will be discussed:

(a) an analysis of the energy contributions, which determine the rotational barrier in singlet trimethylene;

(b) the importance of radical stabilizing substituents (on the rotational barrier).

Theoretical Procedure

Semiempirical SCF calculations were carried out using Dewar's MINDO/2 approximation [10]. In biradical structures the highest occupied MO (HOMO) and the lowest unoccupied MO (LUMO) are in close proximity to each other. This was accounted for by 3×3 variational configuration interaction between the two frontier MO's [11]. Configurations of higher order were not taken into consideration, since it has been shown recently [12] that this has no appreciable effect on the energy of biradicals of this type [13].

The computed total electronic energy was partitioned into one-center (E_{A}) and two-center (E_{AB}) energy contributions of atoms A and B, according to

$$E_{\text{total}} = \sum_{\mathrm{A}} E_{\mathrm{A}} + \sum\sum_{\mathrm{A} \neq \mathrm{B}} E_{\mathrm{AB}} \,. \tag{1.1}$$

For the 3×3 configuration interaction mixture the total energy is given by

$$\begin{aligned} E &= \langle c_1 \psi_1 + c_2 \psi_2 + c_3 \psi_3 \,|\, \tilde{H} \,|\, c_1 \psi_1 + c_2 \psi_2 + c_3 \psi_3 \rangle \\ &= c_1{}^2 \tilde{H}_{11} + c_2{}^2 \tilde{H}_{22} + c_3{}^2 \tilde{H}_{33} \\ &\quad + 2 c_1 c_2 \tilde{H}_{12} + 2 c_1 c_3 \tilde{H}_{13} + 2 c_2 c_3 \tilde{H}_{23} \,. \end{aligned} \tag{1.2}$$

Consequently the total electronic energy is given as sum over the state energies ($\tilde{H}_{11}, \tilde{H}_{22}, \tilde{H}_{33}$) and the mixing among these states ($\tilde{H}_{12}, \tilde{H}_{13}, \tilde{H}_{23}$). Since

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the quantities derived from the energy partitioning scheme depends on the parametrization chosen, we have compared only differences of energy quantities [14], which are less sensitive.

For the computation of the 3×3 CI matrix we started with a single excited configuration which was determined by the method of fractional electrons [15, 16]. We have written a computer program to carry out the energy partitioning within the 3×3 CI scheme [11c] which is available upon request.

Results and Discussion

a) Trimethylene. Our study begins with an analysis of the trimethylene biradical in its singlet ground state. Standard geometries [17] and total optimized geometries have been investigated. The numbering of atoms in relation to the different conformations is given in Figure 1.

The resulting bond lengths and bond angles together with the computed energy barriers are collected in Table 1.

Compared with the recent *ab initio* and VB studies the energy difference between the edge to edge (EE) **1** and edge to face (EF) **2** conformations is overestimated by the semiempirical calculations.

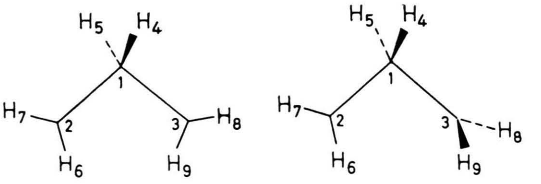


Fig. 1. Numbering of atoms in the different conformations of the trimethylene system.

Table 1. Geometries and relative energies for the different conformations in the trimethylene biradical.

Confor-mation	C_1C_2 (Å)	C_2C_3 (Å)	C_1H_4 (Å)
EE	1.456 (1.500) *	1.459 (1.500)	1.109 (1.093)
EF	1.443 (1.500)	1.476 (1.500)	1.111 (1.093)
	∢ $C_2C_1C_3$ (°)	∢ $H_4C_1H_5$ (°)	
EE	119.4 (120.0)	106.5 (110.0)	
EF	114.0 (120.0)	101.8 (110.0)	
EF−EE	4.9 (6.6) *	this work	
	1.0	ab initio STO-3G (3×3 CI)[4]	
	2.0	GVB[3]	
E (kcal per mole).			

* Values in brackets correspond to assumed geometries.

The energy difference is only slightly affected by the energy optimization of the geometries in **1** and **2**.

The difference of the total energy between the EE and the EF conformation, i.e. the rotational barrier, is written as the sum of the corresponding differences one one-center and two-center energies, in accordance with (1.1) to

$$\begin{aligned} \Delta E_{\text{total}} &= 0.21\ (0.28) \\ &= -\,0.06\ (0.01) + 0.28\ (0.27)\ (\text{eV})\,. \end{aligned}$$

The values in parenthesis correspond to the frozen model geometries. The destabilization of the EF conformation (in reference to the EE conformation) is merely due to a loss of two-center energies. This is in agreement with an energy analysis of the rotational barrier of ethane [14b], where in the optimized and frozen model geometries the two-center energy quantities determine the rotational barrier (the energy difference between staggered and eclipsed ethane).

The contributions ΔE_{AB} can be further partitioned into contributions arising from nearest neighbours (atoms A and B are bound) and non-nearest neighbours (atoms A and B are unbound).

$$\Delta E_{\text{AB}} = \Delta E^{12}_{\text{AB}} + \Delta E^{13}_{\text{AB}} + \Delta E^{14}_{\text{AB}} + \Delta E^{15}_{\text{AB}}\,.$$

The upper indices refer to the type of neighbour interaction between atoms A and B. In more detail, their meaning is as follows: E^{12}_{AB}, the atoms A and B are bound; E^{13}_{AB}, A and B are separated by (two) bonds (over 3 atoms), and so on. For the individual pairs of atoms the $\Delta E^{mn}_{\text{AB}}$ are collected in Table 2.

Since the energy quantities are always with reference to the most stable EE conformation, a positive term (Table 2) corresponds to a destabilization between A and B in the EF conformation.

The sum of the quantities $\Delta E^{12}_{\text{AB}}$ contribute only a small amount to the total energy difference between the two conformations. While the bonds C_1C_2 and C_1C_3 become weakened, this is offset by a simultanous strengthening of the bonds C_1H_4 and C_1H_5.

The main contributions to the rotational barrier arise from the nonbonded interactions. Most notable are the contributions from $\Delta E^{13}_{\text{AB}}$ and $\Delta E^{15}_{\text{AB}}$. They increase in magnitude from the EE to the EF conformation. In the latter the interaction between the atom pairs C_3H_4 and C_3H_5 is more repulsive.

Table 2. Differences of two-center energies for the individual pairs of atoms m and n between the energy optimized structures **2** and **1**. Energies ($E_{\mathrm{AB}}^{mn}(2) - E_{\mathrm{AB}}^{mn}(1)$) are in eV. In parenthesis are the values obtained for the frozen model geometries.

A	B	$\Delta E_{\mathrm{AB}}^{12}$	
1	2	0.24	(0.57)
1	3	0.34	(−0.02)
1	4	−0.24	(−0.22)
1	5	−0.26	(−0.22)
2	6	−0.04	(−0.03)
2	7	0.13	(0.06)
3	8	0.03	(0.05)
3	9	−0.12	(−0.11)
$\sum \Delta E$		0.08	(0.08)

A	B	$\Delta E_{\mathrm{AB}}^{13}$	
1	6	0.00	(−0.02)
1	7	−0.01	(−0.01)
1	8	−0.01	(0.01)
1	9	0.00	(0.01)
2	3	−0.37	(−0.29)
2	4	0.04	(0.01)
2	5	0.04	(0.01)
3	4	0.21	(0.17)
3	5	0.23	(0.17)
6	7	−0.01	(0.00)
4	5	0.01	(0.06)
8	9	0.01	(0.01)
$\sum \Delta E$		0.13	(0.13)

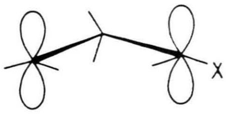
A	B	$\Delta E_{\mathrm{AB}}^{14}$	
2	8	0.06	(0.05)
2	9	−0.09	(−0.09)
3	6	−0.03	(−0.02)
3	7	−0.03	(−0.02)
4	7	0.01	(0.01)
4	6	0.00	(0.00)
5	6	0.00	(0.00)
5	7	0.01	(0.01)
4	8	−0.09	(−0.08)
4	9	0.11	(0.09)
5	8	0.02	(0.01)
5	9	0.00	(−0.01)
$\sum \Delta E$		−0.03	(−0.04)

A	B	$\Delta E_{\mathrm{AB}}^{15}$	
6	8	0.00	(0.00)
6	9	0.09	(0.10)
7	8	0.00	(0.00)
7	9	0.00	(0.00)
$\sum \Delta E$		0.10	(0.10)

In addition the *cis*-standing hydrogens H_6 and H_9 attract each other weakly in **1**. This can be attributed to a general symmetry property of the MO's [18]; hence it should be independent of the parametrization of the semiempirical SCF method. The attraction is lost in the EF conformation.

The trends of the two-center energies in the optimized geometries parallel those in the frozen model geometries. In the optimized geometries the quantities $\Delta E_{23}^{13} + \Delta E_{35}^{13} + \Delta E_{34}^{13} + \Delta E_{69}^{15}$ amount to 3.8 kcal per mole. Thus they constitute about 80% of the total barrier.

b) Radical stabilizing substituents. Because the isomerization mechanism of cyclopropane depends on substituents, it seems desirable to give an interpretation for this. An energy partitioning analysis for the optimized geometries in the EE and EF conformations of **3** and **4** has been carried out. Only the results for the rotation around the bond C_1C_2 will be reported, because an analysis of bond rotation around C_1C_3 reveals the same trend.



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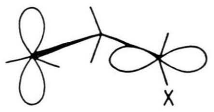

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X = CH_3

For the least steric hindered conformations an energy difference of 3.4 kcal per mole results (in favour of **3**). Performing an energy analysis as before for $E_{\mathrm{EF}} - E_{\mathrm{EE}}$, in accordance with (1.1) this yields:

$$\Delta E = 0.15 = -0.07 + 0.22\,(\mathrm{eV})\,.$$

As before the barrier is determined by the difference in two-center energy contributions.

The sum of contributions arising from the bonded ($m = 1$, $n = 2$) and nonbonded pair of atoms ($m = 1$, $n = 3$ to 6) are:

$$\Delta E_{\mathrm{AB}}^{12} = 0.20\,, \quad \Delta E_{\mathrm{AB}}^{15} = 0.13\,,$$
$$\Delta E_{\mathrm{AB}}^{13} = -0.04\,, \quad \Delta E_{\mathrm{AB}}^{16} = 0.01\ \mathrm{eV}\,.$$
$$\Delta E_{\mathrm{AB}}^{14} = -0.07\,,$$

Thus, contrary to unsubstituted trimethylene the change in contributions from bonded atom pairs contribute considerably to the difference between the EE and EF conformation.

A further analysis, not be recorded in detail indicates, that the change in E_{AB}^{12} is totally due to an increase of two-center energy E_{AB}^{12} in the CH_3 group in the EF conformation. On this basis the reduction of the overall energy barrier can be attributed to an enhanced hyperconjugative stabilization of the EF conformation by methyl substitution.

Conclusions

We have presented an analysis within the energy partitioning scheme for the rotational barrier in the singlet trimethylene biradical. The results of our investigations are summarized as follows:

(1) The main contributions to the rotational barrier in trimethylene arise from four atomic pair contributions. All of them are nonbonding in nature. The diminished repulsive interaction between C_1 and C_3 is opposed by increased repulsion between the atom pairs C_3H_4 and C_3H_5. In addition, in the EE conformation the hydrogens H_6 and H_9 are slightly attractive.

(2) The two-center energies of bonded atoms ($m = 1$, $n = 2$) do not contribute to the overall barrier. Increasing two-center energies between the CC-bonds (C_1C_2 and C_1C_3) is offset by decreasing two-center energies between the atom pairs C_1H_4 and C_1H_5.

(3) Radical stabilizing substituents such as a CH_3 group, attached to atom C_3 (or C_2), lower the rotational barrier in trimethylene. This is due to an increased hyperconjugative interaction (increased two-center energies) with the methyl group in the EF conformation. Therefore our considerations reveal that the disparity in the experimental interpretation of the mechanism for the isomerization of cylcopropane might be attributed in part to electronic effects [19].

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