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Ab initio Calculations of the Potential Energy Surface of the Reaction of Singlet Methylene with the Hydrogen Molecule

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The potential energy surface for the insertion of singlet methylene into H_2 has been computed on the *ab initio* SCF level as well as with inclusion of electron correlation by means of the CEPA method. The results are compared with those of previous semiempirical, *ab initio* SCF and CI calculations. The system is a prototype of a reaction where an allowed and a symmetry-forbidden path can compete. The electron correlation energy was found to be very different for different regions of the surface, but did not have much influence on the optimum reaction path. From the computed heat of the reaction, the heat of formation of singlet methylene was estimated to be 101.5 kcal/mol. According to the calculations the reaction does not need any activation energy.

Key words: Methylene, reaction of singlet ~ with H_2

1. Introduction

The reaction

$$CH_2(^1A_1) + H_2(^1\Sigma_g^+) \rightarrow CH_4(^1A_1) \qquad (1)$$

of singlet methylene with molecular hydrogen to methane can be regarded as a prototype for insertion reactions of singlet methylene into single bonds, e.g. CH bonds. The system (1) is small enough to allow for rather reliable quantum chemical calculations of its potential energy surface, therefore it has been studied in recent years very intensively with different theoretical methods.

Today, there is no doubt about the mechanism of the insertion of singlet methylene into H_2 or CH bonds. It is a direct insertion with an intermediate three-center bond, as probably first discussed by Chanmugam and Burton [1] and Skell and Woodworth [2] (compare also [3]). Such a mechanism has been supported by the

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extended Hückel calculations of Dobson *et al.* [4] and the MINDO/2 studies of Bodor *et al.* [5], both for the reaction of singlet methylene with methane. The first detailed theoretical study of the potential energy surface (PES) of the reaction (1) has been performed by one of the present authors [6] using a modified CNDO procedure.

All these semiempirical calculations lead to the conclusion that the singlet methylene insertion is a non-least-motion process in which two steps can be easily distinguished: 1) An *electrophilic* step in which the empty p-orbital of singlet methylene interacts with the bonding orbital of H_2 or CH, respectively, by forming a three-center bond (optimum $\alpha = 90°$ in Fig. 1).

2) A *nucleophilic* step with the interaction of the lone-pair orbital of methylene with the antibonding σ^*-orbital of H_2. In this step the H–H bond length increases and simultaneously the H_2 subunit rotates from the original position at $\alpha = 90°$ to the final CH_4 structure with $\alpha = 180°$. For a more detailed discussion compare Ref. [6].

These conclusions have been confirmed later on by *ab initio* calculations: Cremaschi and Simonetta [7] using minimum basis set SCF obtained nearly the same activation energy (5.8 kcal/mol) for the electrophilic step as did Kollmar [6] (5 kcal/mol). But by increasing the basis size and by including correlation effects [8, 9] the activation energy disappears.

On the other hand, the least motion pathway of reaction (1)–i.e., maintaining C_{2v} symmetry and fixing α at 180° throughout the reaction–has to pass over a rather high barrier, since this way is forbidden by orbital symmetry [10, 11]. The barrier height has been determined in minimum basis SCF calculations to be in the order of 50 kcal/mol [7, 12]; much more reliable are the CI calculations of Bauschlicher *et al.* [11] who find a value of 26.7 kcal/mol.

Reaction (1) is a prototype for reactions were a symmetry-forbidden and an "allowed" path of low symmetry can compete. SCF calculations will necessarily yield too high energies along the forbidden path. *A priori*, it is not obvious whether the inclusion of electron correlation will only reduce the energy difference between

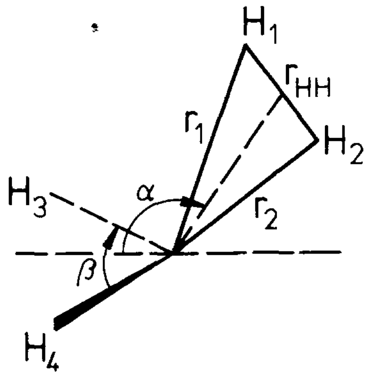

Fig. 1. Geometrical parameters used in the calculation of the potential surface of $CH_2 + H_2 \rightarrow CH_4$

the allowed and the forbidden path or whether correlation will change the qualitative picture of the potential energy surface by shifting the minimum energy path from its SCF position toward the forbidden path. In the case of reaction (1) the question is whether the two phases of the reaction can still be clearly distinguished even when electron correlation is included. We performed *ab initio* SCF and CEPA calculations for the relevant part of the potential surface which includes the whole reaction path. Our study is essentially complementary to the CI calculations of Bauschlicher *et al.* [9] which appeared after our calculations were completed. These authors studied only the electrophilic phase of the reaction in detail and used a double zeta basis set only.

2. Method of Calculation

Basis sets of contracted Gaussian lobe functions have been used throughout this paper. Most of the points have been calculated with a 7.3/3 Huzinaga basis set [13, 14]–i.e. 7*s* and 3*p* functions on the C atom, 3*s* functions on the H atoms–contracted to double zeta quality (DZ basis). In order to check the reliability of this rather small basis set and to explore some parts of the potential surface more thoroughly we also did some calculations with a more extended basis set consisting of a 9.5/5 Huzinaga basis contracted to triple zeta quality and augmented by a set of *d*-functions ($\eta_d = 0.7$) on C and a set of *p*-functions ($\eta_p = 0.75$) on the hydrogens (TZP-basis). The construction of *p*- and *d*-functions from Gaussian lobes and the calculation of integrals followed the rules given by Ahlrichs and Driessler [15, 16].

All the SCF calculations were performed using a conventional Roothaan-type closed shell SCF program. Electron correlation was taken care of using the "coupled electron pair approach" (CEPA) as developed by Meyer [17, 18] and by Ahlrichs *et al.* [19, 20]. This approach amounts to a configuration interaction (CI) calculation including all doubly substituted configurations plus an estimate of the contributions of the unlinked cluster quadrupole and higher substitutions. In addition, a PNO-CI energy was computed which only includes the double substitutions. The PNO-CI total energy has the advantage of representing an upper bound for the total energy, but it does not show the correct dependence on the number of particles [19].

The present CEPA scheme is going to fail for regions on the PES, where the wavefunctions cannot be reasonably approximated by one leading determinant [21]. The ratio of the PNO-CI and the CEPA correlation energies can be used as an internal check for the reliability of a CEPA calculation. This ratio was above 0.85 for all points considered in this paper. That means, the system (1) remains of closed-shell type along the optimum reaction path.

The CEPA calculations were performed in the basis of localized orbitals. While in the TZP basis all valence electron pairs were included, the electron pairs involving only the localized CH bond orbitals of the CH_2 subunit were omitted in the DZ calculations, since these pairs are not expected to vary considerably along the reaction path.

3. Overall Properties of the PES for Reaction (1)

The system CH_2 + H_2 has 9 internal degrees of freedom, 5 of which appear to be of importance for reaction (1): r_1, r_2, r_{HH}, α, and β. (The definition of these coordinates is given in Fig. 1.)

C_s symmetry was imposed. The methylene C–H bond lengths are very similar in singlet CH_2 (1.11 Å [22]) and methane (1.085 Å [23]); they were fixed in our calculations at 1.10 Å. In order to enable a two-dimensional plot exhibiting the most characteristic features of the PES we fixed the methylene angle β at 107°, restricted r_2 to be equal to r_1, and optimized α for each point r_1, r_{HH}. (The optimization of α was done in the SCF approximation; some test calculations showed that correlation changes the optimal α by not more than 1°.) These two-dimensional plots of the PES for reaction (1) are presented in Figs. 2 and 3.

One first observes the close similarity between the SCF and CEPA surfaces. Though there are minor deviations, particularly in the region $r_1 \approx 1.5$ Å, $r_{HH} \approx 0.8$ Å, the essential features of the two surfaces are the same:

1) One can clearly distinguish two phases along the minimum energy path: The approach of H_2 along the entrance valley with r_{HH} close to its equilibrium value of 0.74 Å as long as $r_1 > 1.5$ Å, followed by a rather sudden increase of the H–H distance and a very abrupt descendence into the CH_4 hole. Only a small amount of energy is gained during the first (electrophilic) phase of the reaction where a three-center bond is formed. At $r_1 = r_2 = 1.8$ Å the SCF energy is about 0.8 kcal/mol above the energy of the components, while inclusion of correlation

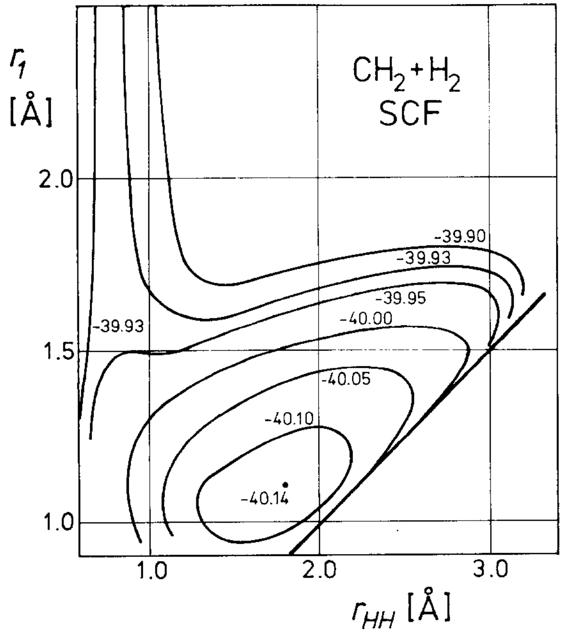

Fig. 2. The Potential Energy Surface of the reaction CH_2 + H_2 calculated with SCF

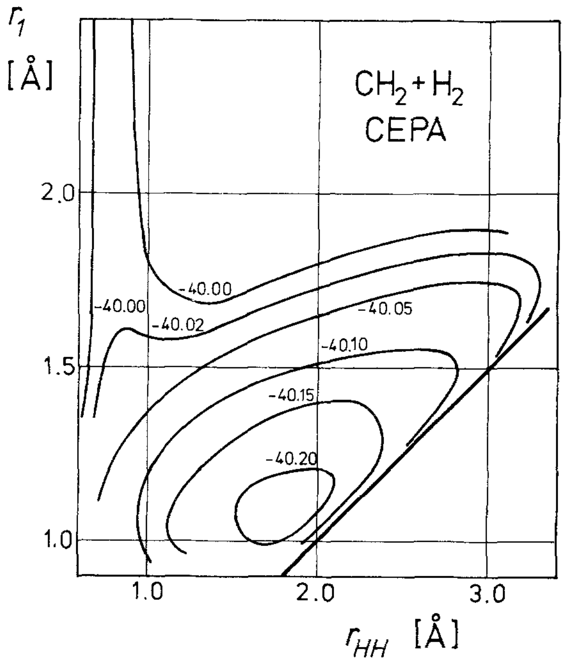

Fig. 3. The Potential Energy Surface of the reaction $CH_2 + H_2$ calculated with CEPA

gives a binding energy of 3 and 7 kcal/mol for the DZ and the TZP basis, respectively. The three-center bond essentially has the role of compensating the repulsion of the components, such that the H_2 can approach close enough to enable the second (nucleophilic) phase of the reaction during which most of the large reaction energy is gained.

The second phase of the reaction is accompanied by a rather sudden rotation of the H_2 group into its final position as can be seen from Table 1. The optimized α changes from the initial value close to 90° to the final value of 180° in a rather small interval of the order of 0.2 Å both for r_1 and r_{HH}. (It has to be noted that in this intermediate region the energy varies very little over a considerable range of α. However, there seems to be no double minimum behavior for α.)

Table 1. Optimum of angle α for different values of r_1 and of r_{HH} (within the restriction $r_1 = r_2$; angle in degree, distances in Å)

r_{HH} \ r_1	1.40	1.50	1.60	1.80
0.70	104	98	95	88
0.80	108	100	96	90
1.00	123	108	102	91
1.20	180	129	106	94
1.40		180	134	100
1.60			180	113
1.70				123
2.00				180

2) Conversely, if one starts from the product CH_4, the path along the smallest gradient would lead to the forbidden least motion path. This is more clearly shown in Fig. 4 presenting cuts through the PES for different r_1 values. For $r_1 > 1.5$ Å both in SCF and CEPA approximation one has double minimum curves, and it is the higher minimum which eventually leads to $CH_2 + H_2$. The very same behavior has been found in the semiempirical calculations [6]. Fig. 2 and 3 of Ref. [6] can be compared directly with our Figs. 2–4 since the coordinates and restrictions are the same in the present study as they were in the previous semiempirical work. The comparison shows, that the mod. CNDO procedure, though giving a very satisfactory overall description of the reaction surface, seems to overestimate the energy gain connected with the formation of the three center bond during the electrophilic phase of reaction. Thus, the double minimum (Fig. 4) appears in the semiempirical work even for considerably smaller r_1 values than in the present calculations.

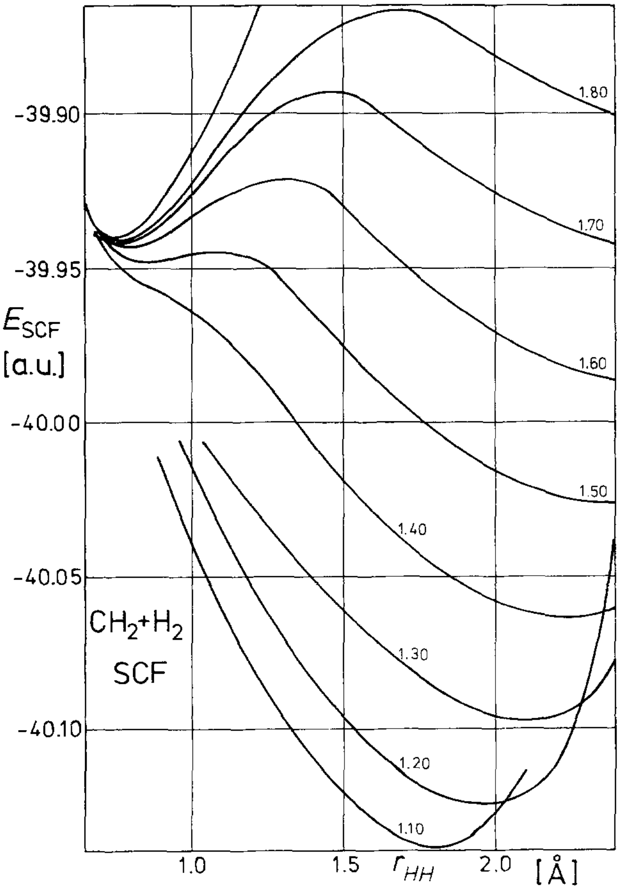

Fig. 4. Total SCF energy in dependence of the two variables r_1 and r_{HH}

3) In agreement with the recent CI calculations [8, 9] we find no barrier at all for the approach of H_2 to CH_2.

4. Details of the PES

In addition to the overall features of the PES for reaction (1) as presented in the previous section we have studied some properties of the PES in more detail:

a) Optimization of the methylene angle β.

It has been observed in the semiempirical study [6] that the methylene angle β changes during the reaction. The *ab initio* calculation of Bauschlicher *et al.* [9] as well as the calculation of Zurawski and Kutzelnigg [24] on the addition of singlet methylene to ethylene have shown that β goes through a maximum though its initial value in methylene (102.4°) and its final value in methane (109°28′) are rather similar. The maximum of β is as high as about 130° and occurs in the same (r_1, r_{HH}) region where the rotation from $\alpha = 90°$ to $\alpha = 180°$ takes place (Table 2). The increase of β is simply the consequence of the orthogonality of the four hybrid orbitals at the carbon atom [25].

It has to be noted that this effect is described very well in SCF approximation and is not changed by correlation.

b) Release of the restriction $r_1 = r_2$.

The restriction $r_1 = r_2$ may seem to be a very severe one, particularly since it does not allow the dissociation to $CH_3 + H$ by forcing the two hydrogen atoms into the

Table 2. Optimized values for the methylene angle β

			β_{opt}		
$r_1 = r_2$ (Å)	r_{HH}(Å)	α	SCF	CEPA	ΔE[a] (10^{-4} a.u.)
∞	0.7	–	104.8	103.8	2.5
1.8	0.8	90	107.3	106.5	0.0
	1.2	104	114.0	115.0	13
	1.7	118	128.0	129.3	108
	1.69	180	137.3	131.5	118
	2.07	180	129.6	127.6	90
	2.95	180	120.3	120.3	41
1.4	0.8	101	114.0	114.4	2
	1.0	116	122.7	123.7	60
	1.18	180	131.0	130.1	120
	1.61	180	122.8	122.8	60
	1.98	180	117.8	118.0	31
	2.294	180	113.9	114.1	13
	2.705	180	105.8	106.5	0
1.1	1.26	180	117.9	118.3	34

[a] Gain in energy by optimization of β with respect to $\beta = 107°$ (CEPA values).

same distance to the C atom. In order to check how much our results are affected by this restriction we optimized r_1 and r_2 separately in the vicinity of the optimal reaction path, i.e. along the entrance valley in the left parts of Figs. 2 and 3.

The results for some points are given in Table 3. We find that the hydrogen atom H_2 (compare Fig. 1) is closer to the C atom than H_1, the difference $r_1 - r_2$ being slightly larger in CEPA than in the SCF approximation. The energy gain as well as $r_1 - r_2$ increase with increasing r_{HH}. Thus, without the restriction $r_1 = r_2$, the maxima in Fig. 4 would be lower (and even vanish for some smaller $\frac{1}{2}(r_1 + r_2)$ values) and the valley along the optimum reaction path would be somewhat broader. For very large H–H distances (second minima in Fig. 4) $r_1 = r_2$ is the optimum. Again, it is quite easy to understand why H_2 wants to come closer to the C-atom than H_1. The interaction between the HOMO of H_2 and the LUMO of CH_2 leads to $r_1 = r_2$, whereas the interaction of the LUMO of H_2 with the HOMO of CH_2 favors $r_1 > r_2$ since the overlap with the $3a_1$ hybrid of CH_2 dominates this interaction.

For $\frac{1}{2}(r_1 + r_2) \geqslant 1.6$ and rather large r_{HH}, however, we expect the difference $r_1 - r_2$ to become large, in particular when correlation is included, since this corresponds to the path $^1CH_2 + H_2 \rightarrow CH_3 + H$. Assuming a dissociation energy of about 110 kcal/mol = 0.1752 a.u. for the $CH_4 \rightarrow CH_3 + H$ dissociation the total energy for $CH_3 + H$ should be −40.039 a.u. (7.3/3 basis, CEPA), i.e. lower than the region of the PES which is represented in the upper right part of Figs. 2–4. While releasing the restriction $r_1 = r_2$ did not change the general features of the PES in the region of the optimum reaction path, it would open up a second valley when correlation is included in the upper right of Fig. 3. This second valley would correspond to the path to (and from) $CH_3 + H$, a reaction which is of minor interest for the present study.

Table 3. Optimum of $r_1 - r_2$ in dependence of $\frac{1}{2}(r_1 + r_2)$ and of r_{HH} (Lengths in Å, energies in 10^{-4} a.u.)

		SCF		CEPA	
$\frac{1}{2}(r_1 + r_2)$	r_{HH}	$r_1 - r_2$	ΔE^a	$r_1 - r_2$	ΔE^a
2.0	0.77	0.11	11	0.16	20
1.8	0.80	0.22	19	0.28	28
1.8	1.20	0.60	133	0.78	247
1.6	0.80	0.24	44	0.30	53
1.6	1.00	0.36	84	0.48	135
1.6	1.20	0.50	107	0.60	221
1.6	1.60	0.00	0	0.00	0
1.4	0.80	0.18	43	0.22	61
1.4	1.00	0.28	79	0.33	109
1.4	1.40	0.00	0	0.00	0

[a] Energy gain by releasing the restriction $r_1 = r_2$.

Since our explanations of the behavior of β and of $r_1 - r_2$ has been essentially based on one-electron arguments, the mod. CNDO calculation of Ref. [6] reproduces the same general trends for these variables as found in our SCF calculations.

c) Activation energy and heat of reaction.

Finally, we performed a series of calculations with the TZP basis set in order to check how reliable the results of the DZ basis are, to get quantitatively correct results for the exothermicity of (1), and to investigate the existence of an activation energy. These calculations were done both in SCF and CEPA approximations, the results are presented in Table 4, where the corresponding figures for the DZ basis set are also included.

As far as the reaction energy ΔE is concerned, there are considerable differences between the two basis sets and between SCF and CEPA treatments. The increase of the basis size changes ΔE by up to 10 kcal/mol rendering the attractive parts more attractive, the repulsive parts more repulsive, but the overall view of the PES remains unchanged. Inclusion of correlation has an effect of about the same size, i.e. up to 10 kcal/mol, except for those points in the repulsive region where r_1 and r_{HH} are large, i.e. where the H_2 molecule dissociates before the new C–H bonds are formed.

The experimental exothermicity of reaction (1) is estimated as follows:

Heat of formation of $CH_2(^1A_1)$	101.7 ± 0.5 kcal/mol [26]
Heat of formation of CH_4	16.0 ± 0.1 kcal/mol [27]
Difference in zero-point vibration	11.2 ± 0.4 kcal/mol
	129 ± 1 kcal/mol

Table 4. Comparison of the two basis sets for different points on the potential energy surface[a]. Energies in kcal/mol relative to $CH_2 + H_2$[b]

			SCF		CEPA	
r_1(Å)	r_{HH}(Å)	α	DZ	TZP	DZ	TZP
∞	0.74	—	0	0	0	0
2.2	0.75	90	−0.3	−0.4	−1.8	−2.3
1.8	0.80	90	+0.8	+0.8	−2.9	−6.7
1.8	1.69	180	56.5	63.2	17.1	28.9
1.8	2.95	180	22.8	32.1	−8.2	+4.6
1.5	0.80	100	−1.8	−8.2	−8.8	−17.8
1.5	1.10	122	2.8	−0.3	−11.7	−16.8
1.5	2.46	180	−50.2	−43.4	−68.0	−61.1
1.1[c]	1.80	180	−122.6	−118.5	−128.2	−128.5

[a] $r_1 = r_2$, $\beta = 107°$.

[b] Total energies of $CH_2 + H_2$ (in a.u.): −39.9439 (DZ, SCF); −40.0196 (TZP, SCF); −40.0097 (DZ, CEPA); −40.1931 (TZP, CEPA).

[c] Structure of methane.

The difference in the zero point energies of CH_4 and $^1CH_2 + H_2$ was estimated in the following way: sum of the harmonic frequencies of methane [28]: 19816 cm^{-1}; sum of the harmonic frequencies of $^1CH_2$ [29, 30] (7500 cm^{-1}) and H_2 (4405 cm^{-1}): 11905 cm^{-1}. The resulting value of 3956 $cm^{-1} \triangleq$ 11.3 kcal/mol has to be reduced by 1–2% to allow for the anharmonic corrections to the zero point energies.

Conversely, the calculated heat of reaction can be used for an estimate for the heat of formation of singlet methylene. For that purpose we performed a calculation for the singlet methylene ($\beta = 103°$ [22]) with an even more extended basis, based on a 9.5/5 Huzinaga basis, containing two sets of d functions and one set of f functions at the carbon atom and two sets of p functions at the hydrogens (=standard basis of Ref. [20]). Using the total energy of CH_4 given in Ref. [20] we obtain a heat of the reaction of $CH_2 + H_2$ of 128.7 kcal/mol with CEPA (117.8 kcal/mol in SCF)

ΔH_f^0 of CH_4	–16.0 kcal/mol
Difference in zero-point vibration	–11.2 kcal/mol
ΔE	128.7 kcal/mol
ΔH_f^0 of CH_2	101.5 kcal/mol

This value is in very good agreement with the experimental value given above.

We do not find an activation energy for the reaction. There seems to be a general trend that the slope of the reaction coordinate in the entrance valley becomes steeper when the basis size is increased and correlation is included. But one has to take into account that basis set unsaturation errors can lead to erroneous conclusions. We have checked how much these effects influence the interaction energy in the region where the activation barrier could be situated by performing calculations for $CH_2 + H_2$ and for CH_2 and H_2 with the full TZP basis set at $r_1 = r_2 = 2.2$ Å, $r_{HH} = 0.75$ Å. The unsaturation errors were 0.0003 a.u. = 0.2 kcal/mol in SCF, 0.0024 a.u. = 1.5 kcal/mol in CEPA approach. This is approximately one half of the total "interaction" energy at this geometry. Our conclusion that no barrier exists remains true, but the small values of ΔE in Table 4 should be taken with care.

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