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Influence of electronic structure of (R)-4-menten-3-one on its restricted rotation and inversion

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Abstract: In this work we was study correlation between electronic structure of (R)-4-menthen-3-one and restricted transitions between its conformers. By NBO analysis, carried out in ab inition methods, we found special orbital interactions and sterical effects in conformers of (R)-4-menthen-3-one, which explained difficults of inversion and rotation. Restrictions of inversion and rotation are linked with steric hindrances arising between CH_3- fragments in i-Pr group and double bonds of enone fragment. Unique orbital and spatial structure of existing preferred conformer well explains unusual reactivity of (R)-4-menten-3-one one vs. conventional enone systems. We found that stable conformer has less electrondeficitic $\pi_{C=C}$ bond, because of less donor transfers from this bond, as result (R)-4-menten-3-one is more reactive in the 1,2- and 1,4- nucleophilic addition reactions.

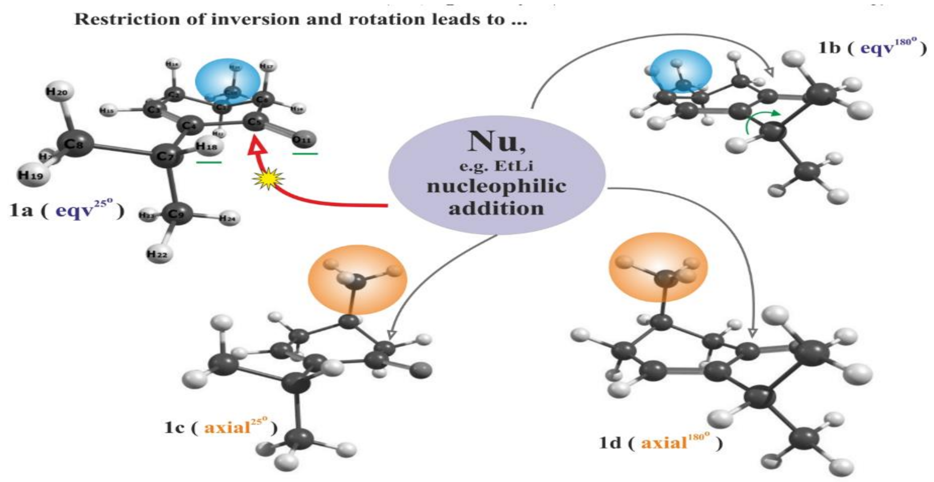
Keywords:Terpenoids, configuration determination, NBO, B3LYP/6-311++G(2d,p), MP2/6-311++G(d,p).

Highlights

1) Prefer position of methyl group in (*R*)-4-menthen-3-one is equatorial.

2) Most stable conformer of (*R*)-4-menthen-3-one methyl radicals of the i-Pr group are oriented to C=C double bond.

Graphical abstracts



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1. Introduction

In our previous work [1] we have shown, that uncharacteristic reactivity of (R)-4-menthen-3-one vs. ordinary enone systems [2, 3] can be explained by predominant content of one conformer. Also our calculation data shown that i-Pr group rotation and inversion of cycle in (R)-4-menthen-3-one is restricted [1]. It's unusually, because the same restrictions in other monoterpenoids with similar structure (figure 1) not found [2]. Another unusual fact is increasing of noted restrictions with temperature growing. This fact followed from experimental found increase of stereoselectivity of 1,4-nuclophilic addition to (R)-4-menthen-3-one with temperature growing [4-6].

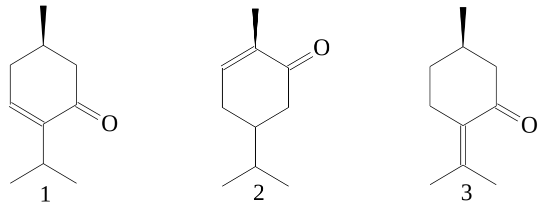


Figure 1. Structure (R)-4-menthen-3-one (**1**), (R)-(−)-carvone (**2**), (R)-(+)-pulegone (**3**)

Taking into account this interesting facts we believe (R)-4-menthen-3-one is not only useful and important compound for the synthesis of a wide range of pheromones [7-19] and chiral synthons [8, 12, 20], but interesting object, which can help to investigate correlation between electronic structure and internal rotation and inversion.

Obviously, calculation of thermodynamics properties, determining the conformers ratio and its dependence of solvent type [1], can't explained restricted rotation and inversion in (*R*)-4-menthen-3-one. Therefore, in this paper we presented results of analysis of (*R*)-4-menthen-3-one electronic structure by modern accuracy method NBO 5.0 [21].

2. Computational Method

Quantum chemical computations were carried out using the "Firefly 8.1.1" [22] software. Final structures are calculated by technology of consecutive approach. In this technology the final equilibrium geometry is in result of a number of consecutive calculations with increasing complexity of approximation. Current calculation on each step also uses approximate Hessian matrix from previous calculation. This technology allows to lower calculation time in 3 and more times. Applicability of such approach for calculation of middle and big molecules has been shown in works [23-25]. In this work we used optimal for speed series {B3LYP/6-311++G(2d, p) / B3LYP/6-31G(d, p) / RHF/3-21G / AM1+Hessian} and {MP2/6-31G(d, p) / MP2(fc)/6-31G(d, p) / RHF/3-21G / AM1+Hessian}. Post-SCF calculation of ZPVE and free Gibbs energy were performed using G4(MP2) [26], B3LYP/6-311++G(2d,p) [27-29] and MP2/6-311++G(d,p) [30]. For G4(MP2) calculations Gaussian-W03 was used [31]. Visualization of molecules and orbitals was performed in ChemCraft software [32].

NBO analysis [33, 34] was carried out by B3LYP/6-311++G(2d,p) and MP2/6-311++G(d,p) methods, because orbital analysis based on this ab initio approaches demonstrate good accuracy [35, 36]. We used NBO calculations with next selected parameters for NBO: NRT ARCHIVE NLMO NRTFDM E2PERT=0.5.

Stabilizations and destabilizations factors were defined based on next interactions:

- second order orbitals perturbations in table "SECOND ORDER PERTURBATION THEORY ANALYSIS"
- steric coupling between atoms (table «NBO/NLMO STERIC ANALYSIS) and pairs of bonds (table «Pairwise steric exchange energies»).

3. Results and discussion

We believe that interactions between bonds in (R)-4-menthen-3-one, e.g. i-Pr group or enone system (C=C-C=O), can play important role in forming rotation and inversion restrictions. The similar interactions can be investigated in terms of second order orbitals interactions in NBO theory [33, 34]. The differences between key donor-acceptor interactions in equatorial and axial conformers of (R)-4-menthen-3-one are presented in table 1, 2 and figure 2.

At first we note that donor-acceptor interactions within C=C-C=O group ($\pi_{C=C} \rightarrow \pi^*_{C=O}$ и $\pi_{C=O} \rightarrow \pi^*_{C=C}$ (figure 3)) weakly depend from i-Pr group rotation. ΔE_{II} for this interactions does not exceed -2.98 kJ/mol in pair of equatorial conformers (**1a,**

1b) and 1.55 kJ/mol in pair of axial conformers (**1c**, **1d**) (table 3).

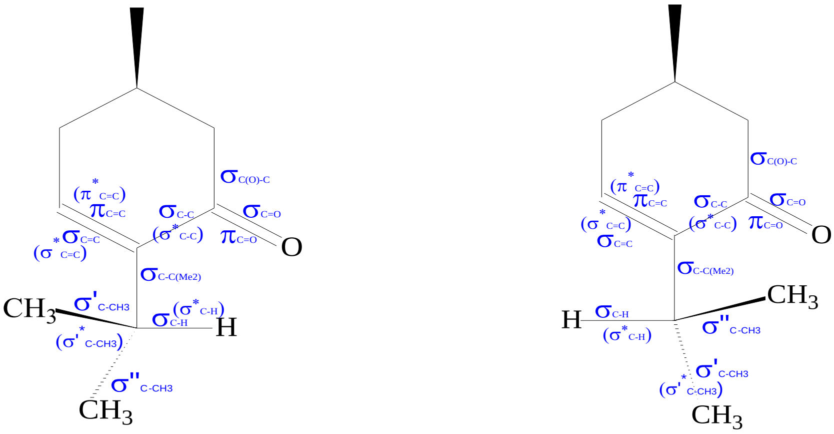


Figure 2. Bonds for NBO second order perturbation analysis

Table 1. The most significant energies of second order orbitals interactions (E_{II}, kJ/mol) in equatorial conformers **1a** and **1b**

1a (1b)	$\pi^*_{C=C}$	$\sigma^*_{C=C}$	σ'^*_{C-CH3}	σ''^*_{C-CH3}	σ^*_{C-H}	σ^*_{C-C}	$\sigma^*_{C=O}$	$\pi^*_{C=O}$	$\sigma^*_{C-C(Me2)}$
$\pi_{C=C}$	-2.85 (-2.68)	-	0.00 (-13.23)	-13.02 (-12.31)	-5.86 (0.00)	-	-	-85.79 (-82.81)	-
$\sigma_{C=C}$	-	-	-	-	-	-8.96 (-11.10)	-6.70 (-8.37)	-	-13.98 (-15.87)
σ'_{C-CH3}	0.00 (-9.38)	0.00 (-5.19)	-	-2.81 (-3.39)	-2.76 (-2.26)	-9.84 (0.00)	-	-	-4.40 (-4.77)
σ''_{C-CH3}	-12.85 (-9.50)	-4.35 (-7.37)	-2.60 (-3.43)	-	-3.01 (-2.30)	-	-	-	-4.14 (-4.90)
σ_{C-H}	-9.38 (0.00)	-13.23 (0.00)	-	-	-	0.00 (-19.30)	-	-	-0.63 (0.00)
σ_{C-C}	-	-11.68 (-11.30)	-6.45 (0.00)	-	0.00 (-2.72)	-	-2.34 (-2.30)	-	-3.94 (-3.89)
$\sigma_{C=O}$	-	-3.85 (-3.68)	-	-	-	-3.89 (-3.94)	-	-	-
$\pi_{C=O}$	-24.03 (-23.70)	-	-	-	-	-	-	-	-
$\sigma_{C-C(Me2)}$	-	-15.95 (-14.53)	-2.47 (-3.06)	-3.06 (-2.97)	-2.55 (0.00)	-3.94 (-4.56)	-	-	-

Table 2. The most significant energies of second order orbitals interactions (E_{II}, kJ/mol) in axial conformers **1c** and **1d**

1c (1d)	$\pi^*_{C=C}$	$\sigma^*_{C=C}$	σ'^*_{C-CH3}	σ''^*_{C-CH3}	σ^*_{C-H}	σ^*_{C-C}	$\sigma^*_{C=O}$	$\pi^*_{C=O}$	$\sigma^*_{C-C(Me2)}$
$\pi_{C=C}$	-2.85 (-3.10)	-	0.00 (-11.97)	-13.52 (-12.18)	-5.74 (0.00)	-	-	-84.41 (-85.96)	-
$\sigma_{C=C}$	-	-	-	-	-	-9.38 (-8.62)	-7.08 (-7.62)	-	-14.57 (-13.06)
σ'_{C-CH3}	0.00 (-8.67)	0.00 (-5.57)	-	-2.93 (-2.60)	-2.93 (-2.55)	-10.13 (0.00)	-	-	-4.61 (-3.98)
σ''_{C-CH3}	-12.60 (-9.09)	-4.27 (-5.23)	-2.68 (-2.60)	-	-3.14 (-2.60)	-	-	-	-4.31 (-3.98)
σ_{C-H}	-9.36 0.00	-13.61 0.00	-	-	-	0.00 (-19.34)	-	-	-2.14 (0.00)
σ_{C-C}	-	-12.10 (-11.30)	-6.49 (0.00)	-	0.00 (-2.68)	-	-2.55 (-2.26)	-	-4.19 (-3.98)
$\sigma_{C=O}$	-	-3.77 (-3.68)	-	-	-	-4.14 (-3.94)	-	-	-

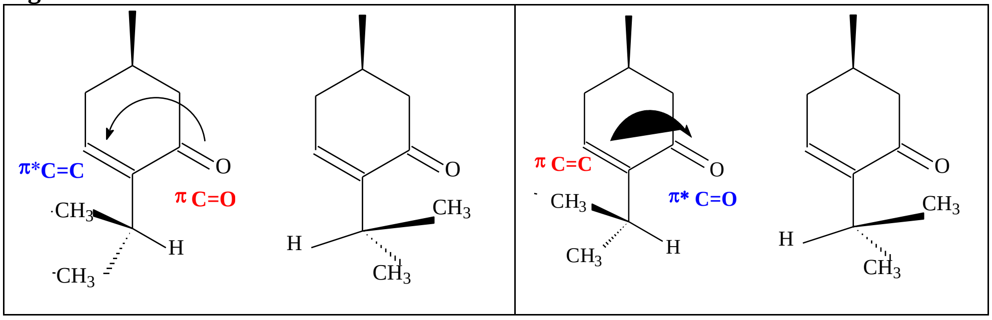
$\pi_{C=O}$	-23.86 (-23.61)	-	-	-	-	-	-	-	-
$\sigma_{C-C(Me2)}$	-	-16.87	-2.60	-3.14	-2.72	-4.10	-	-	-

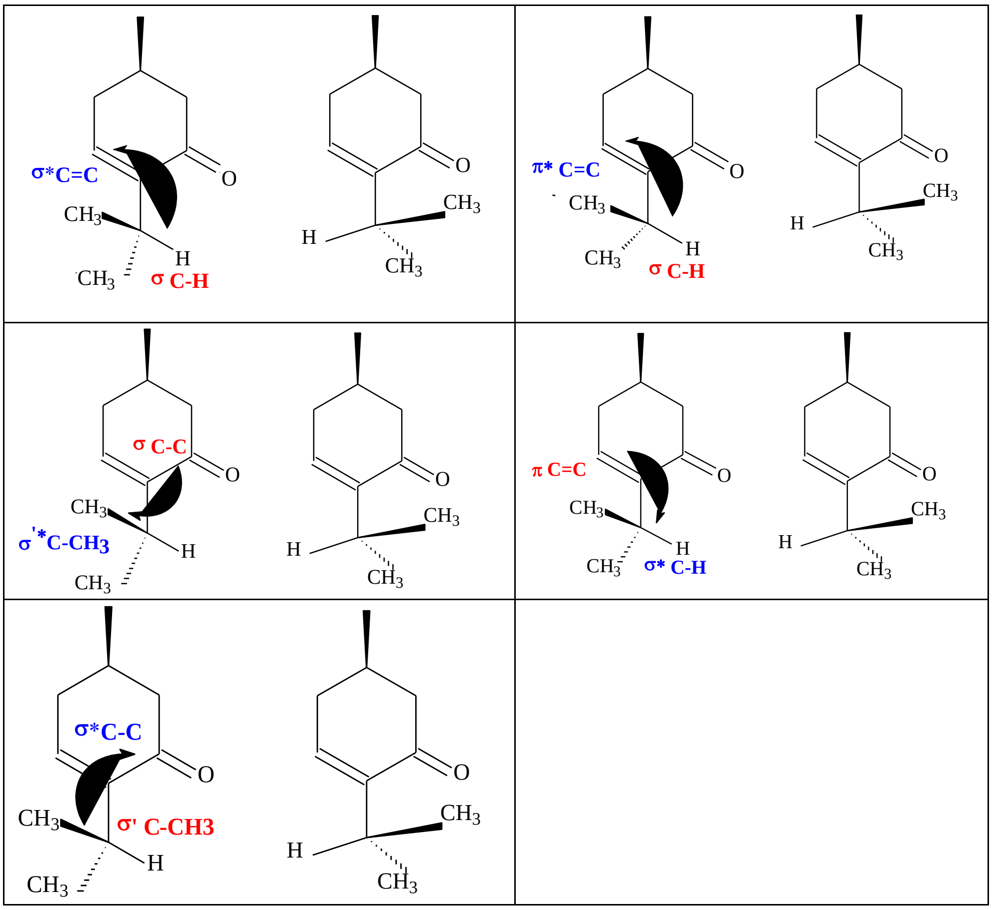
Table 3. Comparison of E_{II} (kJ/mol) in ®-4-menthen-3-one conformers (**1a-d**)

Donor	Acceptor	ΔE_{II} **(1a-1b)**	ΔE_{II} **(1c-1d)**	ΔE_{II} **(1a-1c)**	ΔE_{II} **(1b-1d)**
$\pi_{C=C}$	**$\pi^*_{C=O}$**	-2.98	1.55	-1.38	3.15
$\pi_{C=O}$	**$\pi^*_{C=C}$**	-0.33	0.15	-0.17	0.54
$\pi_{C=C}$	**σ^*_{C-H}**	-5.86	-5.74	-0.12	0.00
$\pi_{C=C}$	**σ'^*_{C-CH3}**	13.23	11.97	0.00	-1.26
$\sigma_{C=C}$	**$\sigma^*_{C=O}$**	1.67	0.54	0.38	-0.75
$\sigma_{C=C}$	**σ^*_{C-C}**	2.14	-0.76	0.42	-2.48
$\sigma_{C=C}$	**$\sigma^*_{C-C(Me2)}$**	1.89	-1.51	0.59	-2.81
σ'_{C-CH3}	**$\pi^*_{C=C}$**	9.38	8.67	0.00	-0.71
σ'_{C-CH3}	**$\sigma^*_{C=C}$**	5.19	5.57	0.00	0.38
σ'_{C-CH3}	**σ^*_{C-C}**	-9.84	-10.13	0.29	0.00
σ''_{C-CH3}	**$\pi^*_{C=C}$**	-3.35	-3.51	-0.25	-0.41
σ''_{C-CH3}	**$\sigma^*_{C=C}$**	3.02	0.96	-0.08	-2.14
σ_{C-H}	**$\pi^*_{C=C}$**	-9.38	-9.36	-0.02	0.00
σ_{C-H}	**$\sigma^*_{C=C}$**	-13.23	-13.61	0.38	0.00
σ_{C-H}	**σ^*_{C-C}**	19.30	19.34	0.00	0.04
σ_{C-C}	**σ'^*_{C-CH3}**	-6.45	-6.49	0.04	0.00
σ_{C-C}	**σ^*_{C-H}**	2.72	2.68	0.00	-0.04
$\sigma_{C-C(Me2)}$	**σ^*_{C-H}**	-2.55	-2.72	0.17	0.00

More significant effects are shown for donor-acceptor interactions between bonds of i-Pr and C=C-C-O groups. Rotation conformers **1a** and **1b** has unique set of orbital interactions (table 3, figure 3). For conformer **1a** we found $\sigma_{C-H}\rightarrow\sigma^*_{C=C}$, $\sigma_{C-H}\rightarrow\pi^*_{C=C}$ and $\pi_{C=C}\rightarrow\sigma^*_{C-H}$ orbital interactions (figure 3). This interactions corresponding coplanar located bonds of i-Pr and C=C-C=O groups. Also for conformer **1a** exist significant interactions $\sigma'_{C-CH3}\rightarrow\sigma^*_{C-C}$ and $\sigma_{C-C}\rightarrow\sigma'^*_{C-CH3}$ between C-C bond of enone system (σ_{C-C}) and C-C bonds in i-Pr group (σ'_{C-CH3}), which is nonplanar located relatively to C=C-C=O group (figure 3). For conformer **1b** the same interactions are absent. Transition to conformer **1b** by rotation of i-Pr group, changes the set of orbitals interactions and $\pi_{C=C}\rightarrow\sigma'^*_{C-CH3}$, $\sigma'_{C-CH3}\rightarrow\pi^*_{C=C}$, $\sigma'_{C-CH3}\rightarrow\sigma^*_{C=C}$, $\sigma_{C-C}\rightarrow\sigma^*_{C-H}$ and $\sigma_{C-H}\rightarrow\sigma^*_{C-C}$ interactions (figure 4) becomes typical. Two last interactions $\sigma_{C-C}\rightarrow\sigma^*_{C-H}$ and $\sigma_{C-H}\rightarrow\sigma^*_{C-C}$ is possible, because C-H bond is coplanar relative to plane of enone system. The energy of $\sigma_{C-H}\rightarrow\sigma^*_{C-C}$ interaction more energy of $\sigma_{C-C}\rightarrow\sigma^*_{C-H}$ by 16.58 kJ/mol, so the C-H bond has a predominantly donor character.

Figure 3. Differences in second order orbitals interactions for conformers **1a** and **1b**





This combinations of donor and acceptor interactions between bonds of C=C-C=O and i-Pr groups are well explain stability of **1a** conformer and restriction of i-Pr group rotation.

The low reactivity of conformer **1b** in nuclophilic addition reactions in comparison with **1a** conformer is also well described by terms of second order orbitals interactions. The sum of energies of donor transfers onto $\pi_{C=C}$ bond in conformer **1b** is more by 7,4 kJ/mol than the same transfer in conformer **1a** (Table 3). Obviously in conformer **1b** bond is more electrondeficitic and therefore worse involved in nuclophilic addition reactions.

Similar reasoning shows that conformer **1a** is more reactive in the 1,2- and 1,4- nucleophilic addition reactions [6], because for it the transfer of electron density to the bonds $\pi^*_{C=O}$ and $\pi^*_{C=C}$ is more pronounced. (Table 3, figure 4).

Steric effects

Next electronic effect, which influence on transitions between conformers of (R)-4-ментен-3-она and it reactivities, is steric factor. In terms of NBO this factor describes, as “Total steric exchange energy” (TSEE), which consists of two contributions - individual bonds repulsions E'_{TSE} [37] and repulsions between pairs of bonds E''_{TSE} [38]. Both contributions presented in table 4 and table 5.

Individual bonds repulsions increment shows that π-bonds in C=C-C=O fragment has the same steric hindrance for all conformers.

More differences between bond repulsion increments are exists for $\sigma_{C\text{-}C}$ bond in C=C-C=O fragment and bonds of i-Pr group (**$\sigma_{C\text{-}C(Me2)}$ $\sigma'_{C\text{-}CH3}$ $\sigma'_{C\text{-}H21}$ $\sigma''_{C\text{-}CH3}$ $\sigma''_{C\text{-}H23}$ $\sigma''_{C\text{-}H24}$).** The steric hindrance for this bonds in axial conformers (**1c** and **1d**) is less, than in equatorial conformers (**1a** and **1b**) (table 4). Obviously this notable differences in steric hindrance leads to rotation restriction of i-Pr group.

Analysis of $\Delta E''_{(1a\text{-}1c)}$ and $\Delta E''_{(1b\text{-}1d)}$ (table 5) shows, that the ring conformation not affected onto difference between the bonds pairwise repulsions contributions for axial (**1c**, **1d**) and equatorial conformers (**1a**, **1b**).

Figure 4. Differences in second order orbitals interactions for conformers **1a** and **1b**

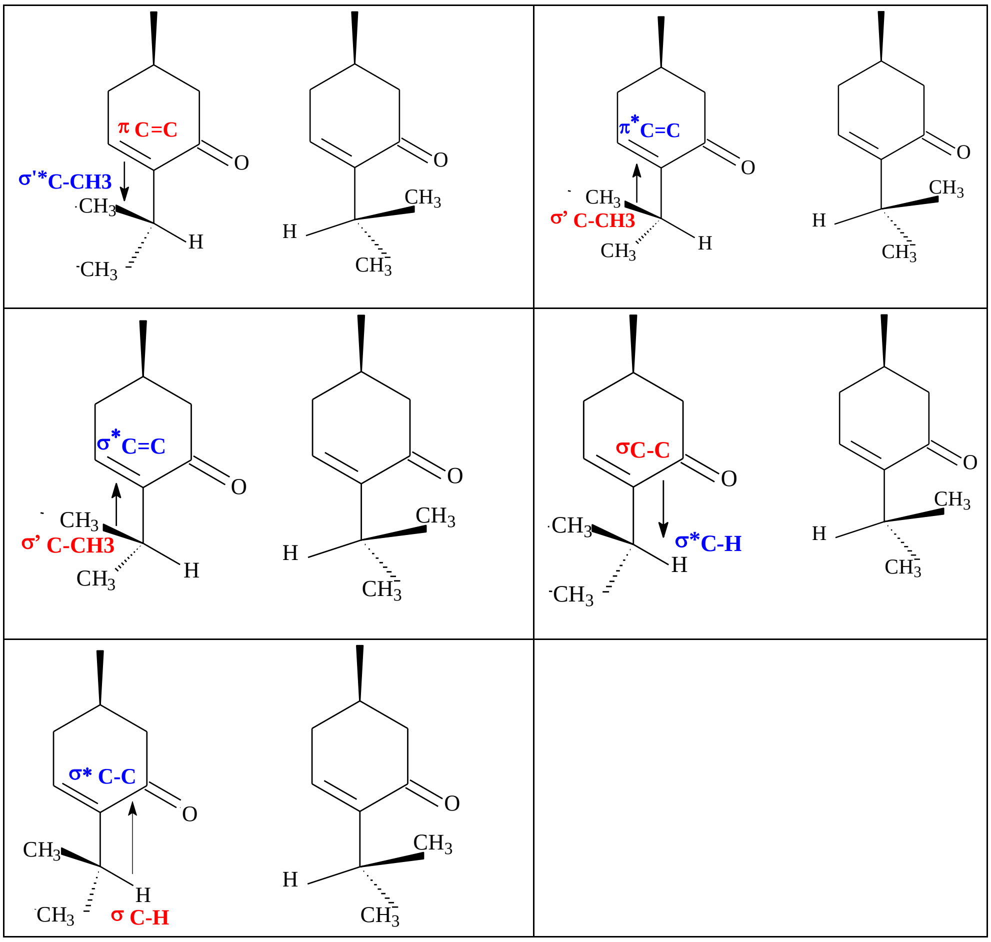


Table 4. Bond repulsion increments in TSEE, (E'_{TSE}) kJ/mol

Bond	E_{TSE} **1a**	E_{TSE} **1b**	E_{TSE} **1c**	E_{TSE} **1d**	ΔE_{TSE} **(1a-1b)**	ΔE_{TSE} **(1c-1d)**	ΔE_{TSE} **(1a-1c)**	ΔE_{TSE} **(1b-1d)**
$\sigma_{C=C}$	-10.13	-10.89	-10.75	-11.13	0.75	0.38	0.62	0.24
$\pi_{C=C}$	-25.71	-25.46	-24.09	-23.30	-0.25	-0.79	-1.62	-2.16
$\pi_{C=O}$	-51.00	-50.83	-50.52	-50.19	-0.17	-0.33	-0.48	-0.64
$\sigma_{C=O}$	-242.71	-243.25	-243.86	-243.78	0.54	-0.08	1.15	0.53
σ_{C-C}	52.71	46.89	52.82	46.56	5.82	6.25	-0.11	0.33
$\sigma_{C(O)-C}$	49.74	50.41	50.98	51.98	-0.67	-1.00	-1.24	-1.57
$\sigma_{C-C(Me2)}$	47.06	42.66	46.44	42.31	4.40	4.13	0.62	0.35
σ'_{C-CH3}	23.24	17.92	23.18	18.97	5.32	4.21	0.06	-1.05
σ'_{C-H19}	-20.47	-20.81	-20.22	-20.63	0.33	0.42	-0.25	-0.18
σ'_{C-H20}	-23.11	-21.69	-23.34	-21.30	-1.42	-2.04	0.23	-0.39
σ'_{C-H21}	-17.75	-25.04	-17.47	-24.43	7.29	6.96	-0.28	-0.61
σ''_{C-CH3}	21.14	18.46	21.93	17.63	2.68	4.29	-0.79	0.83
σ''_{C-H22}	-22.11	-20.31	-22.01	-20.68	-1.80	-1.33	-0.1	0.37
σ''_{C-H23}	-20.14	-24.83	-20.13	-24.89	4.69	4.75	-0.01	0.06
σ''_{C-H24}	-26.04	-21.48	-25.30	-24.55	-4.56	-3.75	-0.74	3.07

Table 5. Bonds pairwise repulsions contributions[a] in TSEE, (E”$_{TSE}$) kJ/mol

Bond$_1$	Bond$_2$	**1a**	**1b**	**1c**	**1d**	ΔE” **(1a-1b)**	ΔE” **(1c-1d)**	ΔE” **(1a-1c)**	ΔE” **(1b-1d)**
		E”(i,j)	E”(i,j)	E”(i,j)	E”(i,j)				
$\sigma_{C=C}$	$\sigma'_{C\text{-}CH3}$	8.46	2.18	8.29	2.34	6.28	5.95	0.17	-0.16
$\sigma_{C=C}$	$\sigma''_{C\text{-}CH3}$	0.00	2.39	0.00	2.18	-2.39	-2.18	0	0.21
$\sigma_{C=C}$	$\sigma_{C\text{-}H}$	6.70	18.63	6.74	18.55	-11.93	-11.81	-0.04	0.08
$\pi_{C=C}$	$\sigma'_{C\text{-}CH3}$	2.89	22.69	3.22	21.48	-19.80	-18.25	-0.33	1.21
$\pi_{C=C}$	$\sigma''_{C\text{-}CH3}$	27.93	21.39	27.93	22.82	6.53	5.11	0	-1.43
$\sigma_{C\text{-}C}$	$\sigma'_{C\text{-}CH3}$	13.44	2.55	13.57	3.31	10.89	10.26	-0.13	-0.76
$\sigma_{C\text{-}C}$	$\sigma''_{C\text{-}CH3}$	0.00	3.06	0.00	2.39	-3.06	-2.39	0	0.67
$\sigma_{C=C}$	$\sigma_{C=O}$	8.79	8.71	8.79	8.67	0.08	0.13	0	0.04
$\pi_{C=C}$	$\pi_{C=O}$	32.62	32.53	32.49	32.53	0.08	-0.04	0.13	0
$\sigma_{C\text{-}C(Me2)}$	$\sigma_{C=O}$	5.15	4.48	5.07	4.35	0.67	0.71	0.08	0.13

[a] exclude geminal bonds

The general differences of this contribution in steric hindrance are exists for rotation conformers. E.g. in conformer 1b bond $\pi_{C=C}$ is more steric hindranced because of near location of CH$_3$-fragments of i-Pr group. Corresponding sum of E”$_{TSE}$ for bonds $\pi_{C=C}$ - $\sigma'_{C\text{-}CH3}$ and $\pi_{C=C}$ – $\sigma''_{C\text{-}CH3}$ in 1b on 13.3 kJ/mol higher than the same sum of repulsions energies for conformer **1a**. The similar ratio of E”$_{TSE}$ occur between axial conformers **1c** and **1d**. So main steric hindrance associated with i-Pr group location instead of ring inversion.

Another interesting fact, which can explain reactivity of conformers **1a-1d** is very low differences of bonds pairwise repulsions contributions associated with $\pi_{C=O}$ and $\sigma_{C=C}$ bonds for all conformers. This is good agree with low stereospecificity in nuclophilic addition reactions for (R)-4-menten-3-one [6].

4. Conclusions

Thus, the uncharacteristic reactivity of (R)-4-menten-3-one vs. conventional enone systems is well described by the steric effects and features of orbital interaction. The most stable conformer, which determinate the unique (R)-4-menten-3-one reactivity, has less electrondeficitic $\pi_{C=C}$, because of less donor transfers from this bond. Also this conformer is more reactive in the 1,2- and 1,4-nucleophilic addition reactions, due to more pronounced second-order orbital interactions involving $\pi^*_{C=O}$ and $\pi^*_{C=C}$ bonds. Restrictions of inversion and rotation, which leads to most stable conformer, are linked with steric hindrances arising between CH$_3$- fragments in i-Pr group and double bonds of enone fragment.

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