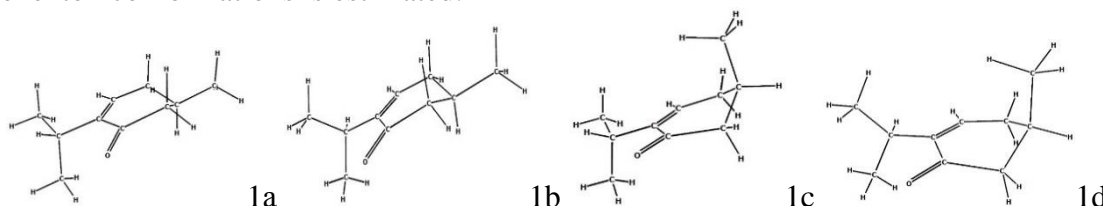


## EVALUATION OF CONFORMAL POPULATION (R)-4-MENTHENONE

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It is shown that (R)-4-menthenone, which is convenient for the synthesis of a whole spectrum of pheromones, has an unusual reactivity in comparison with other enon systems. The unusual behavior of (R)-4-menthenone may be due to the limited rotation of the isopropyl group and its steric effect on the availability of the C = C bond electrons. Using the quantum-chemical non-empirical approximations of different levels of complexity, the relative stability of the (R)-4-menthenone conformations is estimated.



The most stable conformer 1a is characterized by the equatorial orientation of the methyl group at the 4-position and the dihedral angle of the isopropyl group HCCC (= 0) 24°. At this angle, the isopropyl group exerts the greatest screening effect on the C = C bond in the cycle as compared to the conformers 1b and 1d (Table 1).

Table 1

	$\Delta G^{298}$ , kJ/mol			
	1c-1a	1d-1b	1d-1c	1b-1a
B3LYP/6-31G(d,p)	5.96	5.88	1.06	1.13
MP2/6-31G(d,p)	2.40	2.27	0.10	0.16
B3LYP/6-311++G(2d,p)	5.41	5.60	2.57	2.37
MP2/6-311++G(d,p)	8.31	8.00	1.54	1.85
<b>G4 (MP2)</b>	<b>4.04</b>	<b>3.79</b>	<b>2.64</b>	<b>2.87</b>

All other conformers are less favorable, but the difference in energy between them is not more than 8.3 kJ/mol, depending on the calculation method used. It is interesting to note that the calculated values obtained in the DFT methods are closest to the results of the high-precision composite method G4 (MP2). Despite the insignificant difference in energies, the populations of these conformers differ markedly. The share of the most stable conformer 1a is almost 2 times larger than the total fraction of all other conformers and 3 times greater than the nearest one in stability 1b, but having a different orientation of the isopropyl group (Table 2).

Table 2

conformer	1a	1b	1c	1d
w (%)	63.4	19.9	12.4	4.3