Do the Anti-Selectivities of 2,3-*endo,endo*-Dimethylnorbornan-7-one and the Corresponding Diethyl Analog Obey the Cieplak Model? An ab Initio MO Investigation and Application of the Cation Complexation Model

Veejendra K. Yadav*

Department of Chemistry, Indian Institute of Technology, Kanpur 208 016, India

vijendra@iitk.ac.in

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The anti-selectivity of 2,3-*endo,endo*-dimethylbicyclo-[2.2.1]heptan-7-one, **1** (Figure 1), is appreciably inferior to that of the corresponding diethyl derivative, **2**. For instance, in reaction with $LiA1H_4$, the anti/syn selectivity is 55:45 for the dimethyl derivative and 79:21 for the diethyl material.[1] However, if the hyperconjugation effects were indeed the control elements as perceived by the Cieplak model,[2] both the materials will be predicted for syn-selectivity. The Cieplak model considers a C−H bond more electron-donating than a C−C bond, and thus, the C1−C6/C4−C5 bonds must be more electron rich than the C1−C2/C3−C4 bonds. In this paper, we present the results of an application of the cation complexation model[3] and explain (a) why these materials are anti-selective, to begin with, and (b) why the ethyl derivative is better at its selectivity than the corresponding methyl species.

In application of the cation complexation model to bicyclo[2.2.1]heptan-7-ones, we have calculated[4−7] the torsion angles Dl = O−C7−C1−C2, D2 = O−C7−C1−C6, D3 = O−C7−C4−C3, and D4 = O−C7−C4−C5, both before and after complexation, to assess the direction of carbonyl pyramidalization.[3,8] We call the pyramidalization "anti"

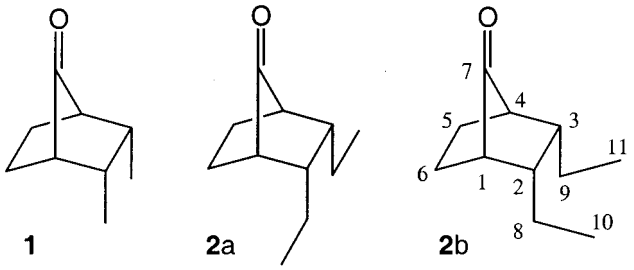

Figure 1. Structures of the molecules studied: 2,3-*endo,endo*-dimethylnorbornan-7-one (**1**) and conformers of 2,3-*endo,endo*-diethynorbornan-7-one (**2**).

Table 1. Selected Becke3LYP/6-31G* Geometrical Parameters on 2,3-*endo,endo*-Disubstituted Bicyclo[2.2.1]heptan-7-ones[a]

substrate	D1	D2	D3	D4	D5	D6	D7[b]
1	121.63	−125.06	−121.63	125.06	−1.14	1.14	−178.80
1-H^+	115.33	−132.28	−115.69	131.97	−6.46	6.02	−173.70
1-Li^+	119.46	−127.70	−119.47	127.70	−3.03	3.02	−176.90
2a	121.22	−125.59	−121.22	125.59	−1.73	1.73	−178.50
2a-H^+	112.57	−135.20	−113.18	134.60	−8.78	8.11	−171.90
2a-Li^+	118.72	−128.61	−118.91	128.45	−3.81	3.74	−176.50
2b	122.46	−124.50	−120.75	126.40	−0.75	1.63	−178.50
2b-H^+	114.21	−133.68	−112.34	135.86	−7.86	8.18	−171.80
2b-Li^+	120.29	−127.15	−118.22	129.38	−2.77	3.77	−176.50

[a] Dl = O−C7−C1−C2; D2 = O−C7−C1−C6; D3 = O−C7−C4−C3; D4 = O−C7−C4−C5; D5 = H−C1−C7−O; D6 = H−C4−C7−O; D7 = C1−C7−O−C4. [b] The D7 torsion angles were calculated using the program ORTEP-3.2.

when Dl and D3 are smaller than D2 and D4 and "syn" when Dl and D3 are larger than D2 and D4, respectively. The anti-pyramidalization leads to anti-addition and the syn-pyramidalization leads to syn-addition of a nucleophile. The directional changes in the torsion angles D5 = H−Cl−C7−O, D6 = H−C4−C7−O, and D7 = C1−C7−O−C4 also provide information about the direction of pyramidalization.[9] The torsion angles Dl−D7 are collected in Table 1.

We have considered two conformations, **2a** and **2b**, for the diethyl derivative.[10] In **2a**, the carbon−carbon bonds of the ethyl groups are antiperiplanar to the C2−C3 bond (C−C−C2−C3 = C−C−C3−C2 = 178.28°). In **2b**, one such bond is near antiperiplanar to the C1−C2 bond (C−C−C2−C1 = 159.90°) and the other near synperiplanar to the C3−H bond (C−C−C3−H = −18.57°). The conformer **2a** is 3.40 kcal mol^{-1} more stable than the conformer **2b**. The torsion angles D1 and D3 are smaller than the torsion angles D2 and D4, respectively, in both

* To whom correspondence should be addressed. Fax: Int. Code-91-512-597436.

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(9) I am indebted to one reviewer who has kindly suggested the torsion angle D7 = C1−C7−O−C4 as a better proof for the direction of carbonyl pyramidalization than the torsion angles D1−D6.

(10) The conformer **2a** was selected on the basis of intuitive chemical knowledge aimed at minimizing the possible steric interactions between the two ethyl groups. The conformer **2b** was a product of geometry optimization of an initial guess wherein the two ethyl carbon−carbon bonds were set synperiplanar to the C−H bonds on C2 and C3.

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Table 2. Becke3LYP/6-31G* Antiperiplanar Effects from the Second-Order Perturbation Theory Analysis of the Fock Matrix in NBO Basis for l and 2 and Their Complexes with H^+ and Li^+

substrate	$\sigma_{C1-C2} - \pi^*_{C7-O}$	$\sigma_{C1-C6} - \pi^*_{C7-O}$	$\sigma_{C3-C4} - \pi^*_{C7-O}$	$\sigma_{C4-C5} - \pi^*_{C7-O}$	$\sigma_{C8-H} - \sigma^*_{C1-C2}$	$\sigma_{C9-H} - \sigma^*_{C3-C4}$	$\sigma_{C8-C10} - \sigma^*_{C1-C2}$	$\sigma_{C9-C11} - \sigma^*_{C3-C4}$
1	3.43	3.27	3.43	3.27	3.53	3.53		
1-H^+	8.60	5.66	8.82	5.66	4.24	4.16		
1-Li^+	6.00	4.52	6.00	4.52	3.93	3.93		
2a	3.48	3.25	3.38	3.25	3.93	3.93		
2a-H^+	9.20	5.30	9.39	5.32	4.71	4.61		
2a-Li^+	6.24	4.39	6.18	4.46	4.38	4.37		
2b	3.33	3.45	3.69	3.06			1.83	1.24
2b-H^+	8.42	5.79	10.3	4.79			2.19	1.57
2b-Li^+	5.79	4.80	6.54	4.13			2.06	1.42

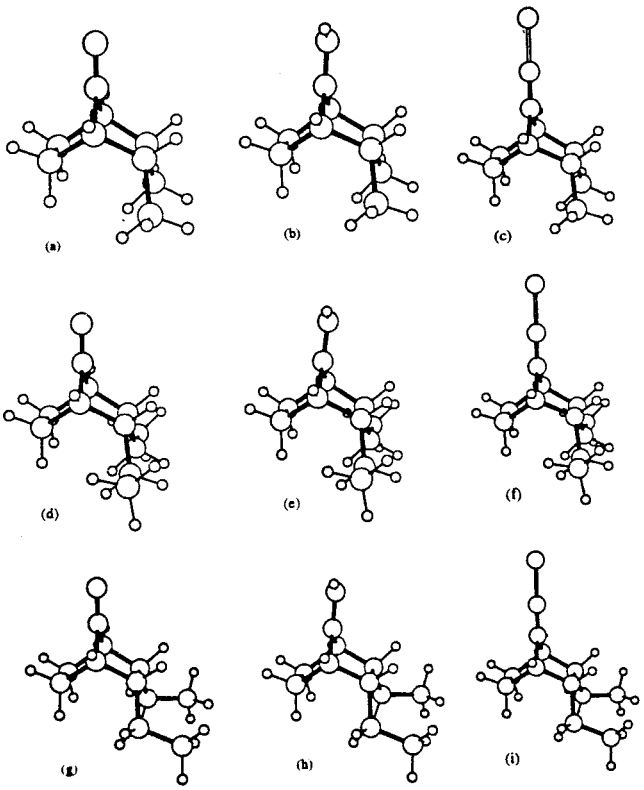

Figure 2. Computed 3D structures of (a) **1**, (b) **1**-H^+, (c) **1**-Li^+, (d) **2a**, (e) **2a**-H^+, (f) **2a**-Li^+, (g) **2b**, (h) **2b**-H^+, and (i) **2b**-Li^+.

1 and **2**. This indicates the anti-pyramidalization tendency of the carbonyl function. On allowing for complexation of a cation with the carbonyl oxygen, D1/D2 and D3/D4 differences are enlarged. Dl and D3 have become smaller and D2 and D4 have become larger than those in the parent molecule. These changes reinforce the above anti-pyramidalization hypothesis. Both the molecules, therefore, must exhibit anti-selectivity as indeed observed from the experiments. The computed 3D structures of **1** and **2** and their complexes with H^+ and Li^+ are collected in Figure 2.

We have traced the origin of the above anti-selectivities in the antiperiplanar effects[11] that are collected in Table 2. In **1**, one of the three C−H bonds of each methyl group is antiperiplanar to C1−C2/C3−C4 bond (H−C−C2−Cl = 175.66°, H−C−C3−C4 = −175.66°) that allows them for mutual interaction. The interaction energy is 3.53 kcal mol^{-1}, which is increased to 4.16−4.24 kcal mol^{-1} on carbonyl protonation. This interaction enhances the electron densities and, hence, the electron donating abilities of the C1−C2 and C3−C4 bonds, which in turn, support anti-pyramidalization. A similar situation exists in **2a**. One of the two methylene hydrogens is antiperiplanar to the C1−C2/C3−C4 bond (H−C8−C2−Cl = −179.44°, H−C9−C3−C4 = 179.44°). However, the interaction energy is somewhat higher at 3.93 kcal mol^{-1} and enhanced to 4.61−4.71 kcal mol^{-1} on carbonyl protonation in comparison to those in **1** and its protonated derivative, respectively. The larger interactions in **2a** and its complexes over those in **1** and its complexes ensure larger carbonyl pyramidalization in **2a** and, hence, the better anti-selectivity.[3c]

In conclusion, we have demonstrated that the anti-selectivities of the title substrates are not controlled by the hyperconjugation effects of the substituents on the carbon adjacent to the carbonyl function but by their antiperiplanar interactions with the electron-deficient carbonyl p orbital. The larger interaction in the diethyl derivative in comparison to that in the dimethyl derivative appears to be responsible for the larger anti-selectivity of the former material.

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Supporting Information Available: The coordinates of **1** and **2** and their complexes with H^+ and Li^+. This material is available free of charge via the Internet at http://pubs.acs.org.

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