Stereoselective 1,3-Dipolar Cycloadditions of a Chiral Nitrone Derived from Erythrulose: An Experimental and DFT Theoretical Study

Miguel Carda, Raul Portolés, Juan Murga, Santiago Uriel, J. Alberto Marco, Luis R. Domingo, Ramón Zaragozá and Harald Röper

Table 1. Total energies (a.u.) and relative energies[a] (kcal/mol, in parentheses) for the transition structures (TS) of the 1,3-DC of nitrone **N1** and acrylonitrile.

	HF/6-31G*	B3LYP/6-31G*	B3LYP/6-31+G*	MP2/6-31+G*// B3LYP/6-31G*	MP3/6-31+G*// B3LYP/6-31G*
TS1	-607.408811 (10.2)	-611.201801 (1.0)	-611.224142 (1.2)	-609.348972 (1.2)	-609.371259 (1.3)
TS2	-607.411547 (8.4)	-611.203034 (0.2)	-611.226015 (0.0)	-609.350805 (0.0)	-609.373366 (0.0)
TS3	-607.425001 (0.0)	-611.203410 (0.0)	-611.225838 (0.1)	-609.337189 (8.5)	-609.371822 (1.0)
TS4	-607.423969 (0.6)	-611.202202 (0.8)	-611.225128 (0.6)	-609.336216 (9.2)	-609.370366 (1.9)

[a] Relative to the most stable TS

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Table 2. B3LYP/6-31G* Imaginary frequency (Frequency, cm^{-1}), Hessian unique negative eigenvalue (Eigenvalue, a. u.), main components of the transition vector (**C**, a. u.), and corresponding geometric parameters (**G**, bonds in Å, angles in degrees) for the transition structures corresponding to the 1,3-DC of nitrone **N1** and methyl propiolate.

TS1			**TS2**		
Imaginary Frequency		394.2i			388.0i
Eigenvalue		-0.03055			-0.03236
	C	**G**		**C**	**G**
O1-C2	0.367	2.335	O1-C3	0.659	1.794
C3-C4	0.765	2.029	C2-C4	0.545	2.440
C4-N5	-0.099	1.352	O1-N5	-0.091	1.313
O1-C2-C10	-0.202	90.9	O1-N5-C4	0.118	121.4
C3-C4-N5	-0.089	95.3	O1-C3-H3	-0.176	97.6
O1-N5-C4-C3	0.114	55.4	C4-C2-C10	-0.255	101.4
O1-N5-C4-C8	0.092	169.1	O1-N5-C4-C2	0.128	46.5
O1-N5-C4-C9	0.309	-48.4	O1-N5-C4-C8	0.140	160.9
C2-O1-N5-C4	-0.135	-50.7	O1-N5-C4-C9	0.267	-41.9

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Table 3. B3LYP/6-31G* Imaginary frequency (Frequency, cm^{-1}), Hessian unique negative eigenvalue (Eigenvalue, a. u.), main components of the transition vector (**C**, a. u.), and corresponding geometric parameters (**G**, bonds in Å, angles in degrees) for the transition structures corresponding to the 1,3-DC of nitrone **N1** and acrylonitrile.

TS3-en			**TS3-ex**		
Imaginary Frequency		407.4i			412.7i
Eigenvalue		-0.03022			-0.02916
	C	**G**		**C**	**G**
O1-C2	0.401	2.298	O1-C2	0.416	2.278
C3-C4	0.766	2.018	C3-C4	0.756	2.014
C4-N5	-0.106	1.360	C4-N5	-0.108	1.361
O1-C2-C10	-0.125	95.7	O1-N5-C4	0.119	120.8
O1-N5-C4	0.111	120.8	H2-C2-O1	-0.138	86.5
H3a-C3-C4	-0.194	94.7	H3a-C3-C4	-0.172	96.8
H3b-C3-C4	-0.115	101.2	H3b-C3-C4	-0.135	99.3
O1-N5-C4-C9	0.285	-52.4	O1-N5-C4-C9	0.276	-52.0
C2-O1-N5-C4	-0.127	-47.3	C2-O1-N5-C4	-0.116	-47.7

TS4-en			**TS4-ex**		
Imaginary Frequency		421.2i			427.4i
Eigenvalue		-0.03438			-0.0351
	C	**G**		**C**	**G**
O1-C3	0.629	1.816	O1-C3	0.622	1.857
C2-C4	0.587	2.334	C2-C4	0.606	2.336
O1-N2-C3	0.122	120.1	O1-N2-C3	0.133	119.9
C4-C2-C10	-0.159	100.8	C4-C2-C10	-0.140	101.8
H2-C2-C4	-0.128	96.8	H3a-C3-O1	-0.184	94.3
H3a-C3-O1	-0.153	98.8	H3b-C3-O1	-0.105	97.2
H3b-C3-O1	-0.142	94.3	C3-O1-N5-C4	-0.104	-52.9
C2-C4-N5-O1	0.105	43.6	C2-C4-N5-O1	0.101	50.2
C8-C4-N5-O1	0.119	160.0	C8-C4-N5-O1	0.141	161.5
C9-C4-N5-O1	0.284	-51.8	C9-C4-N5-O1	0.254	-50.6