Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Conformational equilibria and interaction preference in complex of isoprene-maleic anhydride

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Table S1. The measured transition frequencies of isomer I with quantum numbers and difference to calculated frequencies Δν in the least squares fit.

Transitions		ν/MHz	Δν/MHz
J' K_a' K_c'	J'' K_a'' K_c''		
5 0 5	4 0 4	6755.3681	0.0009
5 1 5	4 1 4	6732.2758	0.0006
5 1 4	4 1 3	7451.2625	0.0006
6 0 6	5 0 5	8034.1955	0.0001
6 1 6	5 1 5	8025.8731	0.0008
6 1 5	5 1 4	8723.1197	-0.0003
7 0 7	6 0 6	9317.8273	-0.0087
7 1 7	6 1 6	9315.0775	0.0027
7 1 6	6 1 5	9975.5716	0.0010
8 0 8	7 0 7	10603.4651	0.0004
8 1 8	7 1 7	10602.5959	-0.0001
8 1 7	7 1 6	11239.1927	0.0001
9 0 9	8 0 8	11889.7999	0.0002
9 1 9	8 1 8	11889.5376	0.0012
3 1 2	2 0 2	5408.2937	-0.0009
3 2 2	2 1 2	5939.2868	-0.0003
3 2 1	2 1 1	5651.0802	0.0008
3 3 1	2 2 1	6518.0685	0.0029
3 3 0	2 2 0	6470.2680	0.0001
4 1 3	3 0 3	7300.4731	-0.0020
4 2 3	3 1 3	7677.8386	0.0003
4 2 2	3 1 2	7250.6856	0.0002
4 3 2	3 2 2	8084.0694	-0.0027
4 3 1	3 2 1	7898.8744	-0.0005
4 4 1	3 3 1	8798.7030	0.0006
4 4 0	3 3 0	8787.7491	-0.0080
5 1 4	4 0 4	9267.4349	-0.0014
5 2 4	4 1 4	9482.8022	0.0005
5 2 3	4 1 3	8976.9898	0.0018
5 3 3	4 2 3	9715.5997	0.0021
5 3 2	4 2 2	9336.7563	0.0008
5 4 2	4 3 2	10314.4195	0.0000
5 4 1	4 3 1	10248.0424	0.0002
5 5 1	4 4 1	11093.5960	0.0003
5 5 0	4 4 0	11091.5913	0.0003
6 1 5	5 0 5	11235.1887	-0.0005
6 2 5	5 1 5	11335.7617	-0.0005
6 2 4	5 1 4	10844.8427	0.0007

6 3 4	5 2 4	11420.3041	0.0010
6 3 3	5 2 3	10866.1333	0.0006
6 4 3	5 3 3	11864.8197	0.0014
6 4 2	5 3 2	11657.7924	-0.0007
6 5 2	5 4 2	12591.6875	-0.0002
6 5 1	5 4 1	12575.2407	-0.0008
6 6 1	5 5 1	13391.7681	-0.0010
6 6 0	5 5 0	13391.4428	0.0013
7 1 6	6 0 6	13176.5649	0.0004
7 2 6	6 1 6	13217.3583	-0.0011
7 2 5	6 1 5	12822.5691	0.0006
7 3 5	6 2 5	13195.1120	0.0030
7 3 4	6 2 4	12534.5243	-0.0008
7 4 4	6 3 4	13469.8126	0.0009
7 4 3	6 3 3	13046.7801	0.0005
7 5 3	6 4 3	14100.0007	0.0004
7 5 2	6 4 2	14028.9154	0.0024
7 6 2	6 5 2	14885.7182	-0.0001
7 6 1	6 5 1	14882.3566	0.0002
7 7 1	6 6 1	15690.4400	0.0012
7 7 0	6 6 0	15690.3900	0.0012
8 1 7	7 0 7	15097.9283	0.0072
8 2 7	7 1 7	15113.0129	-0.0084
8 2 6	7 1 6	14828.7100	-0.0019
8 3 6	7 2 6	15027.0452	0.0000
8 3 5	7 2 5	14361.7584	0.0000
8 4 5	7 3 5	15143.3214	-0.0001
8 4 4	7 3 4	14502.9516	-0.0003
8 5 4	7 4 4	15634.0467	0.0000
8 5 3	7 4 3	15427.7612	-0.0007
8 6 3	7 5 3	16379.6373	-0.0021
8 6 2	7 5 2	16361.3794	0.0005
8 7 2	7 6 2	17183.8333	-0.0018
8 7 1	7 6 1	17183.2206	-0.0005
8 8 1	7 7 1	17989.0605	-0.0023
8 8 0	7 7 0	17989.0605	0.0049
9 2 7	8 1 7	16807.5098	0.0026
9 3 7	8 2 7	16897.8777	-0.0009
9 3 6	8 2 6	16331.5183	-0.0019
9 4 6	8 3 6	16888.7892	0.0018
9 4 5	8 3 5	16099.8564	-0.0007
9 5 5	8 4 5	17213.9219	0.0014
9 5 4	8 4 4	16781.8471	0.0010

9 6 4	8 5 4	17879.2215	0.0003
9 6 3	8 5 3	17810.7984	-0.0008
9 7 3	8 6 3	18674.8140	-0.0009
9 7 2	8 6 2	18670.8342	-0.0012

Table S2. The measured transition frequencies of isomer II with quantum numbers and difference to calculated frequencies Δν in the least squares fit.

Transitions		ν/MHz	Δν/MHz
J' K_a' K_c'	J'' K_a'' K_c''		
4 0 4	3 0 3	5139.8940	-0.0027
4 1 4	3 1 3	5035.4844	-0.0033
4 1 3	3 1 2	5575.2082	0.0002
4 2 3	3 2 2	5337.8483	0.0002
4 2 2	3 2 1	5555.7719	-0.0004
4 3 2	3 3 1	5401.9456	-0.0007
4 3 1	3 3 0	5419.8782	0.0004
5 0 5	4 0 4	6331.7258	0.0016
5 1 5	4 1 4	6262.8832	0.0001
5 1 4	4 1 3	6900.3388	-0.0001
5 2 4	4 2 3	6640.3046	-0.0013
5 2 3	4 2 2	7003.7954	0.0008
5 3 3	4 3 2	6759.1725	0.0009
5 4 2	4 4 1	6754.8867	0.0011
5 4 1	4 4 0	6757.2432	-0.0015
6 0 6	5 0 5	7518.0504	-0.0002
6 1 6	5 1 5	7479.4362	-0.0001
6 1 5	5 1 4	8171.9560	-0.0009
6 2 5	5 2 4	7923.3722	-0.0001
6 2 4	5 2 3	8431.9690	0.0010
6 3 3	5 3 2	8254.4004	0.0000
6 3 4	5 3 3	8110.8022	-0.0009
6 4 3	5 4 2	8121.7624	-0.0003
6 4 2	5 4 1	8132.0870	0.0014
7 0 7	6 0 6	8708.0365	-0.0004
7 1 7	6 1 6	8688.5123	-0.0013
7 1 6	6 1 5	9389.4682	-0.0011
7 2 6	6 2 5	9186.1961	-0.0019
7 2 5	6 2 4	9821.6521	-0.0015
7 3 5	6 3 4	9450.3910	-0.0028
7 3 4	6 3 3	9723.7274	-0.0013
7 4 4	6 4 3	9493.0030	0.0020
7 4 3	6 4 2	9525.7907	0.0006
7 5 3	6 5 2	9469.1375	0.0056
7 5 2	6 5 1	9470.5453	0.0032
8 0 8	7 0 7	9902.2907	-0.0013
8 1 8	7 1 7	9893.0566	0.0031
8 1 7	7 1 6	10571.8297	0.0000

8 2 7	7 2 6	10430.0849	-0.0005
8 2 6	7 2 5	11159.9243	-0.0015
8 3 6	7 3 5	10772.3754	-0.0005
8 3 5	7 3 4	11203.1132	0.0006
8 4 5	7 4 4	10864.6286	-0.0025
8 4 4	7 4 3	10947.9023	-0.0007
8 5 4	7 5 3	10842.3154	0.0004
8 5 3	7 5 2	10847.7906	0.0024
9 0 9	8 0 8	11099.2891	0.0028
9 1 9	8 1 8	11095.1038	-0.0007
9 1 8	8 1 7	11744.4794	0.0004
9 2 8	8 2 7	11658.1903	0.0017
9 2 7	8 2 6	12436.8436	-0.0008
10 0 10	9 0 9	12297.7205	-0.0004
10 1 10	9 1 9	12295.8845	-0.0028
10 1 9	9 1 8	12922.1088	0.0005
10 2 9	9 2 8	12874.5880	0.0000
10 2 8	9 2 7	13652.8064	0.0007
11 0 11	10 0 10	13496.8328	-0.0021
11 1 11	10 1 10	13496.0517	0.0018
11 1 10	10 1 9	14107.6317	0.0001
3 1 2	2 0 2	5002.0230	0.0001
3 2 2	2 1 2	5899.4546	0.0012
3 2 1	2 1 1	5605.1029	0.0006
3 3 1	2 2 1	6819.6586	-0.0018
3 3 0	2 2 0	6796.8568	-0.0019
4 1 3	3 0 3	6656.6616	0.0009
4 2 3	3 1 3	7442.7041	0.0015
4 2 2	3 1 2	6951.0832	0.0025
4 3 2	3 2 2	8202.9735	-0.0005
4 3 1	3 2 1	8100.0468	-0.0000
4 4 1	3 3 1	9264.0556	-0.0020
4 4 0	3 3 0	9261.2965	0.0003
5 1 4	4 0 4	8417.1044	0.0015
5 2 4	4 1 4	9047.5219	0.0011
5 2 3	4 1 3	8379.6670	-0.0002
5 3 3	4 2 3	9624.2989	0.0013
5 3 2	4 2 2	9362.9918	0.0003
5 4 2	4 3 2	10616.9965	-0.0004
5 4 1	4 3 1	10598.6644	0.0013
5 5 1	4 4 1	11716.8477	-0.0021
5 5 0	4 4 0	11716.5730	-0.0038
6 1 5	5 0 5	10257.3325	-0.0030

6 2 5	5 1 5	10708.0112	0.0011
6 2 4	5 1 4	9911.2952	-0.0011
6 3 4	5 2 4	11094.7940	-0.0007
6 3 3	5 2 3	10613.5974	0.0002
6 4 3	5 3 3	11979.5877	-0.0004
6 4 2	5 3 2	11912.0332	0.0014
6 5 2	5 4 2	13064.5484	-0.0001
6 5 1	5 4 1	13062.1780	0.0002
6 6 0	5 5 0	14170.5427	0.0079
7 1 6	6 0 6	12128.7558	0.0015
7 2 6	6 1 6	12414.7679	-0.0037
7 2 5	6 1 5	11560.9911	-0.0019
7 3 5	6 2 5	12621.8180	0.0016
7 3 4	6 2 4	11905.3570	-0.0009
7 4 4	6 3 4	13361.7877	0.0018
7 4 3	6 3 3	13183.4244	0.0028
7 5 3	6 4 3	14411.9171	-0.0006
7 5 2	6 4 2	14400.6317	-0.0025
7 6 2	6 5 2	15517.8841	-0.0004
7 6 1	6 5 1	15517.6250	0.0000
7 7 0	6 6 0	16624.2322	-0.0021

Table S3. Comparison of theoretical (with different methods) and experimental spectroscopic constants of isomers I and II.

	Isomers	*A* [MHz]	*B* [MHz]	*C* [MHz]
Exp.	I	1149.541060	830.244541	643.462812
	II	1227.008821	739.493310	600.064693
CP-B2PLYP-D3(BJ)/def2-TZVP	I	1144.1 (-0.5%)[a]	838.8(1.0%)	646.3 (0.4%)
	II	1217.4 (-0.8%)	752.8(1.8%)	604.4 (0.7%)
B2PLYP-D3(BJ)/def2-TZVP	I	1144.2 (-0.5%)	855.3 (3.0%)	656.2 (2.0%)
	II	1217.4 (-0.8%)	766.8 (3.7%)	612.71 (2.1%)
CP-B3LYP-D3(BJ)/def2-TZVP	I	1143.8 (-0.5%)	851.3 (2.5%)	652.9 (1.5%)
	II	1214.0 (-1.3%)	768.1 (3.9%)	611.3 (1.9%)
B3LYP-D3(BJ)/def2-TZVP	I	1143.2 (-0.6%)	857.3 (3.3%)	656.2 (2.0%)
	II	1213.9 (-1.1%)	773.6 (4.6%)	614.6 (2.4%)
CP-MP2/def2-TZVP	I	1152.1 (0.2%)	857.7 (3.3%)	656.2 (2.0%)
	II	1225.2 (0.1%)	771.3 (4.3%)	616.6 (2.8%)
MP2/def2-TZVP	I	1158.3 (3.1%)	890.6 (9.1%)	682.6 (9.4%)
	II	1227.9 (0.1%)	802.3 (8.5%)	636.2 (6.0%)

[a] The error with respect to experiment is indicated as percentage between parentheses.

Table S4. CP-B2PLYP-D3(BJ)/def2-TZVP calculated geometries of isomer I.

Bond lengths (Å)		Valence angles (°)		Dihedral angles (°)	
O2O1	2.267				
O3O2	2.266	O3O2O1	161.2		
C4O3	1.192	C4O3O2	31.3	C4O3O2O1	-5.5
C5O1	1.192	C5O1O2	31.2	C5O1O2C4	2.3
C6C4	1.484	C6C4O3	130.1	C6C4O3O2	179.4
C7C6	1.331	C7C6C4	108.2	C7C6C4O3	-178.8
H8C7	1.077	H8C7C6	129.7	H8C7C6C4	-179.9
H9C6	1.077	H9C6C4	122.0	H9C6C4O3	1.3
C10C5	3.413	C10C5C7	92.6	C10C5C7C6	-96.3
C11C7	3.468	C11C7C6	90.3	C11C7C6C4	-79.4
C12C11	1.462	C12C11C10	125.5	C12C11C10C5	82.3
C13C12	1.502	C13C12C11	118.9	O13C12C11C10	4.3
C14C12	1.341	C14C12C11	119.4	C14C13C11C10	-175.3
H15C10	1.081	H15C10C11	121.1	H15C10C11C12	179.1
H16C10	1.081	H16C10C11	122.1	H16C10C11C12	-0.4
H17C11	1.086	H17C11C12	115.6	H17C11C12C14	3.9
H18C13	1.091	H18C13C12	111.4	H18C13C12C14	121.6
H19C13	1.092	H19C13C12	110.6	H19C13C12C14	-119.2
H20C13	1.088	H20C13C12	110.8	H20C13C12C14	1.3
H21C14	1.083	H21C14C12	121.1	H21C14C12C11	-1.3
H22C14	1.081	H22C14C12	121.6	H22C14C12C11	179.1

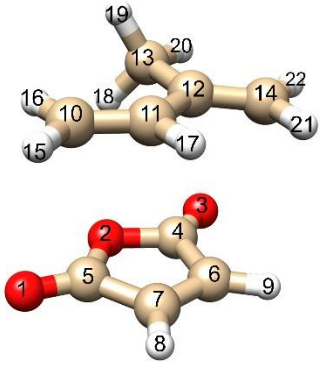


Table S5. CP-B2PLYP-D3(BJ)/def2-TZVP calculated geometries of isomer II.

Bond lengths (Å)		Valence angles (°)		Dihedral angles (°)	
O2O1	2.265				
O3O2	2.267	O3O2O1	161.2		
C4O3	1.193	C4O3O2	31.2	C4O3O2O1	1.0
C5O1	1.193	C5O1O2	31.2	C5O1O2C4	-0.9
C6C4	1.484	C6C4O3	130.0	C6C4O3O2	179.2
C7C5	1.485	C7C5O1	130.0	C7C5O1O2	-180.0
H8C6	1.078	H8C6C7	129.7	H8C6C7C5	179.8
H9C7	1.077	H9C7C5	122.1	H9C7C5O1	-0.03
C10H9	3.365	C10H9C7	89.4	C10H9C7C5	-68.0
C11C7	3.381	C11C7C6	96.6	C11C7C6C4	-89.6
C12C11	1.501	C12C11C10	121.6	C12C11C10H9	-83.7
C13C11	1.461	C13C11C10	119.7	O13C12C10H9	95.5
C14C13	1.337	C14C13C11	125.4	C14C13C11C10	-176.8
H15C10	1.082	H15C10C11	121.3	H15C10C11C13	-0.2
H16C10	1.082	H16C10C11	121.5	H16C10C11C13	179.9
H17C13	1.085	H17C13C11	115.7	H17C13C11C10	2.2
H18C12	1.088	H18C12C11	111.0	H18C12C11C10	-1.0
H19C12	1.092	H19C12C11	111.0	H19C12C11C10	-121.6
H20C12	1.093	H20C12C11	111.0	H20C12C11C10	119.6
H21C14	1.081	H21C14C13	121.0	H21C14C13C11	178.8
H22C14	1.082	H22C14C13	122.2	H22C14C13C11	-1.1

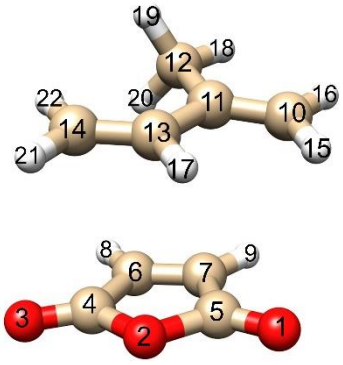


Table S6. Intensities (in arbitrary units) of isomers I and II for several selected μ_c-type transitions.

Transitions	Isomers	Frequencies	Intensities
$3_{3\,0} \leftarrow 2_{2\,0}$	I	6470.2680	0.0093
	II	6796.8591	0.0036
$4_{3\,1} \leftarrow 3_{2\,1}$	I	7898.8750	0.0107
	II	8100.0479	0.004
$5_{3\,2} \leftarrow 4_{2\,3}$	I	9336.7572	0.0225
	II	9362.9912	0.0067
$5_{3\,3} \leftarrow 4_{2\,3}$	I	9715.5975	0.0227
	II	9624.2973	0.0083
$5_{4\,1} \leftarrow 4_{3\,1}$	I	10248.0416	0.0107
	II	10598.6617	0.0033
$5_{4\,2} \leftarrow 4_{3\,2}$	I	10314.4195	0.0079
	II	10616.9940	0.0024
$6_{4\,3} \leftarrow 5_{3\,3}$	I	11864.8182	0.0115
	II	11979.5889	0.0035
$6_{5\,1} \leftarrow 5_{4\,1}$	I	12575.2411	0.009
	II	13062.1782	0.0028

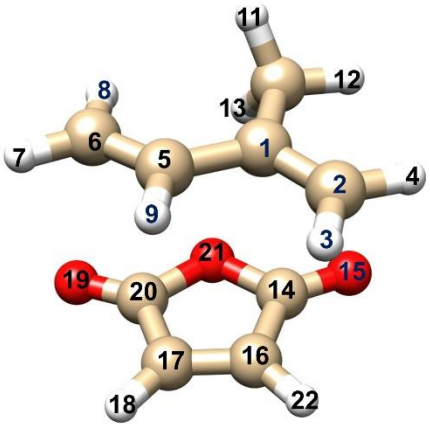
Table S7. SAPT analysis (all values in kJ mol^{-1}).

	Electrostatic	Induction	Dispersion	Exchange	Total
ISO-MA- Ⅰ	-19.4 (**33.2%**)[a]	-5.2 (**8.8%**)	-33.9 (**58.0%**)	35.1	-23.4
ISO-MA- Ⅱ	-19.4 (**34.0%**)	-4.9 (**8.6%**)	-32.7 (**57.4%**)	34.6	-22.4
$(Dibenzofuran)_2$	-29.5(**25.2%**)	-6.7(**5.7%**)	-80.9(**69.1%**)	65.6	-51.5
$(Benzene)_2$	-9.2(**20.8%**)	-2.6(**5.8%**)	-32.47(**73.4%**)	33.5	-27.7

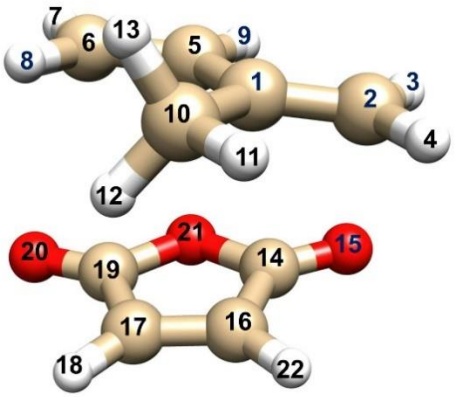
[a] Percentage contribution to total attracting energy.

Table S8. Stabilization energy contributions ($E^{(2)} \geq$ 0.40 kJ mol^{-1}) for isomers I and II of ISO-MA.

Isomer I		
Donor NBO	Acceptor NBO	$E^{(2)}$[kJ mol^{-1}]
from ISO to MA		
BD (2) C1 - C2	RY*(3) C16	0.75
BD (2) C1 - C2	BD*(2) C14 - O15	1.59
BD (2) C1 - C2	BD*(2) C16 – C17	3.09
BD (2) C5 - C6	BD*(2) C16 - C17	1.17
BD (2) C5 - C6	BD*(2) C19 - O20	1.80
from MA to ISO		
BD (2) C16 - C17	BD*(2) C5 - C6	1.46
BD (2) C19 - O20	BD*(2) C5 - C6	0.71
LP (2) O21	BD*(1) C10 - H13	0.46
Isomer II		
Donor NBO	Acceptor NBO	$E^{(2)}$[kJ mol^{-1}]
from ISO to MA		
BD (2) C1 - C2	RY*(3) C16	0.67
BD (2) C1 - C2	BD*(2) C16 – C17	3.47
BD (1) C5 - C6	RY*(8) C19	0.50
BD (2) C5 - C6	BD*(2) C14 - O15	0.54
BD (2) C5 - C6	BD*(2) C16 - C17	0.54
BD (2) C5 - C6	BD*(2) C19 - O20	2.38
from MA to ISO		
BD (2) C16 - C17	BD*(2) C1 - C2	0.92
BD (2) C19 - O20	BD*(2) C5 - C6	0.54



Isomer I



Isomer II