Electronic Supplementary Material (ESI) for RSC Advances

SUPPORTING INFORMATION

Understanding the local reactivity in polar organic reactions through electrophilic and nucleophilic Parr functions*

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S2 Complete citation for reference 24.

S3 **Table S1**. B3LYP/6-31G* total and relative energies of the stationary points involved in the polar Diels-Alder reactions of captodative ethylene **5** with enamine **12**.

S4 B3LYP/6-31G* computed total energies, unique imaginary frequency, and cartesian coordinates of the stationary points involved in the polar Diels-Alder reactions of captodative ethylene **5** with enamine **12**.

Complete citation for reference 24

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09, Revision A.01, Gaussian, Inc., Wallingford CT, **2009**.

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Table S1. B3LYP/6-31G* total (E, in au) and relative (ΔE, in kcal mol^{-1}, relative to **5**+**12**) energies of the stationary points involved in the polar Diels-Alder reactions of captodative ethylene **5** with enamine **12**.

	E	ΔE
5	-417.057179	
12	-212.562347	
TS3no	-629.600898	11.7
TS3nm	-629.570572	30.7
CA3no	-629.647366	-17.5
CA3nm	-629.632726	-8.3

B3LYP/6-31G* computed total energies, unique imaginary frequency, and cartesian coordinates of the stationary points involved in the polar Diels-Alder reactions of captodative ethylene **5** with enamine **12**.

5
E(RB3LYP) = -417.057179332 A.U.

O	2.38440700	0.31031600	0.29080700
N	1.35644100	-0.22294900	-0.11799600
C	0.06721900	0.53851600	0.04346700
C	0.18056500	1.86143600	0.22547300
H	-0.69505000	2.48216800	0.36941700
H	1.15276900	2.33326000	0.21540400
N	-1.07312300	-0.21543500	-0.15480900
O	1.30471500	-1.32626000	-0.65601700
C	-2.28654300	0.53082100	-0.45306000
H	-2.08426000	1.26010100	-1.24235500
H	-3.04782300	-0.17025300	-0.80834100
H	-2.69502100	1.06332400	0.42314900
C	-1.30008600	-1.38141100	0.70518600
H	-2.02485000	-2.04108000	0.21880000
H	-0.37359200	-1.93792500	0.83748800
H	-1.69530500	-1.08952400	1.69135700

12
E(RB3LYP) = -212.562346657 A.U.

C	-2.00298300	-0.11135000	0.12127200
H	-2.14806300	0.94851400	0.29905700
H	-2.88881700	-0.73617200	0.12072200
C	-0.80244000	-0.66415100	-0.12033200
H	-0.72955200	-1.74060700	-0.27029700
N	0.42131700	-0.02108400	-0.25999100
C	1.60716000	-0.76190500	0.13953900
H	1.52020200	-1.80042900	-0.19546600
H	1.76894900	-0.76784700	1.23170800
C	0.46474300	1.40520000	-0.00481700
H	-0.28574400	1.91218500	-0.61985400
H	0.27005600	1.65879500	1.05216200
H	2.49343300	-0.32504000	-0.33388100
H	1.45143800	1.79142400	-0.27818900

TS3no
E(RB3LYP) = -629.600897601 A.U.
1 imaginary frequency -354.0205 cm-1

C	0.00000000	0.00000000	0.00000000
H	0.00000000	0.00000000	1.08589739
H	0.99652138	0.00000000	-0.43438132
C	-0.93896564	-0.77936757	-0.68896669
H	-0.78273957	-0.94291908	-1.75095941
N	-2.06584994	-1.34849496	-0.22401016
C	-3.10620748	-1.69956135	-1.18755362
H	-2.64849824	-2.04989299	-2.11600179
H	-3.70780343	-0.80613559	-1.40643207
C	-2.55603676	-1.17326491	1.13684110
H	-1.73390248	-0.95484264	1.81912231
H	-3.29114297	-0.35745894	1.17794291
O	-2.54749605	1.28740970	-1.63239933
N	-2.75240181	1.88053360	-0.52955475

C	-1.63493049	2.35158501	0.17102713
C	-0.38751452	1.95513357	-0.33904275
H	0.49029944	2.34698789	0.16870615
H	-0.29266641	1.89443797	-1.41524580
H	-3.73324454	-2.49630041	-0.77738069
H	-3.04300688	-2.09893243	1.46187835
N	-1.85052128	3.05211686	1.36674668
O	-3.90000196	1.96982793	-0.02823255
C	-0.83284283	4.01892100	1.73596650
H	-0.52945543	4.59070317	0.85400001
H	-1.25259898	4.71510475	2.47190221
H	0.07207990	3.56935429	2.18757386
C	-2.43676899	2.35547561	2.50674219
H	-2.78277290	3.09615486	3.23664625
H	-3.30152104	1.78317418	2.16979670
H	-1.72018511	1.68623952	3.01900931

TS3nm

E(RB3LYP) = -629.570571916 A.U.

1 imaginary frequency -448.6929 cm-1

C	0.00000000	0.00000000	0.00000000
H	0.00000000	0.00000000	1.08708603
H	1.00431257	0.00000000	-0.41442919
C	-0.89499194	-0.93576449	-0.63043138
H	-0.58883851	-1.44681437	-1.53495387
N	-1.92529346	-1.52484560	0.04830585
C	-2.90900675	-2.24801753	-0.73595802
H	-2.40485359	-2.83385713	-1.51162664
H	-3.61485774	-1.56306257	-1.23460718
C	-2.29745579	-1.07919908	1.38694485
H	-1.53802192	-1.39045595	2.11552795
H	-2.39927489	0.01947349	1.45889385
C	-2.43511996	1.50248188	-1.20642244
C	-1.81301574	0.76660244	-2.20988296
H	-0.77359609	0.92583704	-2.44620160
H	-2.42579017	0.33400896	-2.99318016
N	-1.64074903	1.91399638	-0.14760072
O	-0.35043377	1.59236223	-0.30834450
H	-3.46892732	-2.93466874	-0.09607515
H	-3.24266786	-1.54998035	1.66357553
N	-3.78834857	1.81058654	-1.19409408
C	-4.65379142	1.49667411	-0.05773421
H	-4.09507951	1.63820489	0.86454007
H	-5.51165169	2.17838866	-0.07018855
H	-5.03994778	0.46355020	-0.11152584
C	-4.48301087	1.81031410	-2.47067730
H	-3.84469607	2.24099939	-3.24590484
H	-4.80115818	0.80407290	-2.79684608
H	-5.38426973	2.42688312	-2.37802249
O	-2.07351016	2.12543492	1.04300442

CA3no

E(RB3LYP) = -629.647366379 A.U.

C	0.53798200	1.68768300	0.65400000
H	0.38582800	1.22458100	1.63258900
H	0.90485900	2.70334000	0.83850900
C	1.58717400	0.91251600	-0.16245800
H	2.19640100	1.61579000	-0.73762700
N	2.48238200	0.11066500	0.61235900
C	3.65719800	-0.32303900	-0.14580600
H	4.12662100	0.54231400	-0.62584100
H	3.41530700	-1.06484800	-0.92313900
C	1.88455700	-1.01970200	1.32909500
H	1.06322200	-0.68444900	1.96890800
H	1.50155300	-1.79596800	0.64937500

O	0.91823600	0.20147700	-1.27747100
N	-0.30248800	-0.48929500	-0.92041000
C	-1.21688200	0.28621800	-0.37690900
C	-0.80074000	1.71311100	-0.10831300
H	-1.56317700	2.22130700	0.48647800
H	-0.68457100	2.27332400	-1.04507600
H	4.38510700	-0.76498100	0.54297200
H	2.64670300	-1.46261500	1.97877600
N	-2.43912800	-0.25878700	-0.00148800
O	-0.33282400	-1.71726700	-1.17483800
C	-3.55487400	0.64400400	0.21128500
H	-3.56928400	1.42237900	-0.55666500
H	-4.48529800	0.07226400	0.12461100
H	-3.55245600	1.12840200	1.20425700
C	-2.46248100	-1.47693900	0.80503400
H	-3.43427900	-1.96653200	0.68098400
H	-1.68131400	-2.15274100	0.45237200
H	-2.31547800	-1.26644400	1.87819100

CA3nm

E(RB3LYP) = -629.632726347 A.U.

C	-1.04385600	-1.71162900	-0.03062500
H	-0.93787100	-1.62769000	1.05751600
H	-1.76579400	-2.49829000	-0.26492600
C	-1.44348600	-0.33665500	-0.62853000
H	-2.18136000	-0.48504100	-1.44316700
N	-2.01661500	0.52728700	0.41658000
C	-2.37452300	1.85920300	-0.06711400
H	-3.08075000	1.83728100	-0.92042100
H	-1.48945000	2.42462900	-0.36832100
C	-3.20430900	-0.09123600	1.00962300
H	-4.01941600	-0.24682700	0.27542300
H	-2.96161700	-1.05869000	1.45614400
C	1.06773400	-0.04065600	-0.43499400
C	-0.15206200	0.23551500	-1.27793300
H	-0.04290100	-0.25942200	-2.24971000
H	-0.24653900	1.30169900	-1.47554200
N	1.27654300	-1.30434500	-0.12622100
O	0.19277500	-2.17730500	-0.58322400
H	-2.85011500	2.41443100	0.74743300
H	-3.58650800	0.55234800	1.80826000
N	1.95680900	0.91879400	0.02836500
C	2.26601400	0.93555800	1.45801700
H	2.40882300	-0.09054400	1.80372700
H	3.19666700	1.49105500	1.61272300
H	1.46627900	1.41461700	2.04572000
C	1.98179200	2.21328100	-0.62549500
H	1.94281200	2.09509400	-1.71210600
H	1.16203200	2.88472900	-0.31255700
H	2.92683300	2.70859600	-0.37850700
O	2.17696200	-1.85149700	0.54191700