Supporting Information

Spin-Coupled Study of the Electronic Mechanism of the Hetero-Diels-Alder Reaction of Acrolein and Ethene

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Supplementary Information: Numerical data used to construct Figure 4.

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Table S1. Evolution of overlap integrals $\langle\psi_\mu|\psi_\nu\rangle$ between nearest-neighbor active SC orbitals along the MP2/6-31G(d) IRC for the gas-phase cycloaddition reaction of *s-cis*-acrolein and ethene. These data are illustrated in Figure 4a, with the numbering scheme and phases of the orbitals shown in Figure 3. The corresponding overlap integrals in isolated *s-cis*-acrolein, (with $P_1^{CC} = 0.938$) are $\langle\psi_1|\psi_2\rangle = 0.623$, $\langle\psi_3|\psi_4\rangle = 0.632$ and $\langle\psi_2|\psi_3\rangle = 0.307$.

R_{IRC} (amu^{½}bohr)	$\langle\psi_1\|\psi_2\rangle$	$\langle\psi_3\|\psi_4\rangle$	$\langle\psi_5\|\psi_6\rangle$	$\langle\psi_4\|\psi_5\rangle$	$\langle\psi_2\|\psi_3\rangle$	$\langle\psi_1\|\psi_6\rangle$
–1.19482	0.615	0.631	0.626	0.284	0.338	0.175
–0.89489	0.613	0.631	0.625	0.298	0.347	0.190
–0.59503	0.612	0.631	0.624	0.309	0.358	0.207
–0.29569	0.611	0.630	0.622	0.315	0.373	0.226
0	0.618	0.598	0.588	0.302	0.403	0.273
+0.09910	0.545	0.367	0.232	0.633	0.657	0.614
+0.29711	0.488	0.357	0.233	0.680	0.662	0.611
+0.59685	0.420	0.335	0.240	0.701	0.651	0.603
+0.89673	0.377	0.308	0.237	0.720	0.639	0.603
+1.19671	0.347	0.280	0.225	0.738	0.632	0.612

Table S2. Chirgwin-Coulson weights (P_k^{CC}) of the Rumer spin functions included in the active-space spin-coupling pattern for the gas-phase cycloaddition reaction of *s*-*cis*-acrolein and ethene. These data are illustrated in Figure 4b, with the Rumer functions $\Theta_{00;k}^{6}$ depicted in Figure 1 and the ordering of the orbitals shown in Figure 3.

R_{IRC} (amu^{½}bohr)	P_1^{CC}	P_2^{CC}	P_3^{CC}	P_4^{CC}	P_5^{CC}
–1.19482	0.798	0.076	0.076	0.032	0.018
–0.89489	0.760	0.078	0.097	0.044	0.022
–0.59503	0.710	0.079	0.122	0.061	0.028
–0.29569	0.645	0.080	0.152	0.087	0.035
0	0.499	0.067	0.213	0.162	0.059
+0.09910	0.163	0.066	0.212	0.462	0.097
+0.29711	0.132	0.059	0.198	0.531	0.080
+0.59685	0.092	0.045	0.161	0.644	0.057
+0.89673	0.059	0.033	0.122	0.743	0.043
+1.19671	0.037	0.024	0.091	0.815	0.034

Table S3. Values of the generalized Wiberg indices (W_{AB}) for nearest-neighbor atoms, numbered as in Scheme 1. These data are illustrated in Figure 4c.

R_{IRC} (amu^{½}bohr)	W_{12}	W_{34}	W_{56}	W_{45}	W_{23}	W_{16}
–1.19482	0.666	0.663	0.733	0.075	0.120	0.031
–0.89489	0.648	0.634	0.702	0.104	0.137	0.042
–0.59503	0.625	0.594	0.661	0.144	0.160	0.059
–0.29569	0.592	0.543	0.605	0.200	0.191	0.083
0	0.507	0.427	0.473	0.335	0.274	0.155
+0.09910	0.340	0.266	0.301	0.528	0.438	0.303
+0.29711	0.294	0.218	0.246	0.595	0.488	0.355
+0.59685	0.228	0.157	0.176	0.687	0.562	0.434
+0.89673	0.174	0.109	0.121	0.764	0.625	0.507
+1.19671	0.134	0.075	0.082	0.824	0.671	0.566