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Corrigendum

Diels-Alder Transition State Geometry

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Our original surface for this concerted reaction [1] was constructed using a single determinant, *ab initio*, minimal basis set (STO-3G) LCAO method. The procedure consisted in optimizing first the bond lengths and then the bond angles for selected distances of the ethylene carbons to the terminal butadiene carbons (parameter, R_{16}). Our failure to reoptimize the bond lengths after finding a set of angles led to our being trapped in a false minimum.

The cause of this trap is the dependence of the bond lengths on the lowering of the internal butadiene hydrogens (parameters μ and ν). Inspection of the molecular orbital coefficients shows that this lowering causes a concentration of the butadiene π system on the central CC bond and a weakening of the ethylene π system.

A straightforward way to account for this dependence is to form a grid of points for a certain R_{16} where the angle μ is plotted against various sets of bond lengths (R_{12}, R_{23} and R_{56}). Fig. 1 is an isoenergetic contour diagram constructed from this grid wherein the set of bond lengths is represented by the ethylene bond length R_{56} (any of the three lengths could be used). After the best μ and set of bond lengths were found for various values of R_{16}, the other angles were optimized. After each parameter was optimized, μ was checked to see if there was an interdependence with another parameter. It was found that the only interdependence was that between μ (or ν) and the bond lengths.

Table 1 gives the values of the geometric parameters and the total energies for the chosen values of R_{16} (R_{45}). It is to be noted that the transition state is now at $R_{16} = 2.26 \pm 0.02$ Å and that its geometric parameters are more intermediate between product- and reactant-like structures than previously reported. The electronic properties remain similar to those found in the original study. For example, the centroids of charge [2] for points VI, VII and VIII retain their reactant-like aspect, and the charge transfer to ethylene, $t_{\text{eth.}}$ (Table 1), increases until just before the transition state. The activation energy, calculated as the energy difference between points VII and I (Table 1), is now 40.3 kcal/mole as opposed to 44.6 kcal/mole found in the original study (STO-3G results).

Table 1. Geometric parameters (defined in Ref. [1]) for several points along the reaction path

State	$R_{16} = R_{45}$ (Å)	R_{12} (Å)	R_{23} (Å)	R_{56} (Å)	α (°)	β (°)	γ (°)	ϵ (°)	δ (°)	μ (°)	ν (°)	E_T (a.u.)	$t_{eth.}$
I	5.000	1.314	1.497	1.310	72	0	126	0	0	0	0	−230.088419	0.0000
II	3.167	1.314	1.497	1.310	72	0	126	0	0	0	0	−230.087223	0.0002
III	2.867	1.314	1.497	1.310	72	0	126	0	0	0	0	−230.077537	−0.0040
IV	2.567	1.314	1.497	1.310	72	0	123	0	0	0	0	−230.058055	0.0000
V	2.367	1.330	1.465	1.330	70	0	123	5	5	15	15	−230.038375	−0.0207
VI	2.300	1.350	1.455	1.350	66	5	120	12	8	22	25	−230.024376	−0.0207
VII	2.240	1.375	1.410	1.380	62	5	120	17	13	30	32	−230.024174	−0.0119
VIII	2.200	1.375	1.410	1.380	62	5	120	17	13	35	37	−230.026651	0.0016
IX	2.167	1.400	1.360	1.410	62	5	120	17	13	35	37	−230.031781	0.0119
X	1.504	1.504	1.325	1.542	0	15	122	0	120	105	135	−230.255489	–

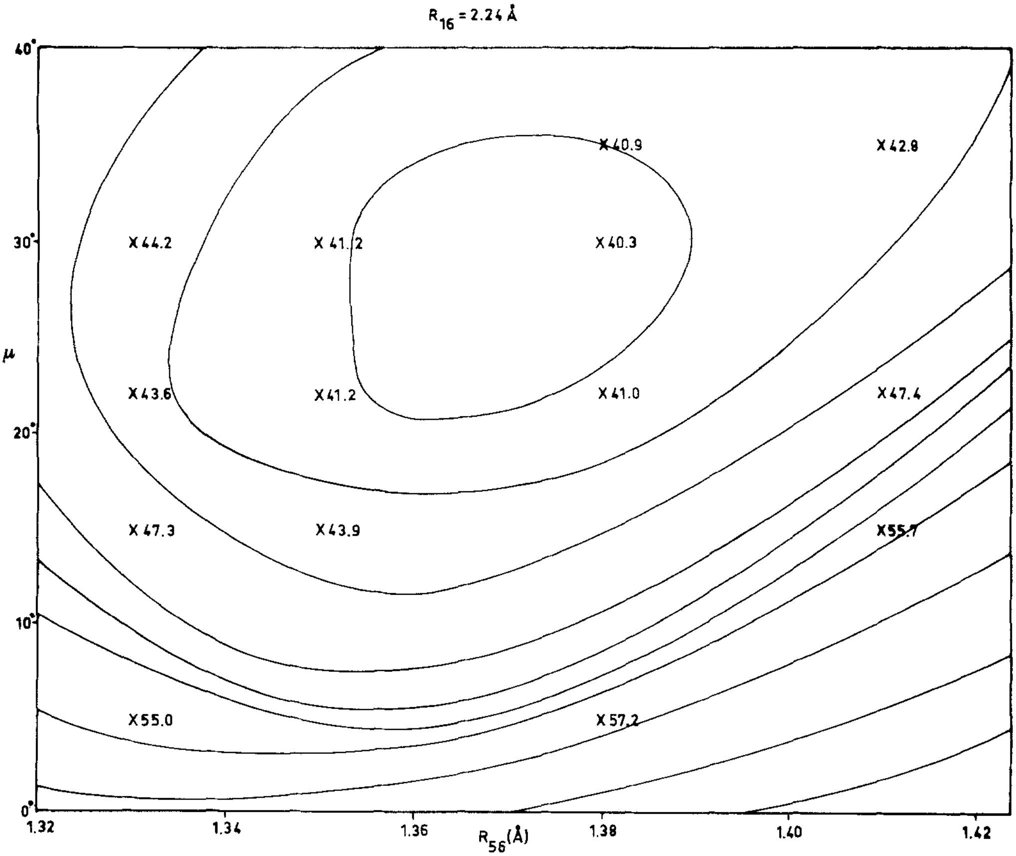

Fig. 1. An isoenergetic contour diagram comparing angle μ with the ethylenic bond length, R_{56} (Å) at $R_{16} = R_{45} = 2.240$ Å. Each line represents a change of 2.5 kcal/mole. The numbers indicated are the differences in energy (kcal/mole) between a particular point and the supermolecule at $R_{16} = 5.0$ Å.

In a similar study of the Diels-Alder reaction Salem and coworkers [3] found the concerted transition state to be geometrically similar to product cyclohexene with R_{16} = 2.21 Å. The reason for this discrepancy may be in part due to the difference in methods employed for constructing the hypersurfaces, theirs being an SCF (STO-3G) plus a (3 x 3) configuration interaction method and ours being only an SCF (STO-3G) method. We are at present investigating the influence of various limited configuration interactions on the geometry of the transition state and on the value of the activation energy.

References

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