Single-Electron Induces Double-Reaction by Charge Delocalization

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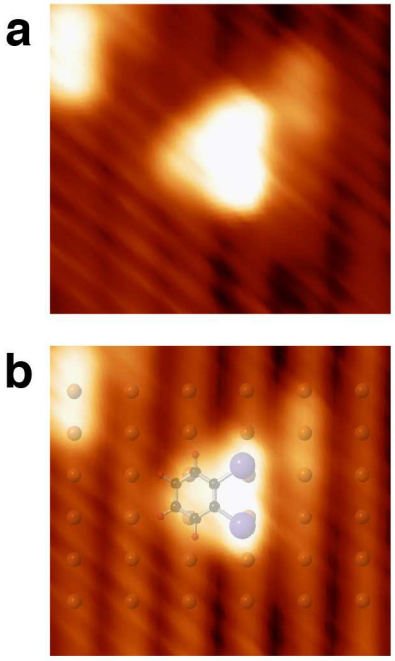
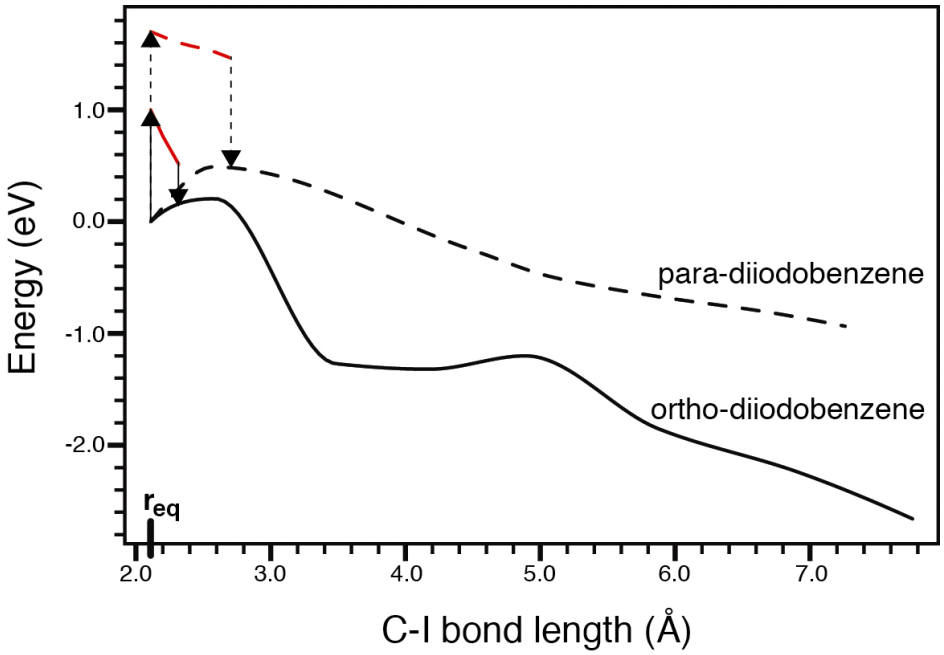
Supporting notes:

Supporting Figure S1. Experimental STM image of the initial state. (a) STM image of the physisorbed o-DIB on the Cu surface. (b) The same image as (a) after Fourier filtering to enhance the location of the Cu rows with an overlay of the calculated geometry. The STM image (2.0 nm × 1.7 nm) was taken at 0.3 nA and + 0.2 V.



Supporting Figure S2. Comparison of ground state barrier heights and exothermicity of para-DIB against ortho-DIB reaction.

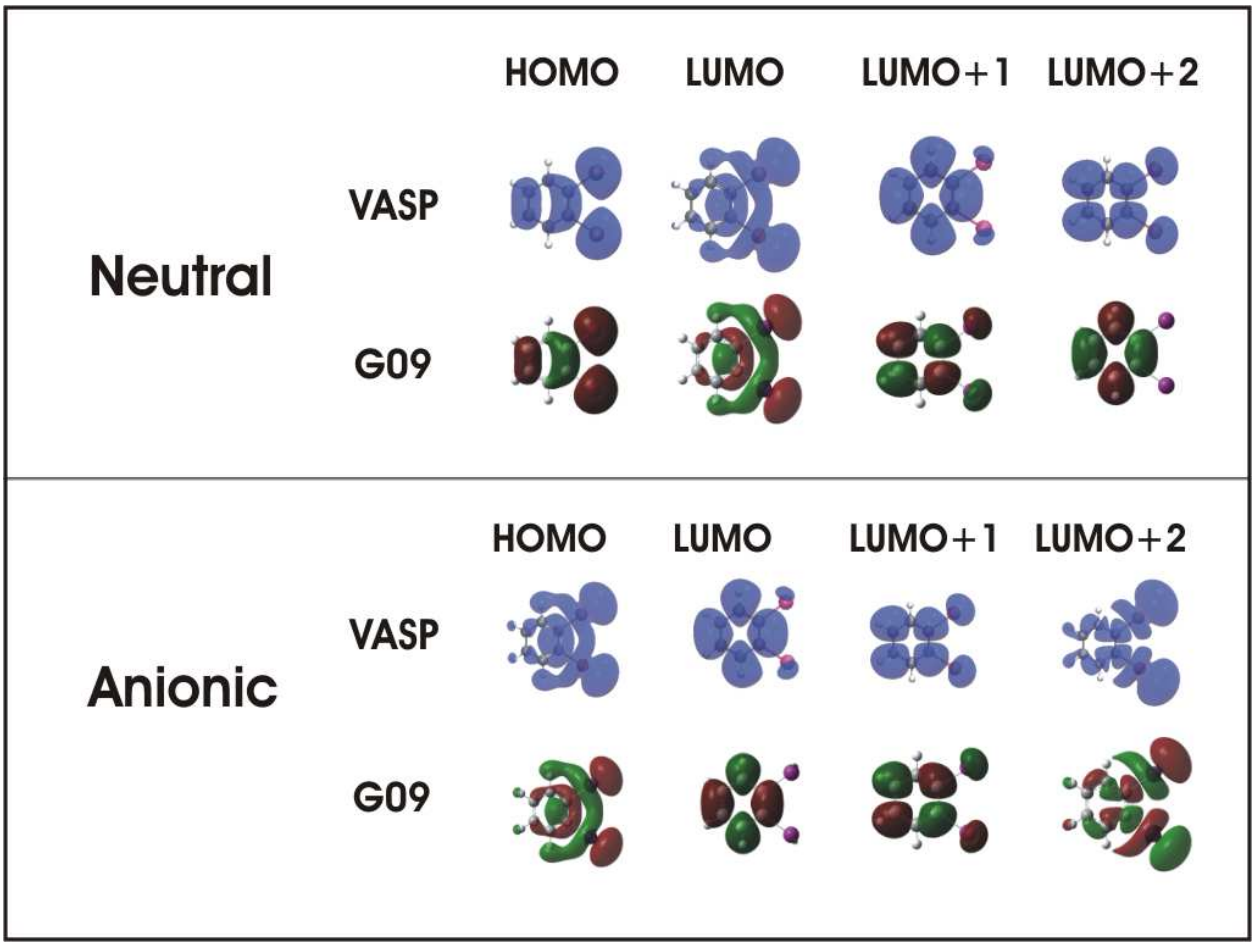


The figure above illustrates graphically the minimum energy pathways for para-DIB in breaking one C-I bond (dashed lines) and ortho-DIB in breaking two C-I bonds (solid lines), plotted along the C-I bond length. The red curves represent the modeled ionic trajectories taken by ortho-DIB (solid red) and para-DIB (dashed red) when half an electron is added on each I-atom using the ionic psedopotential method.

Comparing anionic models obtained from pseudopotential method against corresponding anionic state in Gaussian09

As a more rigorous check on the ionic pseudopotential method, the anionic state of molecular ortho-DIB was modeled using the ionic pseudopotential method in VASP and was compared with the calculated anionic state in Gaussian09. The neutral ground state and negative ionic state of $(\text{ortho-DIB})^-$ were calculated using the PBE functional with all-electron atomic basis sets (6-311G** for C,H and MidiX for I) in Gaussian09 and PAW potential in VASP respectively. The ionic pseudopotential was constructed with ionic configuration $4d^{9.5}5s^{2}5p^{5.5}$ and applied to both iodine atoms in the ortho-DIB molecule (ionic charge $Q1=Q2=0.5e^-$). We compared the optimized molecular orbitals, C-I bond lengths and energy gaps in VASP and Gaussian09 as follows:

Supporting Figure S3. Molecular orbital of neutral ground state and anionic state for the isolated ortho-DIB molecule calculated both in VASP and Gaussian09



Supporting Table S1. C-I bond-length (Å) in ortho-DIB and $(\text{ortho-DIB})^-$

	VASP	Gaussian09
Neutral	2.10	2.10
Anionic	2.43	2.37

Supporting Table S2. The comparison of energy gaps (eV). In the table below, we show the changes of energy gaps between neutral ground-state and the ionic state. The ionic pseudopotential approach shows consistency with the all-electron calculation at least in the level of HOMO-LUMO gap (note: H = HOMO, L = LUMO).

	Neutral			Anionic		
Gaps(eV)	H-L	L-(L+1)	(L+1)-(L+2)	H-L	L-L+1	(L+1)-(L+2)
VASP	3.50	0.59	0.02	1.06	0.01	0.13
G09	3.52	0.58	0.02	1.08	0.08	0.91

Supporting Movie S1 is available online separately.