

Electronic Supplementary Information (ESI) for the manuscript:

Nucleophilicity and electrophilicity of the C(*sp*³)–H bond: methane and ethane binary complexes with iodine

Alberto Baggioli, Stefano V. Meille, Antonino Famulari

Dipartimento di Chimica, Materiali e Ingegneria Chimica “G. Natta”, Politecnico di Milano, via Mancinelli 7, I-20131 Milano, Italia.

Content:

Results of a Natural Bond Orbital (NBO) analysis carried out on each of the complexes discussed.

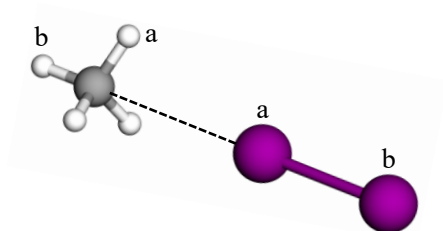
For each complex, Cartesian coordinates of the equilibrium geometry and atom labelling is also listed.

E⁽²⁾ refers to the second order perturbation energy, reported in kcal mol^{−1}, associated with electron density delocalization from a high occupancy natural bond orbital from a low occupancy one; ΔN_D and ΔN_A refer to the occupancy change of the donor and acceptor orbitals respectively, relative to the occupancy of the same orbital in the isolated molecule, reported in atomic units.

Symmetry-related multiplicity is explicitly marked (*e.g.* ^{×2}, ^{×3}).

<i>complex M1</i>	S2
<i>complex M2</i>	S3
<i>complex M3</i>	S4
<i>complex E1</i>	S5
<i>complex E2</i>	S6
<i>complex E3</i>	S7
<i>complex E4</i>	S8

Complex M1



C	0.116447	-0.006213	-0.112354
H	1.082574	-0.231964	0.327029
H	0.207317	-0.010921	-1.193093
H	-0.607812	-0.756637	0.187197
H	-0.214876	0.974601	0.212686
I	-0.180510	0.009679	3.431860
I	-0.403140	0.021455	6.086680

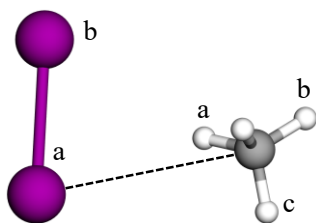
From methane to iodine

donor → acceptor	$E^{(2)}$	ΔN_D	ΔN_A
$\sigma(C-H_a) \rightarrow \sigma^*(I-I) \times 3$	0.24	-1.46×10^{-3}	$+5.85 \times 10^{-3}$
$\sigma(C-H_b) \rightarrow \sigma^*(I-I)$	0.11	-2.93×10^{-3}	$+5.85 \times 10^{-3}$
$\sigma(C-H_a) \rightarrow Ry^*(I_a) \times 3$	0.08	-1.46×10^{-3}	$+0.73 \times 10^{-3}$

From iodine to methane

donor → acceptor	$E^{(2)}$	ΔN_D	ΔN_A
$\sigma(I-I) \rightarrow Ry^*(C)$	0.69	-1.70×10^{-3}	$+1.05 \times 10^{-3}$
$LP(I_a) \rightarrow \sigma^*(C-H_b)$	0.37	-1.70×10^{-3}	$+1.33 \times 10^{-3}$
$\sigma(I-I) \rightarrow \sigma^*(C-H_b)$	0.12	-1.70×10^{-3}	$+1.33 \times 10^{-3}$

Complex M2



C	-0.047323	0.081763	0.226979
H	0.244158	-0.424301	1.140884
H	0.836758	0.319723	-0.354357
H	-0.694794	-0.564501	-0.355516
H	-0.575637	0.996517	0.472366
I	0.783309	-1.356473	-3.662486
I	-0.546473	0.947272	-3.747864

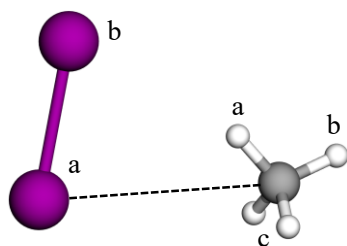
From methane to iodine

donor → acceptor	$E^{(2)}$	ΔN_D	ΔN_A
$\sigma(C-H_a) \rightarrow Ry^*(I_b) \times 2$	0.09	-0.43×10^{-3}	$+0.31 \times 10^{-3}$
$\sigma(C-H_a) \rightarrow Ry^*(I_a) \times 2$	0.05	-0.43×10^{-3}	$+0.17 \times 10^{-3}$

From iodine to methane

donor → acceptor	$E^{(2)}$	ΔN_D	ΔN_A
$LP(I_a) \rightarrow \sigma^*(C-H_b)$	0.24	-0.76×10^{-3}	$+0.09 \times 10^{-3}$
$\sigma(I-I) \rightarrow Ry^*(C)$	0.18	-1.44×10^{-3}	$+0.47 \times 10^{-3}$
$\sigma(I-I) \rightarrow Ry^*(H_a) \times 2$	0.18	-1.44×10^{-3}	$+0.51 \times 10^{-3}$

Complex M3



C	-0.091546	-0.003778	0.228527
H	0.433051	0.216922	1.151632
H	-0.487566	-1.012575	0.268921
H	-0.907322	0.698848	0.098291
H	0.592794	0.080609	-0.608559
I	-0.731893	-0.571463	-3.888542
I	1.849874	0.071972	-3.786113

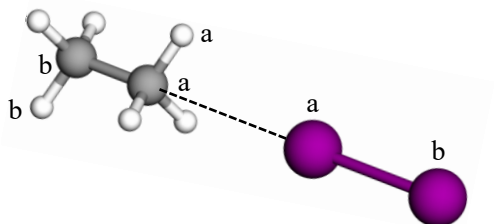
From methane to iodine

donor → acceptor	$E^{(2)}$	ΔN_D	ΔN_A
$\sigma(C-H_a) \rightarrow Ry^*(I_b)$	0.29	-0.92×10^{-3}	$+0.51 \times 10^{-3}$
$\sigma(C-H_a) \rightarrow Ry^*(I_a)$	0.09	-0.92×10^{-3}	$+0.18 \times 10^{-3}$

From iodine to methane

donor → acceptor	$E^{(2)}$	ΔN_D	ΔN_A
$\sigma(I-I) \rightarrow Ry^*(H_a)$	0.65	-1.54×10^{-3}	$+1.36 \times 10^{-3}$
$LP(I_b) \rightarrow \sigma^*(C-H_a)$	0.50	-1.23×10^{-3}	$+1.30 \times 10^{-3}$
$LP(I_a) \rightarrow \sigma^*(C-H_b)$	0.18	-0.58×10^{-3}	$+0.51 \times 10^{-3}$
$LP(I_b) \rightarrow Ry^*(H_a)$	0.08	-1.23×10^{-3}	$+1.36 \times 10^{-3}$
$\sigma(I-I) \rightarrow Ry^*(C)$	0.07	-1.54×10^{-3}	$+0.21 \times 10^{-3}$

Complex E1



C	-0.000005	0.000003	0.027730
C	0.000003	-0.000002	1.547144
H	1.016301	0.000004	-0.360898
H	-0.508161	-0.880144	-0.360893
H	-0.508161	0.880152	-0.360887
H	-1.013919	-0.000003	1.938088
H	0.506967	-0.878087	1.938077
H	0.506967	0.878081	1.938083
I	0.000001	-0.000001	-3.501875
I	0.000009	-0.000005	-6.166567

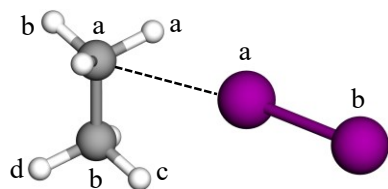
From ethane to iodine

donor → acceptor	$E^{(2)}$	ΔN_D	ΔN_A
$\sigma(C_a-H_a) \rightarrow \sigma^*(I-I) \times 3$	0.28	-1.56×10^{-3}	$+6.81 \times 10^{-3}$
$\sigma(C_a-H_a) \rightarrow Ry^*(I_a) \times 3$	0.09	-1.56×10^{-3}	$+0.88 \times 10^{-3}$

From iodine to ethane

donor → acceptor	$E^{(2)}$	ΔN_D	ΔN_A
$\sigma(I-I) \rightarrow Ry^*(C)$	0.73	-1.94×10^{-3}	$+0.11 \times 10^{-3}$
$LP(I_a) \rightarrow \sigma^*(C-C)$	0.40	-1.06×10^{-3}	$+1.50 \times 10^{-3}$
$\sigma(I-I) \rightarrow \sigma^*(C-C)$	0.16	-1.94×10^{-3}	$+1.50 \times 10^{-3}$

Complex E2



C	-0.208587	0.000000	-0.041368
C	0.039912	0.000000	1.456668
H	0.725824	0.000000	-0.597436
H	-0.773065	-0.878117	-0.343839
H	-0.773064	0.878118	-0.343839
H	-0.894278	0.000000	2.012935
H	0.597899	-0.882437	1.765291
H	0.597898	0.882438	1.765290
I	3.587385	0.000000	1.259511
I	6.215079	0.000000	0.816791

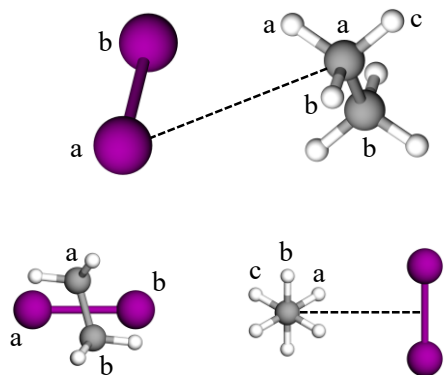
From ethane to iodine

donor → acceptor	$E^{(2)}$	ΔN_D	ΔN_A
$\sigma(C_a-H_a) \rightarrow \sigma^*(I-I) \times 2$	0.47	-3.30×10^{-3}	$+8.07 \times 10^{-3}$
$\sigma(C_a-H_a) \rightarrow Ry^*(I_a) \times 2$	0.24	-3.30×10^{-3}	$+1.37 \times 10^{-3}$
$\sigma(C_b-H_c) \rightarrow Ry^*(I_a)$	0.20	-0.75×10^{-3}	$+0.24 \times 10^{-3}$
$\sigma(C_a-H_b) \rightarrow \sigma^*(I-I)$	0.10	-2.11×10^{-3}	$+8.07 \times 10^{-3}$

From iodine to ethane

donor → acceptor	$E^{(2)}$	ΔN_D	ΔN_A
$\sigma(I-I) \rightarrow Ry^*(C_a)$	0.47	-1.54×10^{-3}	$+0.73 \times 10^{-3}$
$LP(I_a) \rightarrow \sigma^*(C_a-H_a) \times 2$	0.26	-0.66×10^{-3}	$+0.70 \times 10^{-3}$
$LP(I_a) \rightarrow \sigma^*(C_b-H_c)$	0.17	-0.70×10^{-3}	$+0.27 \times 10^{-3}$
$LP(I_a) \rightarrow \sigma^*(C_b-H_d) \times 2$	0.11	-0.65×10^{-3}	-0.28×10^{-3}
$\sigma(I-I) \rightarrow Ry^*(H_a) \times 2$	0.08	-1.54×10^{-3}	$+0.30 \times 10^{-3}$
$\sigma(I-I) \rightarrow \sigma^*(C_a-H_b)$	0.08	-1.54×10^{-3}	$+1.11 \times 10^{-3}$
$LP(I_a) \rightarrow \sigma^*(C_a-H_b)$	0.06	-0.70×10^{-3}	$+1.11 \times 10^{-3}$

Complex E3



C	0.021728	0.406067	-0.063581
C	0.093446	-0.219577	1.317696
H	0.862319	1.073816	-0.236497
H	0.038371	-0.354639	-0.840704
H	-0.891423	0.983257	-0.187016
H	-0.752336	-0.880190	1.494089
H	1.000702	-0.806872	1.436860
H	0.086277	0.541338	2.094446
I	-0.615637	-3.701025	-0.673715
I	-2.907577	-2.349403	-0.708239

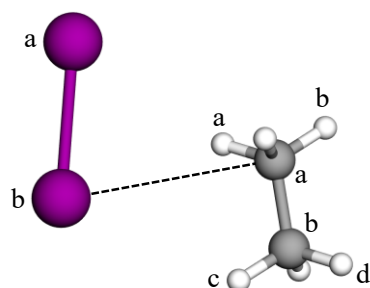
From ethane to iodine

donor → acceptor	$E^{(2)}$	ΔN_D	ΔN_A
$\sigma(C_a-H_a) \rightarrow Ry^*(I_b) \times 2$	0.20	-0.68×10^{-3}	$+0.38 \times 10^{-3}$
$\sigma(C_a-H_a) \rightarrow Ry^*(I_a) \times 2$	0.11	-0.68×10^{-3}	$+0.60 \times 10^{-3}$

From iodine to ethane

donor → acceptor	$E^{(2)}$	ΔN_D	ΔN_A
$\sigma(I-I) \rightarrow Ry^*(H_a) \times 2$	0.43	-2.57×10^{-3}	$+1.02 \times 10^{-3}$
$LP(I_a) \rightarrow \sigma^*(C_a-H_a) \times 2$	0.29	-1.17×10^{-3}	$+0.87 \times 10^{-3}$
$LP(I_a) \rightarrow \sigma^*(C_a-H_c) \times 2$	0.17	-1.17×10^{-3}	$+0.44 \times 10^{-3}$
$\sigma(I-I) \rightarrow Ry^*(C) \times 2$	0.10	-2.57×10^{-3}	$+0.31 \times 10^{-3}$

Complex E4



C	0.419945	0.638432	0.218085
C	-0.213251	-0.265626	1.260310
H	1.125000	0.090363	-0.402504
H	-0.331796	1.066224	-0.441076
H	0.958000	1.460107	0.684830
H	-0.750356	-1.086016	0.790424
H	0.538445	-0.695404	1.917713
H	-0.920068	0.281600	1.879090
I	0.248954	0.217915	-3.940252
I	-1.074871	-1.707594	-2.666616

From ethane to iodine

donor → acceptor	$E^{(2)}$	ΔN_D	ΔN_A
$\sigma(C_b-H_c) \rightarrow Ry^*(I_b)$	0.19	-0.59×10^{-3}	$+0.44 \times 10^{-3}$
$\sigma(C_a-H_a) \rightarrow Ry^*(I_a) \times 2$	0.13	-0.54×10^{-3}	$+0.54 \times 10^{-3}$
$\sigma(C_a-H_a) \rightarrow Ry^*(I_b) \times 2$	0.08	-0.54×10^{-3}	$+0.23 \times 10^{-3}$

From iodine to ethane

donor → acceptor	$E^{(2)}$	ΔN_D	ΔN_A
$\sigma(I-I) \rightarrow Ry^*(C_a)$	0.34	-1.98×10^{-3}	$+0.78 \times 10^{-3}$
$LP(I_b) \rightarrow \sigma^*(C_a-H_b)$	0.25	-1.39×10^{-3}	$+0.54 \times 10^{-3}$
$LP(I_b) \rightarrow \sigma^*(C_b-H_c)$	0.23	-1.39×10^{-3}	$+0.65 \times 10^{-3}$
$\sigma(I-I) \rightarrow \sigma^*(C_a-H_a) \times 2$	0.18	-1.98×10^{-3}	$+0.14 \times 10^{-3}$