Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Proton leap: Shuttling of protons onto benzonitrile

Nemanja Pavković, Branislav Milovanović, Ana Stanojević, Mihajlo Etinski, and Milena Petković*
University of Belgrade – Faculty of Physical Chemistry, Studentski trg 12-16, 11 158 Belgrade, Serbia
* *E-mail: milena@ffh.bg.ac.rs*

Supplementary Information

Figure S1: Energy change along the reaction coordinate defined as: A) N–H distance, r_{NH}: B) distance between reactants' centres of masses, r_{COM}; C) distance between r_{COM} defined as being negative/positive before/beyond the turning point (turning point TP corresponds to the shortest r_{COM} value). The arrows indicate the direction of the reaction.
Figure S2: A) Deformation energies and B) propagation energies for BN (red), H_2 (green), H^+ (blue) and the whole system (black).
Figure S3: A) Classical; B) non-classical; and C) total interaction energies for BN–H^+ (blue), H_2–H^+ (turquoise), BN–H_2 (orange) and the whole system (black).
Figure S4: Difference between corresponding energy terms with and witout the carrier H_2: classical (black, dashed), nonclassical (black, dotted), total interaction (black, solid) energy, as well as promotion energy for BN (red) and H^+ (blue).
Figure S5: Optimized structure of the adduct N-ethyl benzonitrilium cation.
Table S1: Reaction rate constants obtained from the classical Langevin capture model using *ab initio* molecular dynamics calculations at 10 K and 100 K.

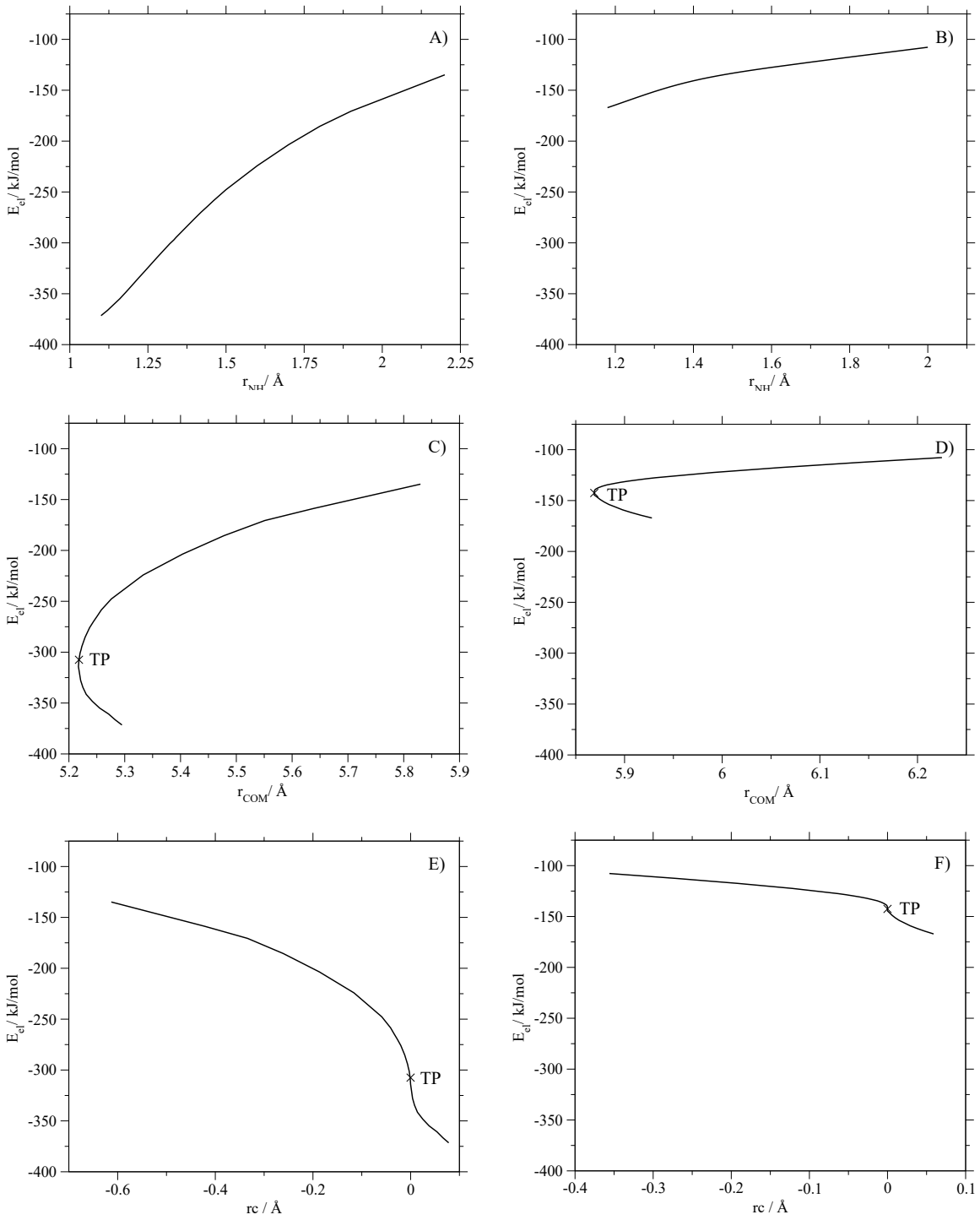

Fig. S1 Energy change along the reaction coordinate defined as: A) N–H distance, r_{NH}: B) distance between reactants' centres of masses, r_{COM}; C) distance between r_{COM} defined as being negative/positive before/beyond the turning point (turning point TP corresponds to the shortest r_{COM} value). The arrows indicate the direction of the reaction.

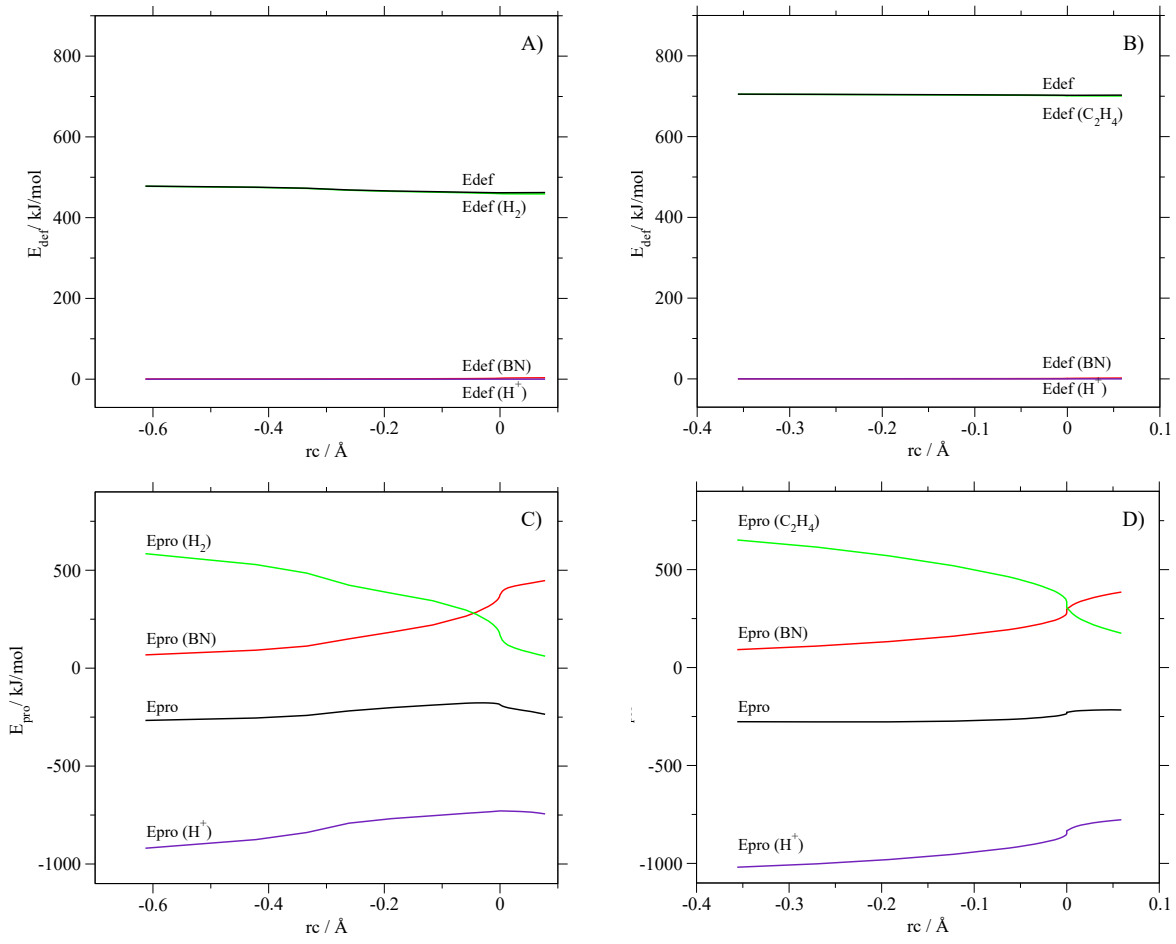

Fig. S2 A) Deformation energies and B) propagation energies for BN (red), H_2 (green), H^+ (blue) and the whole system (black).

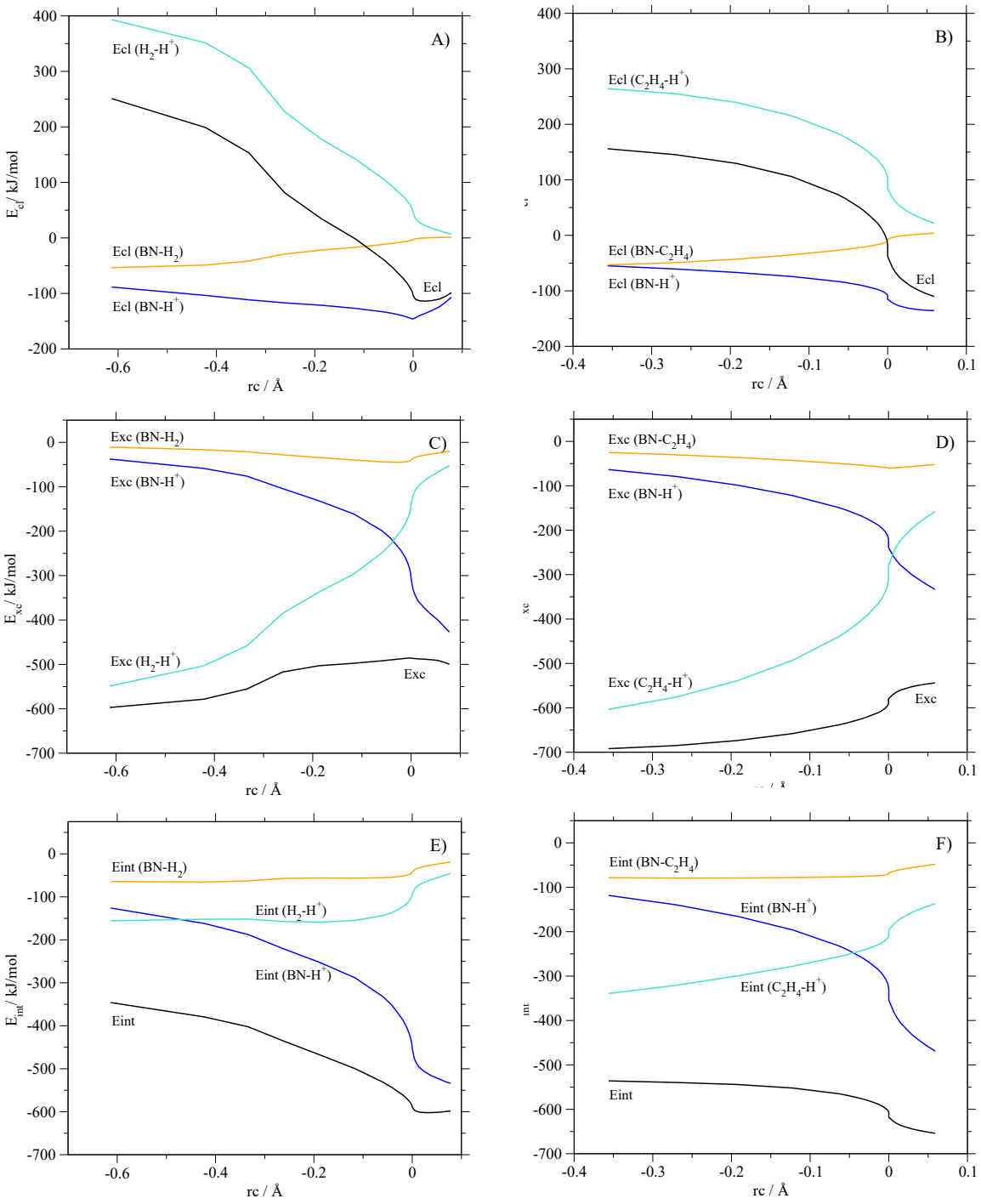

Fig. S3 A) Classical; B) non-classical; and C) total interaction energies for BN–H^+ (blue), H_2–H^+ (turquoise), BN–H_2 (orange) and the whole system (black).

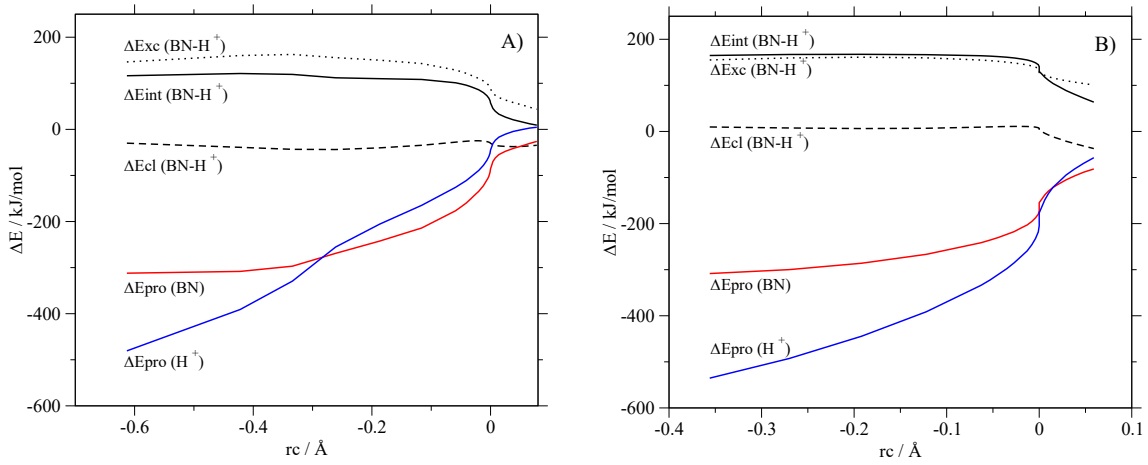

Fig. S4 Difference between corresponding energy terms with and witout the carrier H_2: classical (black, dashed), nonclassical (black, dotted), total interaction (black, solid) energy, as well as promotion energy for BN (red) and H^+ (blue).

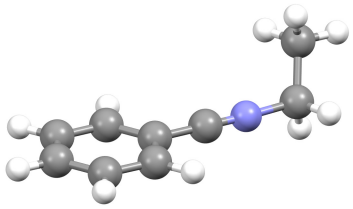

Fig. S5 Optimized structure of the adduct N-ethyl benzonitrilium cation.

Table S1 Reaction rate constants obtained from the classical Langevin capture model using *ab initio* molecular dynamics calculations at 10 K and 100 K.

System	T/ K	C / kJ mol^{-1}Å^n	n	R^2	k / cm^{3}s^{-1}	$\bar{k}$ / cm^{3}s^{-1}
$BN-H_3^+$	10	$2.358{\cdot}10^5$	4.171	0.9769	$2.5191{\cdot}10^{-8}$	$2.5253{\cdot}10^{-8}$
		$2.395{\cdot}10^5$	4.187	0.9755	$2.5393{\cdot}10^{-8}$	
		$2.355{\cdot}10^5$	4.170	0.9811	$2.5175{\cdot}10^{-8}$	
	100	$1.809{\cdot}10^5$	4.155	0.9891	$2.2064{\cdot}10^{-8}$	$2.8327{\cdot}10^{-8}$
		$4.350{\cdot}10^5$	4.557	0.9895	$3.4215{\cdot}10^{-8}$	
		$3.061{\cdot}10^5$	4.406	0.9891	$2.8701{\cdot}10^{-8}$	
$BN-C_2H_5^+$	10	$6.974{\cdot}10^4$	3.533	0.9951	$4.9288{\cdot}10^{-9}$	$4.6989{\cdot}10^{-9}$
		$6.941{\cdot}10^4$	3.532	0.9949	$4.9171{\cdot}10^{-9}$	
		$5.187{\cdot}10^4$	3.398	0.9969	$4.4251{\cdot}10^{-9}$	
	100	$9.888{\cdot}10^4$	3.772	0.9956	$5.8689{\cdot}10^{-9}$	$6.6449{\cdot}10^{-9}$
		$1.138{\cdot}10^5$	3.874	0.9914	$6.2961{\cdot}10^{-9}$	
		$1.733{\cdot}10^5$	4.083	0.9898	$7.7696{\cdot}10^{-9}$	