

# Photoelectron spectroscopic study of 2-naphthyl nitrene and its thermal rearrangement to cyanoindenes

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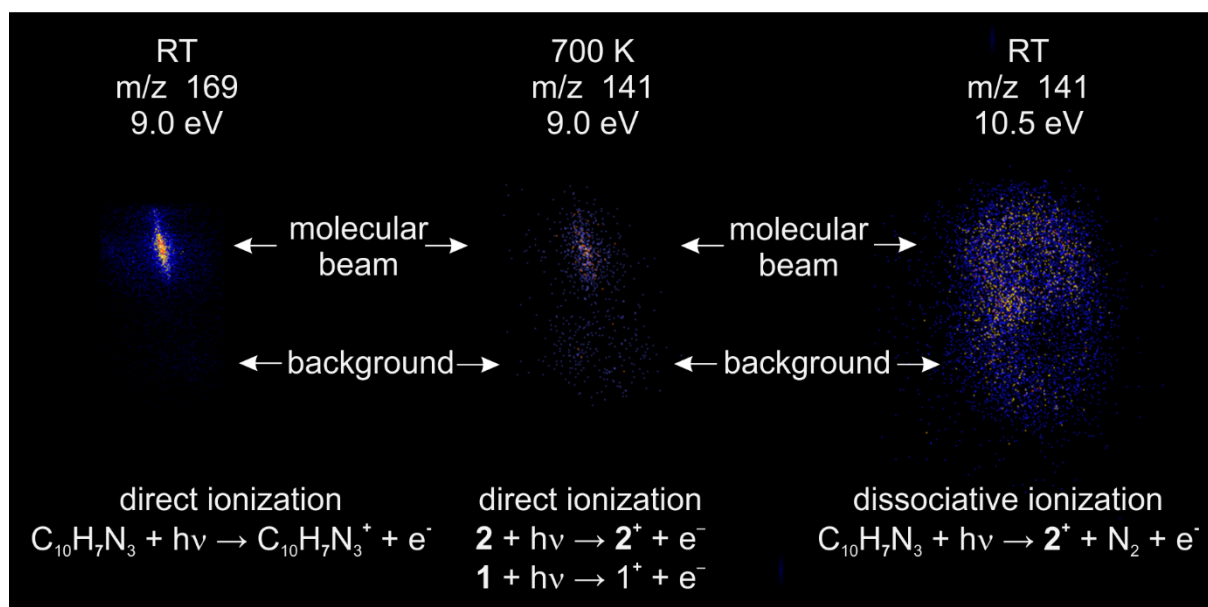
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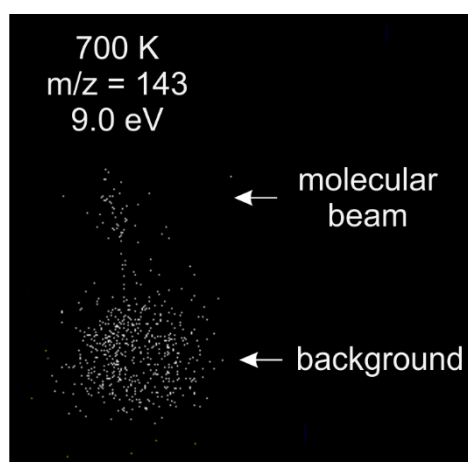
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## Velocity Map Imaging



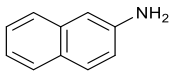
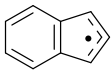
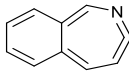
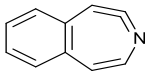
**Figure S1.** Ion velocity map imaging allows to distinguish the molecular beam from the room temperature background (formed via collisions within the vacuum chamber), as well as direct ionization from dissociative ionization (kinetic energy release of the fragments), which is an essential tool, when reactive and open-shell molecules are investigated. Selected ion images showing the direct ionization and dissociative ionization of 2-naphthylazide **3** (m/z 169) at 9.0 and 10.5 eV under RT (left and right) as well as the direct ionization of naphthyl nitrene **2** / cyanoinidene **1** (m/z 141), upon FVP at 700 K and 9.0 eV (center).



**Figure S2.** The ion image of 2-aminonaphthalene **6** (m/z 143) at 9 eV shows a strong background signal, while the molecular beam component is negligible. This is intriguing as the mass spectra in Figure 1, clearly show that m/z 143 is solely formed via pyrolysis from azide **3**. The absence of a molecular beam signature can be rationalized as follows: pyrolysis of azide **3** forms nitrene **2** selectively in the gas phase. Upon leaving the hot reactor a molecular beam is formed which travels towards the ionization region. A large fraction of the molecular beam is not ionized and collides with the chamber walls, where it rethermalizes and retrieves a room temperature Boltzmann distribution, which translates to the broad background signal in the VMI. Due to the high reactivity of nitrene **2**, H-abstraction from the chamber walls, from e.g. adsorbed water, quenches the reactive molecules to form **6**, with a strong signature only background of the ion image.

## Quantum Chemical Calculations

**Table S1.** Adiabatic ionization energies (in eV) of FVP products at different levels of theory.

method	 <b>6</b>	 <b>4</b>	 <b>5</b>	 <b>7</b>	 <b>8</b>
B3LYP-D3/def2-TZVP	7.03	7.93	7.48	6.72	7.34
CBS-QB3	7.34	7.89	7.64	7.05	7.73
G4	7.36	7.95	7.60	7.01	7.82

## Cartesian Coordinates

Optimized geometries at B3LYP-D3/def2-TZVP level of theory.

<b>T-2</b>		<b>D-2<sup>+</sup></b>					
C	-2.80501578	0.44613674	0.00000000	C	-2.76670544	0.47015151	0.00000000
C	-1.71420507	1.28938367	0.00000000	C	-1.66305143	1.31817838	0.00000000
C	-0.40618376	0.77645249	0.00000000	C	-0.37604550	0.79515434	0.00000000
C	-0.21625487	-0.64210785	0.00000000	C	-0.22453404	-0.64754328	0.00000000
C	-1.35848440	-1.48330081	0.00000000	C	-1.38625720	-1.48969267	0.00000000
C	-2.62341230	-0.95015037	0.00000000	C	-2.63386950	-0.93438159	0.00000000
H	0.58971759	2.69908912	0.00000000	H	0.63762107	2.71542973	0.00000000
H	-3.80648885	0.85687154	0.00000000	H	-3.75981053	0.90261766	0.00000000
H	-1.85644233	2.36355526	0.00000000	H	-1.80905051	2.39038567	0.00000000
C	0.74396386	1.62620173	0.00000000	C	0.78869135	1.64323261	0.00000000
C	1.08788856	-1.16296275	0.00000000	C	1.03452252	-1.18632967	0.00000000
H	-1.21523491	-2.55707046	0.00000000	H	-1.25193446	-2.56398154	0.00000000
H	-3.48683257	-1.60303677	0.00000000	H	-3.51714916	-1.55781167	0.00000000
C	2.22077754	-0.30897427	0.00000000	C	2.20836660	-0.31732834	0.00000000
C	2.00274527	1.12513414	0.00000000	C	2.03537970	1.13474849	0.00000000
H	2.86992175	1.77121468	0.00000000	H	2.92144466	1.75329348	0.00000000
N	3.43828067	-0.79882314	0.00000000	N	3.35448813	-0.87142382	0.00000000
H	1.24648037	-2.23373763	0.00000000	H	1.19847970	-2.25710523	0.00000000
<b>Q-2<sup>+</sup></b>		<b>1c</b>					
C	-2.83520454	0.42713067	0.00000000	C	0.04083709	-0.25076805	0.30462218
C	-1.74228990	1.28001030	0.00000000	C	0.69592117	0.93277390	-0.06618385
C	-0.41134436	0.76798346	0.00000000	C	2.05659616	0.91902681	-0.34818186
C	-0.20151360	-0.65271493	0.00000000	C	2.74220609	-0.29050323	-0.26196583
C	-1.32436472	-1.48723239	0.00000000	C	2.08183802	-1.46337218	0.09763921
C	-2.62619690	-0.94845643	0.00000000	C	0.71592102	-1.45159209	0.38623321
H	0.54357244	2.69472697	0.00000000	C	-1.41784189	0.07455105	0.58096318
H	-3.83951406	0.82723460	0.00000000	C	-1.49237579	1.55848805	0.25660214
H	-1.88866450	2.35340645	0.00000000	C	-0.28321176	2.01886396	-0.08501288
C	0.69240095	1.62162817	0.00000000	H	2.57293722	1.82706777	-0.63335888
C	1.11140488	-1.16764303	0.00000000	H	3.80181509	-0.32163431	-0.48178583
H	-1.19368944	-2.56215634	0.00000000	H	2.63210696	-2.39379322	0.15111623
H	-3.47307914	-1.62269838	0.00000000	H	0.20079396	-2.36514805	0.65610724
C	2.23246450	-0.29106957	0.00000000	H	-1.63957089	-0.08045590	1.64482818
C	1.99825392	1.11457792	0.00000000	H	-2.41264676	2.11802911	0.32110312
H	2.84793880	1.78518223	0.00000000	C	-2.36304294	-0.73862791	-0.18156480
N	3.48008877	-0.74634057	0.00000000	N	-3.10935998	-1.38285588	-0.77354877
H	1.28115316	-2.23659655	0.00000000	H	-0.05099870	3.04288394	-0.34207291
<b>D-1c<sup>+</sup></b>		<b>1b</b>					
C	0.01563287	-0.26925394	0.33106115	C	-0.52741307	-0.70720806	0.00000000
C	0.70983777	0.92579412	-0.05350587	C	-0.50457671	0.69979948	0.00000000
C	2.09574379	0.89998425	-0.34999577	C	-1.68874605	1.43186192	0.00000000
C	2.74505992	-0.30582867	-0.27350867	C	-2.89484506	0.74003840	0.00000000
C	2.04166102	-1.47965173	0.09216735	C	-2.91629831	-0.65484800	0.00000000
C	0.66555100	-1.46803586	0.39522126	C	-1.73015090	-1.38941447	0.00000000
C	-1.43506218	0.08492691	0.60210304	C	0.88513764	-1.22281649	0.00000000
C	-1.46152832	1.55578389	0.25854095	C	1.69551434	0.05642484	0.00000000
C	-0.20638535	2.00247701	-0.08827599	C	0.88093960	1.13490105	0.00000000
H	2.61300071	1.80632830	-0.63509779	H	-1.67154686	2.51451652	0.00000000
H	3.80111994	-0.37487856	-0.49633959	H	-3.82840195	1.28797795	0.00000000
H	2.58178012	-2.41693767	0.14171544	H	-3.86639445	-1.17368784	0.00000000

H	0.15481909	-2.38373891	0.66210027	H	-1.75709225	-2.47229436	0.00000000
H	-1.67279624	-0.04376105	1.66744703	H	1.10761177	-1.83649013	0.87815400
H	-2.36457639	2.14932079	0.29055886	H	1.10761177	-1.83649013	-0.87815400
C	-2.38930005	-0.69902423	-0.17942799	H	1.20870380	2.16463312	0.00000000
N	-3.11983794	-1.32016335	-0.81198900	C	3.10932952	0.07325312	0.00000000
H	0.03825555	3.02178003	-0.35273803	N	4.26373745	0.05426916	0.00000000
<b>D-1b<sup>+</sup></b>				<b>1a</b>			
C	-0.51461530	-0.74077269	0.00000000	C	-0.82643551	-0.89392180	0.00000000
C	-0.49425291	0.69588531	0.00000000	C	0.00138819	0.23872602	0.00000000
C	-1.69492419	1.45144428	0.00000000	C	-0.52969619	1.52149966	0.00000000
C	-2.88179948	0.76576733	0.00000000	C	-1.91486577	1.65802794	0.00000000
C	-2.89079399	-0.65013641	0.00000000	C	-2.74228307	0.53593893	0.00000000
C	-1.70859730	-1.41124908	0.00000000	C	-2.20238599	-0.75052301	0.00000000
C	0.89655796	-1.25216502	0.00000000	C	0.03232245	-2.13128391	0.00000000
C	1.68743567	0.02841386	0.00000000	C	1.42746042	-1.57725148	0.00000000
C	0.84112480	1.13485448	0.00000000	C	1.39496762	-0.22892576	0.00000000
H	-1.66339907	2.53281844	0.00000000	H	0.11769643	2.38928510	0.00000000
H	-3.82326497	1.29781484	0.00000000	H	-2.35536705	2.64680392	0.00000000
H	-3.84439420	-1.16342646	0.00000000	H	-3.81709121	0.66493351	0.00000000
H	-1.75696925	-2.49198946	0.00000000	H	-2.85253857	-1.61709039	0.00000000
H	1.13069574	-1.86416175	0.87702800	H	-0.14667754	-2.76418483	0.87633300
H	1.13069574	-1.86416175	-0.87702800	H	-0.14667754	-2.76418483	-0.87633300
H	1.17226565	2.16398050	0.00000000	C	2.52290263	0.63666957	0.00000000
C	3.08531394	0.08288441	0.00000000	N	3.41417983	1.36763266	0.00000000
N	4.24309646	0.10850955	0.00000000	H	2.32114802	-2.18272800	0.00000000
<b>D-1a<sup>+</sup></b>							
C	-0.84083668	-0.91496007	0.00000000				
C	0.01413539	0.23490500	0.00000000				
C	-0.50466238	1.55244533	0.00000000				
C	-1.86806775	1.69790791	0.00000000				
C	-2.70969562	0.55878268	0.00000000				
C	-2.19971986	-0.75414741	0.00000000				
C	0.00979929	-2.15533541	0.00000000				
C	1.38987095	-1.60168574	0.00000000				
C	1.36433094	-0.21184011	0.00000000				
H	0.16210740	2.40483191	0.00000000				
H	-2.31458154	2.68280776	0.00000000				
H	-3.78274229	0.70455200	0.00000000				
H	-2.87486153	-1.59947137	0.00000000				
H	-0.16089751	-2.79548612	0.87390200				
H	-0.16089751	-2.79548612	-0.87390200				
C	2.50336373	0.63139479	0.00000000				
N	3.41278532	1.33896967	0.00000000				
H	2.29126770	-2.19933758	0.00000000				