The Dynamics of Hydrogen and Methyl Radical Loss from Ionized Dihydro-Polycyclic Aromatic Hydrocarbons: A Tandem Mass Spectrometry and Imaging-PEPICO Study of Dihydronaphthalene and Dihydrophenanthrene

Brandi West,[a] Christine Joblin,[b, c] Valerie Blanchet,[d] Andras Bodi,[e] Bálint Sztáray[f] and Paul M Mayer[a*]

[a] Chemistry Department, University of Ottawa, Ottawa, Canada K1N 6N5

[b] Université de Toulouse; UPS-OMP; IRAP; Toulouse, France

[c] CNRS; IRAP; 9 Av. colonel Roche, BP 44346, F-31028 Toulouse cedex 4, France

[d] Laboratoire des Collisions Agrégats Réactivité, Univ. Toulouse-CNRS, Toulouse, France

[e] Molecular Dynamics Group, Paul Scherrer Institut, Villigen 5232 Switzerland

[f] Chemistry Department, University of the Pacific, Stockton, California 95211, United States

*Corresponding author: Paul M Mayer, pmmayer@uottawa.ca, 1-613-562-5800 ext 6038

Supporting Information

Complete Reference 24

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Laham, A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 03, Revision C.02, 2003.

Description of deconvolution process.

It was necessary to use a deconvolution procedure to extract the fractional abundances of the overlapping parent, H-loss and 2H-loss peaks. This is based on the idea of finding the weighted center of the TOF distribution. For example, the molecular ion $M^{+\bullet}$ has a peak with a certain time-of-flight (TOF) centre and full width half-maximum. As the $[M\text{-}H]^+$ peak grows with increasing photon energy, the center of the TOF distribution of the peak cluster shifts towards the TOF of the $[M\text{-}H]^+$ ion, the shift being proportional to the relative abundance of the two peaks. This procedure can be generalized for a cluster of three peaks, making use of the 2nd moment of the TOF distribution around the peak center. In the present case, this involves either of the combinations $[M\text{-}H]^+$, $M^{+\bullet}$, $^{13}C\text{-}M^{+\bullet}$ or $[M\text{-}2H]^{+\bullet}$, $[M\text{-}H]^+$, $M^{+\bullet}$.

If we consider three peaks with relative abundances a, b and c, with arrival times of t_1, t_2 and t_3, and each with the same full-width-half-maximum (due to the low mass of H the difference in the peak widths due to kinetic energy release broadening of the fragment ions relative to the parent ion should be negligible), one can derive the following expressions for a, b and c:

$$a = \left(\sigma^2 - \sigma_p^2 - \mu(t_2 + t_3) + t_2 t_3\right) / \left((t_1 - t_2)(t_1 - t_3)\right) \quad (1)$$

$$b = \left(\sigma^2 - \sigma_p^2 - \mu(t_1 + t_2) + t_1 t_2\right) / \left((t_3 - t_2)(t_3 - t_1)\right) \quad (2)$$

$$c = \left(\sigma^2 - \sigma_p^2 - \mu(t_1 + t_3) + t_1 t_3\right) / \left((t_2 - t_1)(t_2 - t_3)\right) \quad (3)$$

Where $\mu = \frac{\int tTOF(t)dt}{\int TOF(t)dt}$, $\sigma^2 = \frac{\int (t-t_0)^2 TOF(t)dt}{\int TOF(t)dt}$, t_0 refers to the moment centre and σ^2_p refers to the parent ion. After deconvolution of the three peaks in question, ^{13}C contributions were taken into account prior to the calculation of final relative abundances for use in the breakdown diagrams.

Figure S1: Determination of the ionization energy for dihydrophenanthrene.

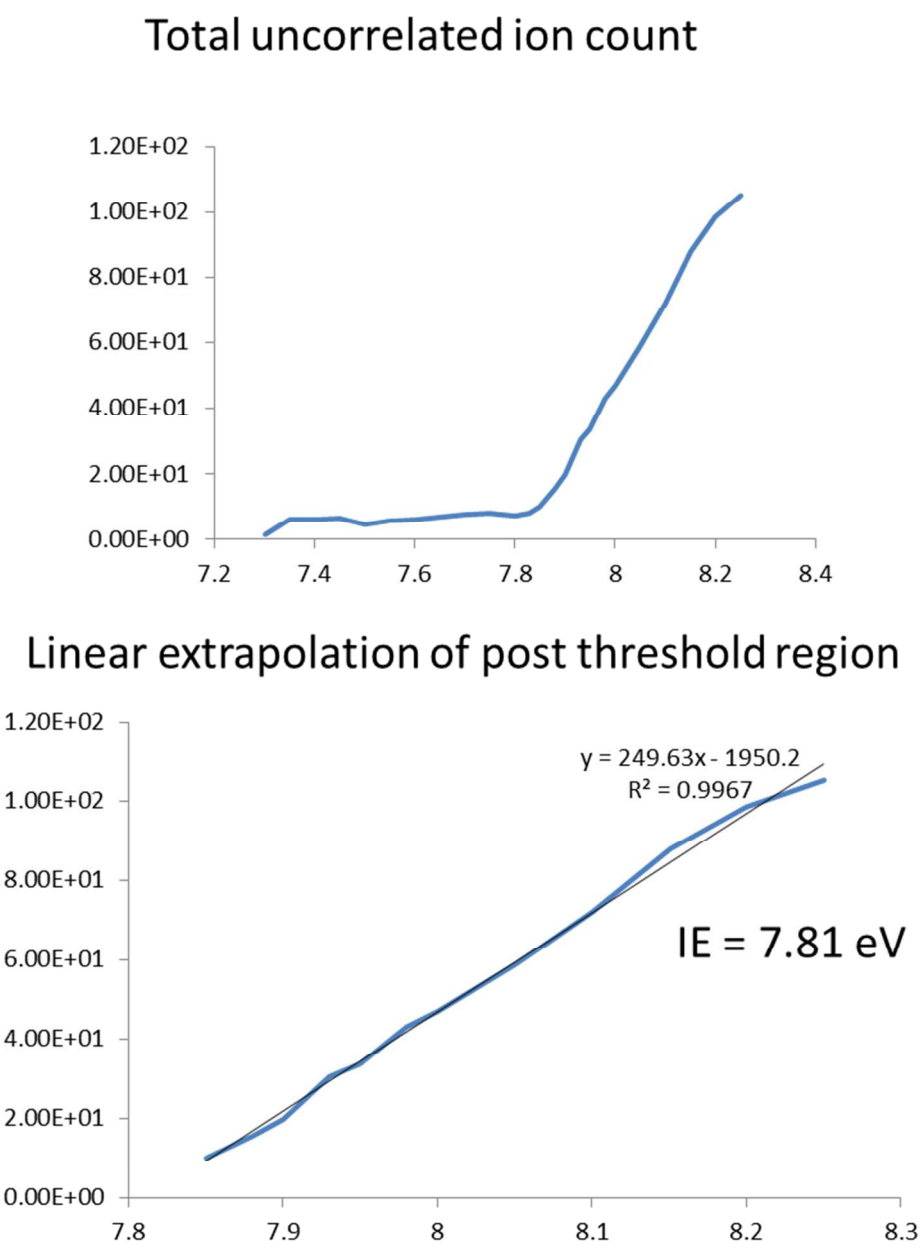


Figure S2: Plot of 0K activation energy for all three primary channels (R1a-b, R2) versus isomerization barrier energy ranging from 1.5-2.0 eV.

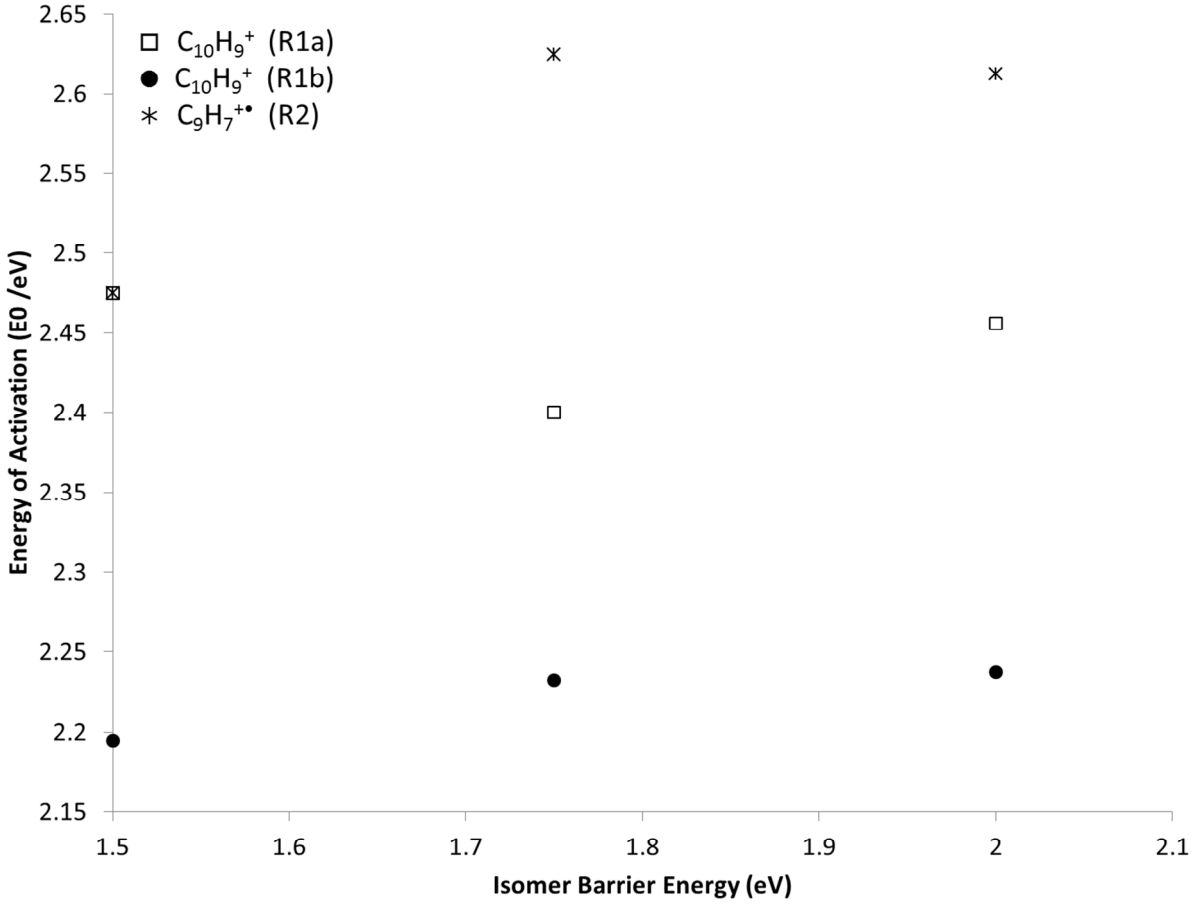


Figure S3: Representative TOF fits, for 9,10-dihydrophenanthrene, calculated during the RRKM fitting of experimental iPEPICO data. The region shown is the $C_{13}H_9^+$ region, as this peak was the only asymmetric TOF peak which was not obscured due to its proximity to other peaks. As photon energy increases, it can be seen that the peak becomes increasingly Gaussian in shape.

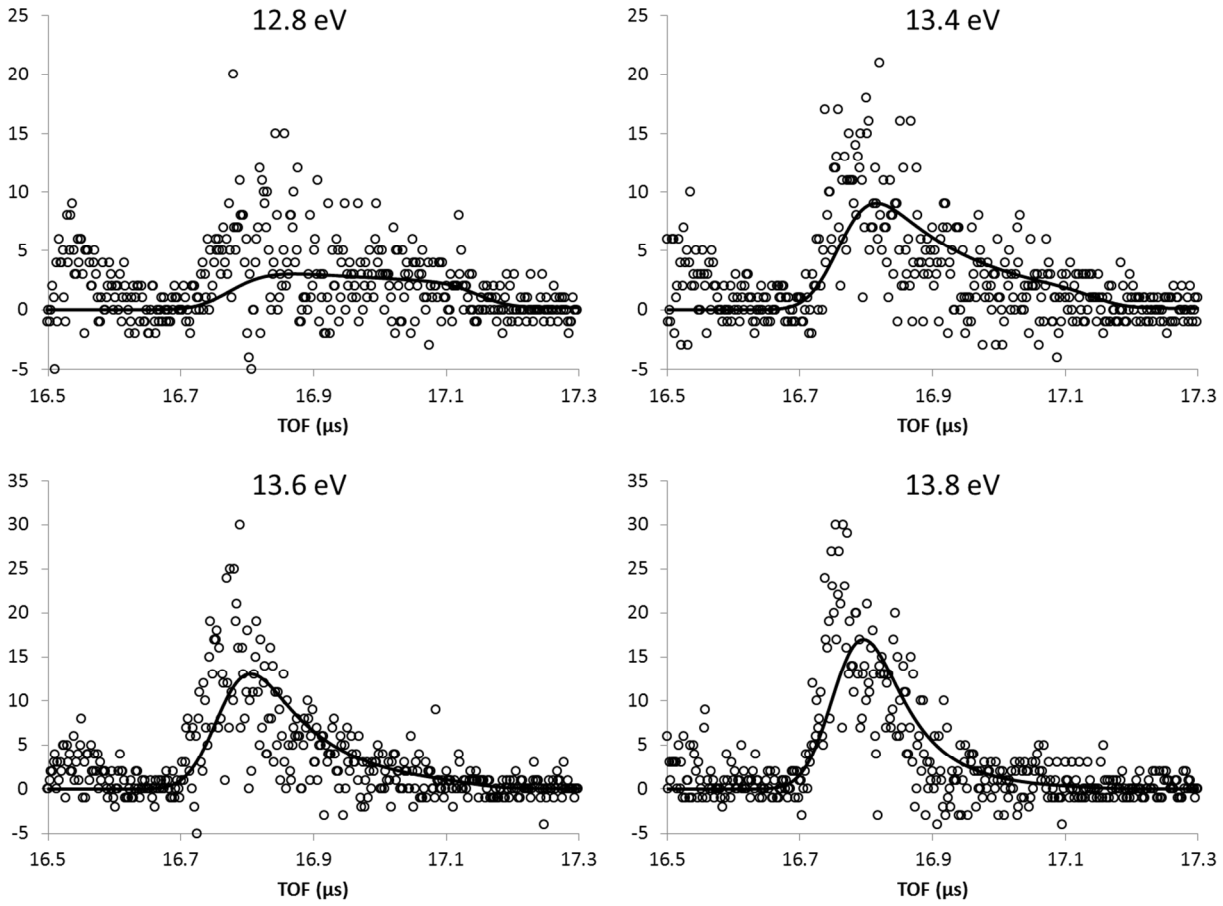
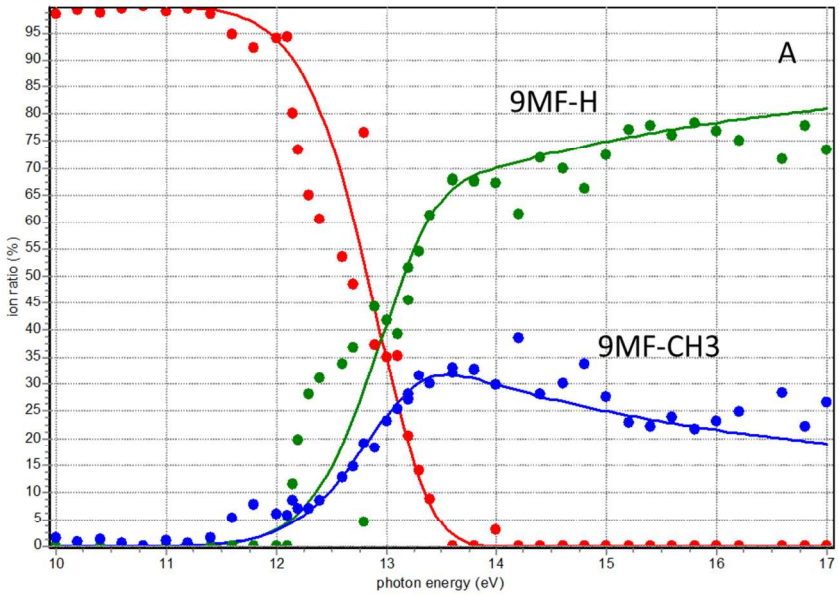


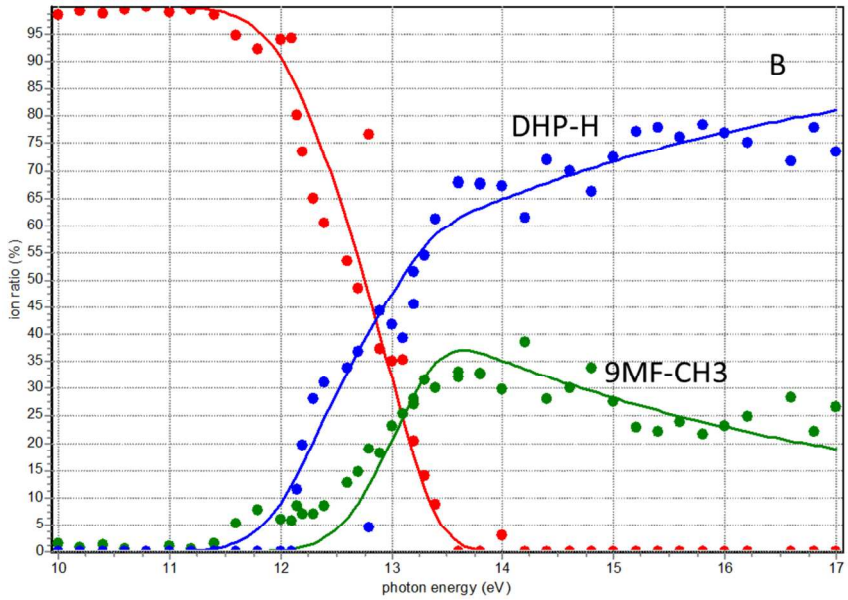
Figure S4: Various iPEPICO RRKM fittings for 9,10-dihydrophenanthrene to demonstrate (A) the effect of choosing to remove hydrogen from 9-methylfluorene, (B) the effect of barrier height on energetic values.



2 eV barrier height
No restrictions to calculation

Demonstrating unreasonable Δ‡S(1000K) values when using 9MF-H instead of DHP-H

transition	E0 (eV)	Δ‡S(1000K)
DHP → 9MF	2.18	93.1391
DHP ← 9MF	2.15	82.0243
9MF-H	2.34	-9.0746
9MF-CH3	2.74	-31.9366



1.75 eV barrier

No restrictions on calculation

transition	E0 (eV)	Δ‡S(1000K)
DHP → 9MF	1.90	-19.1715
DHP ← 9MF	2.08	-30.2863
DHP-H	2.25	0.3535
9MF-CH3	2.50	11.3751

Table S1. Vibrational frequencies (cm-1) used in the RRKM calculations outlined in this paper. Frequencies in parenthesis were removed for the transition state.

1,2-dihydronaphthalene

$C_{10}H_{10}$ (M)	$C_{10}H_{10}^{+\cdot}$ ($M_{DHN}^{+\cdot}$)	$C_{10}H_{10}^{+\cdot}$ ($M_{MI}^{+\cdot}$)	TS $(DHN\text{-}MI)^{+\cdot}$	TS $(M_{DHN}\text{-}H)^{+}$	TS $(M_{MI}\text{-}H)^{+}$	TS $(M_{MI}\text{-}CH_3)^{+}$	$(M_{DHN}\text{-}H)^{+}$	TS $[(M_{DHN}\text{-}H)\text{-}H]^{+\cdot}$	TS $[(M_{DHN}\text{-}H)\text{-}H_2]^{+}$
140	120	94	(706)	(3120)	(3001)	(1001)	121	(3206)	(3206)
161	144	155	104	78	132	48	175	97	97
278	244	229	170	94	217	79	253	140	140
366	351	250	252	158	321	117	357	202	202
408	370	263	275	228	349	127	410	286	286
440	433	385	290	240	369	134	439	328	328
506	486	431	433	433	385	385	497	439	439
520	502	483	486	486	431	431	503	497	497
583	518	501	502	502	483	483	506	503	503
615	597	540	518	518	501	501	613	506	506
722	706	596	597	597	540	540	680	613	613
735	722	716	722	706	596	596	749	680	680
785	759	729	759	722	716	716	751	749	749
794	801	758	801	759	729	729	792	751	751
833	830	785	830	801	758	758	801	792	792
854	859	836	859	830	785	785	867	801	801
931	930	863	930	859	836	836	930	867	867
934	941	894	941	930	863	863	934	930	930
985	974	911	974	941	894	894	973	934	934
1006	1014	976	1014	974	911	911	1000	973	973
1040	1050	994	1050	1014	976	976	1026	1000	1000
1048	1062	1001	1062	1050	994	994	1041	1026	1026
1072	1074	1009	1074	1062	1001	1009	1049	1041	1041

1100	1077	1019	1077	1074	1009	1019	1050	1049	1049
1104	1087	1063	1087	1077	1019	1063	1114	1050	1050
1181	1193	1092	1193	1087	1063	1092	1157	1114	1114
1223	1216	1098	1216	1193	1092	1098	1180	1157	1157
1227	1239	1140	1239	1216	1098	1140	1193	1180	1180
1244	1245	1177	1245	1239	1140	1177	1201	1193	1193
1265	1261	1184	1261	1245	1177	1184	1218	1201	1201
1281	1301	1246	1301	1261	1184	1246	1271	1218	1218
1305	1317	1266	1317	1301	1246	1266	1300	1271	1271
1362	1357	1280	1357	1317	1266	1280	1341	1300	1300
1372	1412	1317	1412	1357	1280	1317	1374	1341	1341
1434	1437	1380	1437	1412	1317	1380	1393	1374	1374
1441	1461	1412	1461	1437	1380	1412	1449	1393	1393
1492	1513	1422	1513	1461	1412	1422	1475	1449	1449
1548	1520	1445	1520	1513	1422	1445	1488	1475	1475
1554	1537	1457	1537	1520	1445	1457	1544	1488	1488
1561	1546	1497	1546	1537	1457	1497	1584	1544	1544
1593	1572	1497	1572	1546	1497	1497	1609	1584	1584
1695	1610	1509	1610	1572	1497	1509	1653	1609	1609
1730	1631	1550	1631	1610	1509	1550	2972	1653	1653
1776	1721	1644	1721	1631	1550	1644	2975	2972	2972
3094	3084	3001	3084	1721	1644	3001	3168	2975	2975
3107	3120	3047	3120	3084	3047	3047	3177	3168	3168
3173	3198	3123	3198	3198	3123	3123	3181	3177	3177
3178	3216	3125	3216	3216	3125	3125	3185	3181	3181
3269	3303	3187	3303	3303	3187	3187	3192	3185	3185
3274	3312	3196	3312	3312	3196	3196	3204	3192	3192
3279	3315	3200	3315	3315	3200	3200	3206	3204	3204
3292	3318	3205	3318	3318	3205	3205			
3294	3325	3210	3325	3325	3210	3210			
3309	3337	3223	3337	3337	3223	3223			

9,10-dihydrophenanthrene

$C_{14}H_{12}$ (M)	$C_{14}H_{12}^{+\cdot}$ ($M_{DHP}^{+\cdot}$)	$C_{14}H_{12}^{+\cdot}$ ($M_{9MF}^{+\cdot}$)	TS $(DHP\text{-}9MF)^{+\cdot}$	TS $(M_{DHP}\text{-}H)^{+}$	TS $(M_{9MF}\text{-}CH_3)^{+}$
86	72	69	(288)	(3194)	(1080)
104	94	121	40	46	65
177	157	123	70	60	114
209	198	197	71	101	116
269	258	218	114	126	185
318	288	238	127	165	205
392	383	279	383	288	238
397	393	340	393	383	279
456	433	399	433	393	340
468	459	421	459	433	399
470	474	466	474	459	421
504	477	496	477	474	466
554	500	512	500	477	496
578	529	513	529	500	512
612	588	564	588	529	513
636	620	614	620	588	564
721	704	618	704	620	614
739	718	709	718	704	618
741	720	741	720	718	709
759	772	753	772	720	741
784	778	773	778	772	753
792	809	797	809	778	773
818	816	798	816	809	797
880	880	821	880	816	798
882	882	890	882	880	821
908	892	893	892	882	890
959	983	987	983	892	893
959	991	990	991	983	987
988	994	991	994	991	990
990	1003	1001	1003	994	991
993	1018	1016	1018	1003	1001
1023	1019	1017	1019	1018	1016
1049	1034	1023	1034	1019	1017
1068	1048	1027	1048	1034	1023
1069	1052	1062	1052	1048	1027
1111	1115	1080	1115	1052	1062
1150	1156	1132	1156	1115	1132
1181	1182	1134	1182	1156	1134
1184	1187	1177	1187	1182	1177
1188	1195	1183	1195	1187	1183

1208	1199	1190	1199	1195	1190
1217	1229	1197	1229	1199	1197
1224	1236	1234	1236	1229	1234
1278	1285	1260	1285	1236	1260
1304	1299	1302	1299	1285	1302
1306	1318	1335	1318	1299	1335
1328	1353	1360	1353	1318	1360
1335	1360	1380	1360	1353	1380
1362	1379	1403	1379	1360	1403
1380	1398	1421	1398	1379	1421
1471	1455	1442	1455	1398	1442
1474	1459	1459	1459	1455	1459
1484	1471	1485	1471	1459	1485
1485	1473	1498	1473	1471	1498
1516	1495	1500	1495	1473	1500
1521	1507	1512	1507	1495	1512
1602	1537	1538	1537	1507	1538
1622	1548	1565	1548	1537	1565
1637	1615	1608	1615	1548	1608
1646	1635	1650	1635	1615	1650
2990	2996	3016	2996	1635	3016
3002	3009	3045	3009	2996	3045
3066	3095	3118	3095	3095	3118
3066	3096	3119	3096	3096	3119
3154	3184	3185	3184	3184	3185
3155	3184	3186	3184	3184	3186
3166	3194	3193	3194	3194	3193
3168	3195	3195	3195	3195	3195
3178	3202	3198	3202	3202	3198
3182	3205	3199	3205	3205	3199
3189	3214	3209	3214	3214	3209
3193	3226	3210	3226	3226	3210