

**Supporting Information: Metadynamics for Automatic Sampling of Quantum
Property Manifolds: Exploration of Molecular Biradicality Landscapes**

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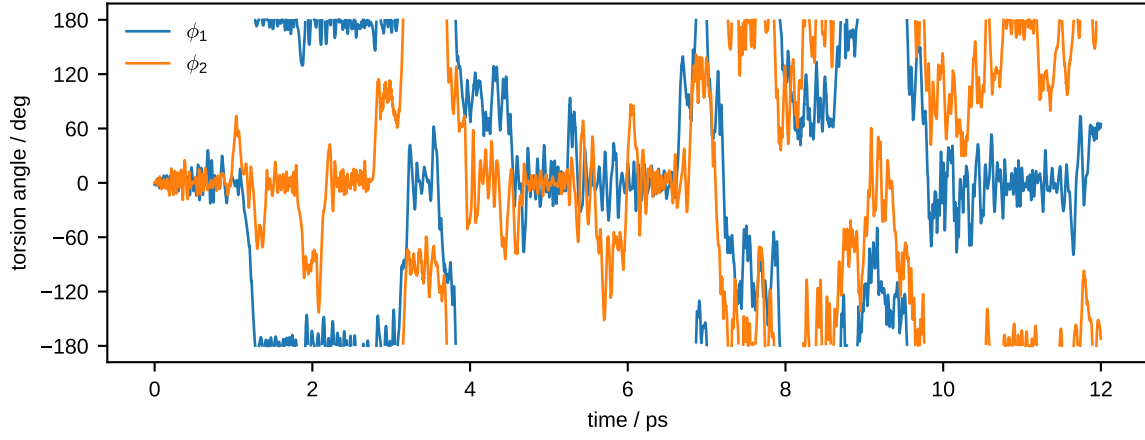
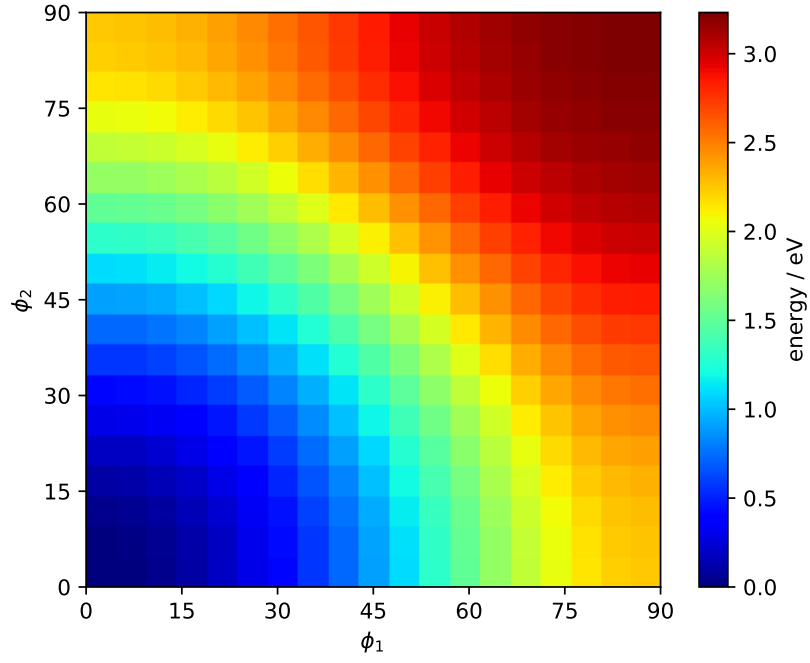
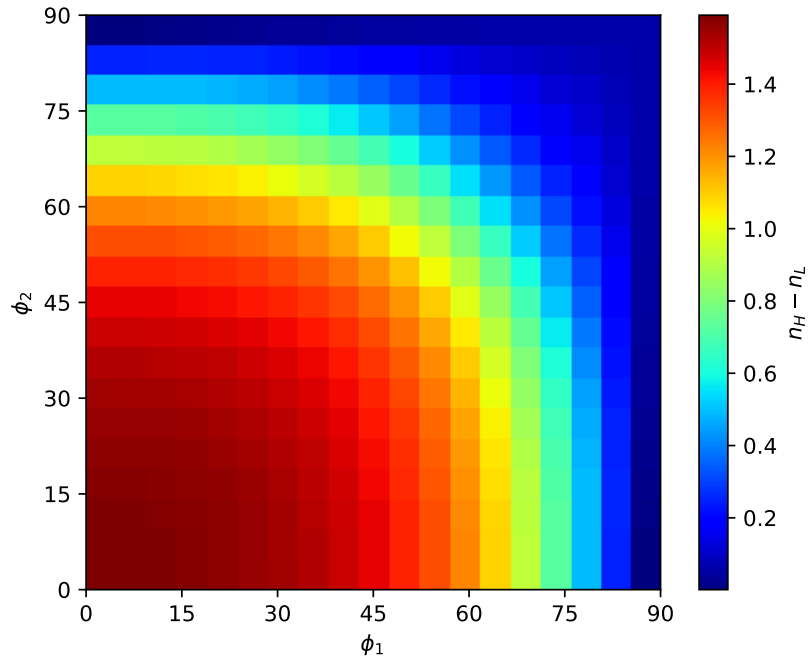


FIG. S1: Torsion angles ϕ_1 and ϕ_2 along the ASQPM trajectory of *p*-xylylene.



(a)



(b)

FIG. S2: a) Ground state energy and b) gap between frontier NOONs along a fixed scan of the two CVs ϕ_1 and ϕ_2 in *p*-xylylene using an increment of 5 degrees.

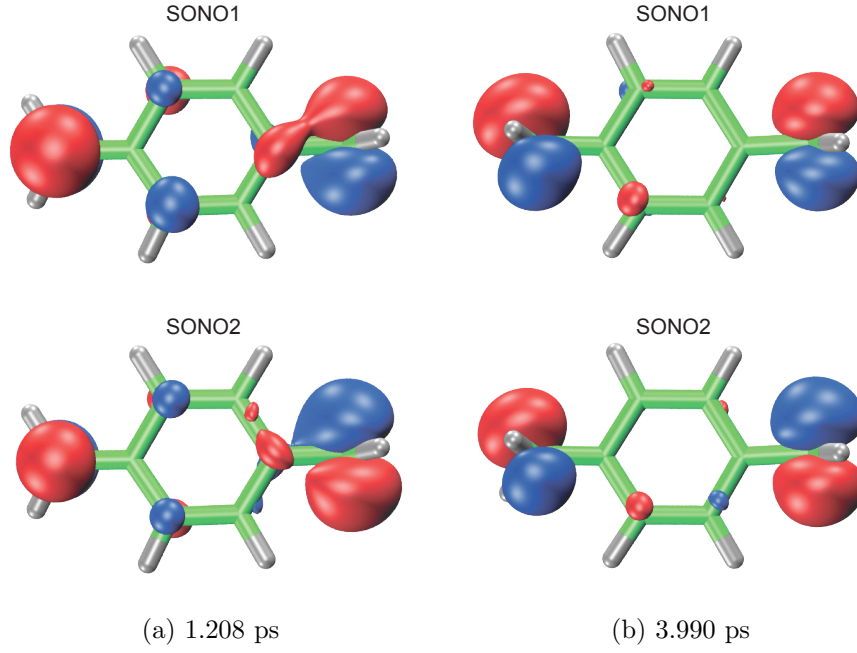


FIG. S3: SONOs of *p*-xylylene at different time steps with a) one rotated methylene unit and b) two rotated methylene units.

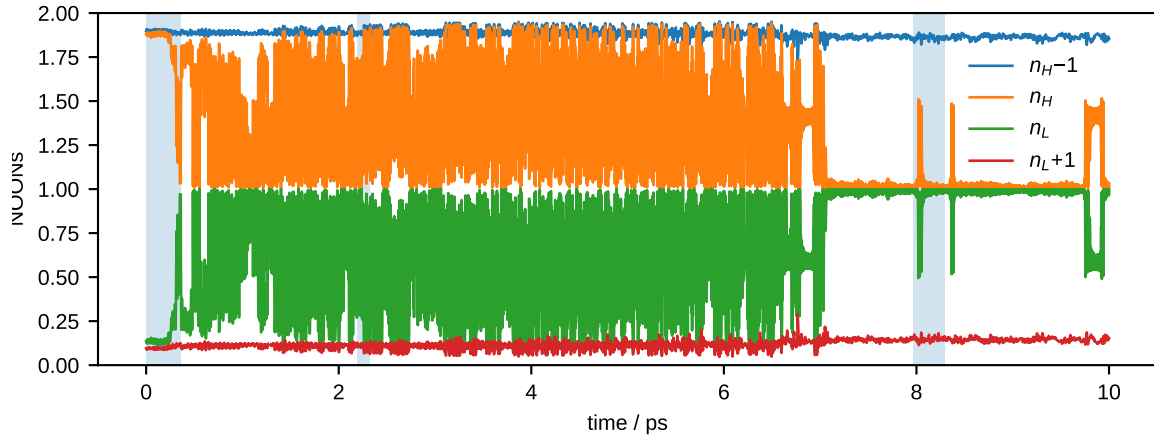


FIG. S4: NOONS along the ASQPM trajectory of [8]annulene. The regions shown in Fig. 3 of the main article are highlighted with blue background.

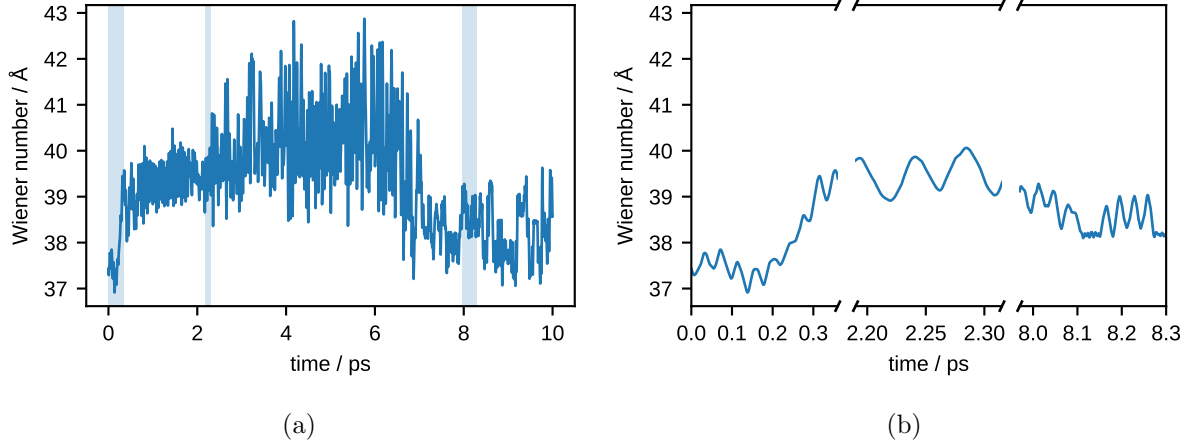


FIG. S5: Wiener number along the ASQPM trajectory of [8]annulene. a) Complete time evolution of the 10 ps trajectory. The regions shown in Fig. 3 of the main article are highlighted with blue background. b) Zoomed to the representative regions shown in Fig. 3 of the main article.

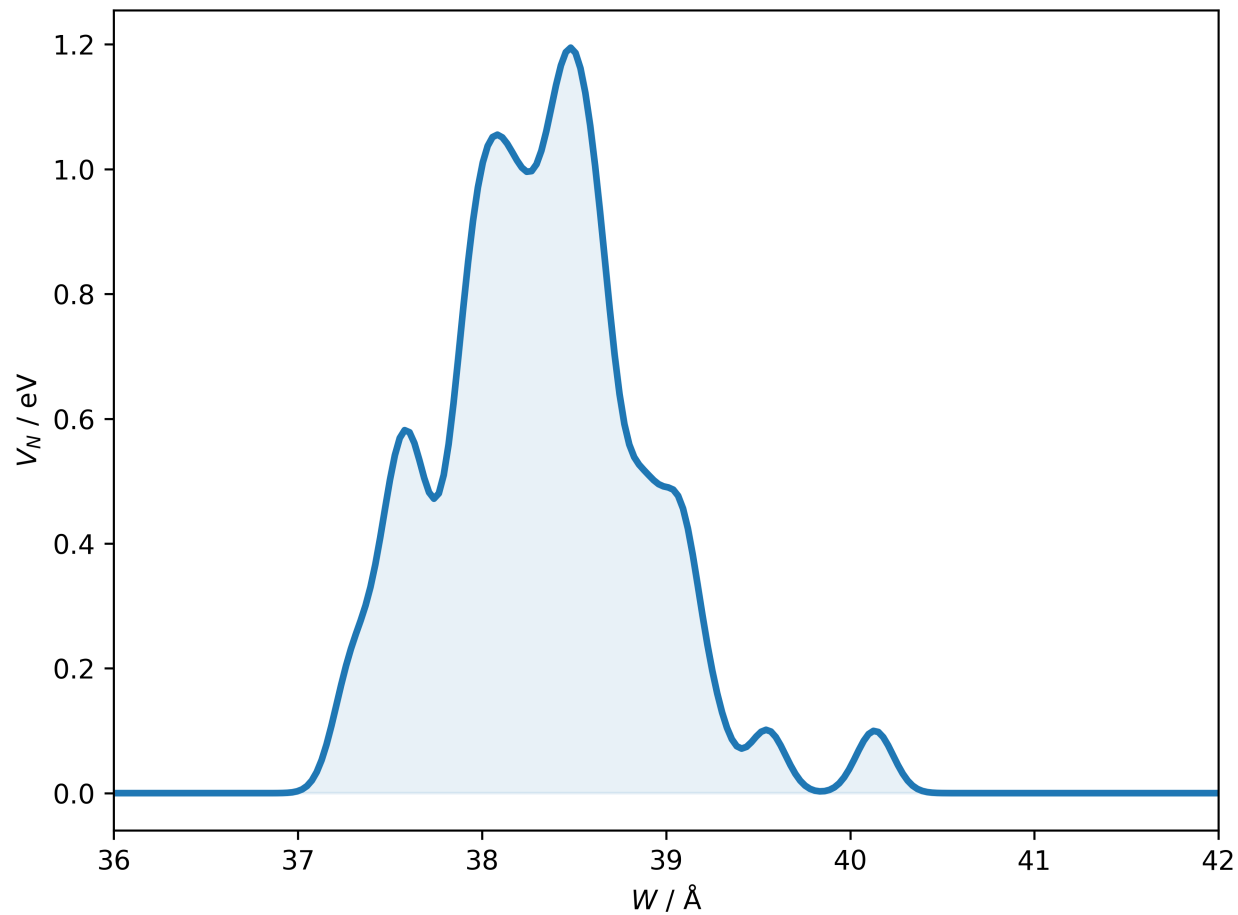


FIG. S6: Bias potential V_N in dependence of the Wiener number W , obtained from the ASQPM trajectory of [8]annulene after 10 ps, when 59 Gaussians have been added.

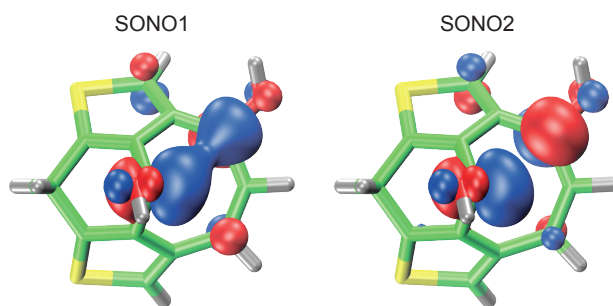


FIG. S7: Optimized structure and SONOs of the stabilized biradical **B2**.

TABLE S1: Cartesian coordinates of the optimized geometry of [8]annulene in Å on the CASSCF(8, 8)/6-31G level of theory ($E = -307.53180233$ a.u.).

C	-1.5830145777	0.2808515314	0.4304507653
C	-1.2921523200	-1.0354077273	0.4043890949
C	-0.2469717743	-1.6998044437	-0.4021610608
C	1.0693053815	-1.4086073491	-0.4237177604
C	1.7610559362	-0.3594075741	0.3538525632
C	1.4701486624	0.9568843864	0.3790355063
C	0.3940685061	1.6444599919	-0.3647949833
C	-0.9222504678	1.3534816475	-0.3421442385
H	-2.4192584592	0.5985718360	1.0310041868
H	-1.9110653678	-1.6981959869	0.9861516444
H	-0.5853137206	-2.5390744312	-0.9868922547
H	1.7114187327	-2.0306067013	-1.0249579002
H	2.6206437139	-0.6944034225	0.9102626244
H	2.1124850714	1.6021790304	0.9548877056
H	0.7091754800	2.5011436933	-0.9371550193
H	-1.5875112669	1.9926022891	-0.8986628435

TABLE S2: Cartesian coordinates of the optimized geometry of **B1** in Å on the CASSCF(8, 8)/6-31G level of theory ($E = -1291.58989906$ a.u.).

C	-1.4906566719	0.3543665167	0.7460648330
C	-1.7759335667	-0.7004577140	-0.2249453588
C	-0.6869022731	-1.5210095772	-0.7324828926
C	0.6925999274	-1.3772860520	-0.1988337635
C	1.4047877325	-0.2572350908	0.0693296858
C	1.2182773240	1.1942049259	-0.0530776426
C	0.0300038559	1.9429811645	-0.4967878064
C	-1.3046502013	1.5505121967	-0.0716572361
C	-1.0282257111	-2.1476750885	-1.8938835242
H	2.4011113576	-0.4705204675	0.4180948726
C	-0.0118851705	2.8241123716	-1.5139900914
C	-2.3137747376	1.8919830171	-0.9201030568
C	-3.4655589287	0.8991044472	-1.1184928961
H	-4.1908089058	0.9907867214	-0.3175471307
H	-3.9820016321	1.0732290731	-2.0501588609
C	-2.8062020109	-0.4861988163	-1.0931129797
H	-0.9376173319	0.1786415082	1.6447150876
H	2.1317588720	1.7534536840	0.0310470387
H	1.2216114441	-2.3012578569	-0.0456018864
S	-2.6617091111	-1.6261468899	-2.5048344020
S	-1.6917493399	3.0896606711	-2.1371453970
H	0.8055996290	3.2840623646	-2.0243518321
H	-0.4311345499	-2.7937911090	-2.4988647604

TABLE S3: Cartesian coordinates of the optimized geometry of **B2** in Å on the CASSCF(8, 8)/6-31G level of theory ($E = -1441.22883733$ a.u.).

C	-1.4766746189	0.3402677967	0.7625665170
C	-1.7484442231	-0.7467223757	-0.1989843396
C	-0.6495247606	-1.5104751013	-0.7573204184
C	0.7407446498	-1.3638601257	-0.2528862428
C	1.4460524301	-0.2467674314	0.0145610072
C	1.2270746695	1.2012858132	-0.0715947021
C	0.0473141569	1.9424014808	-0.5131407413
C	-1.2686389461	1.5012396091	-0.1154383734
C	-1.0150089983	-2.1353929916	-1.9128964328
H	2.4574120699	-0.4217576674	0.3329647233
C	-0.0203339531	2.8673601963	-1.5214538591
C	-2.2713095319	1.8216883809	-0.9370113014
C	-3.4566586761	0.8552302102	-1.0634969143
H	-4.1476529304	0.9876615054	-0.2401256141
H	-3.9967239592	1.0118228305	-1.9843997843
C	-2.8198692891	-0.5484151785	-1.0247921144
O	-2.3121498065	0.5387479034	1.8469703072
O	2.4400315740	1.8765565845	-0.0787223334
H	1.2795355254	-2.2849225005	-0.1218412745
S	-2.6857927785	-1.6615267062	-2.4574403787
S	-1.7237591255	3.0767153558	-2.1210732155
H	0.7768566026	3.3471603570	-2.0438540914
H	-0.4296766157	-2.7754797910	-2.5351693257
H	-2.5098668971	-0.2569012871	2.3294581439
H	2.3728234320	2.7983431327	0.1435507586