Supplementary Material (ESI) for New Journal of Chemistry

The effect of benzoannulation on the transition state and the proton transfer equilibrium in di(2-pyridyl)methane derivatives

Borys Ośmiałowski[a*], Tadeusz M. Krygowski[b],
Justyna Dominikowska[c], Marcin Palusiak[c]

[a] *Faculty of Chemical Technology and Engineering, University of Technology and Life Sciences, Seminaryjna 3, PL-85-326 Bydgoszcz, Poland,* [b] *Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland*
[c] *Department of Theoretical and Structural Chemistry, University of Łódź, Tamka 12, 91-403 Łódź, Poland*

Supporting Information file

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Optimized geometry and its energy for system pp at M05/6-31G(2d,p) level of theory.

E2 and E2' form

N	-2.12272568	4.00533219	0.00000000
C	-0.93194210	4.65899058	0.00000000
C	0.29381173	3.91540500	0.00000000
C	0.42441714	2.54247453	0.00000000
N	-0.68216937	1.71148524	0.00000000
C	-0.61724250	0.36041382	0.00000000
C	0.57531391	-0.29324427	0.00000000
C	1.75880576	0.50163957	0.00000000
C	1.68819494	1.85999816	0.00000000
C	-3.24776669	4.72097210	0.00000000
C	-3.29689490	6.10428033	0.00000000
C	-2.07732758	6.78849551	0.00000000
C	-0.90022245	6.07439646	0.00000000
H	1.21513607	4.48476754	0.00000000
H	-1.57310069	-0.15011944	0.00000000
H	0.61190613	-1.37352938	0.00000000
H	2.72818100	0.01422718	0.00000000
H	2.58587835	2.46651064	0.00000000
H	-4.17132235	4.14455288	0.00000000
H	-4.24572891	6.62643908	0.00000000
H	-2.05648493	7.87399016	0.00000000
H	0.05793342	6.58217995	0.00000000
H	-1.57089030	2.21933217	0.00000000

E= -534.3076873 a.u.

Optimized geometry and its energy for system pp at M05/6-31G(2d,p) level of theory.

M form

N	-1.59127942	-0.74838313	-1.45014828
C	-1.21636392	-0.91023749	-0.17807279
C	0.02159678	-1.73952937	0.06459228
C	1.23601882	-0.86113281	0.24548275
N	1.60478416	-0.59721441	1.50219645
C	2.66295075	0.19345439	1.68398712
C	3.40015383	0.75649743	0.65027071
C	3.00380268	0.48385628	-0.65423758
C	1.90488005	-0.33512765	-0.86282172
C	-2.67063669	-0.00234170	-1.68749260
C	-3.42386164	0.61366943	-0.69641488
C	-3.02115876	0.44734916	0.62394543
C	-1.90028378	-0.32383326	0.89000715
H	-0.09779359	-2.34089574	0.96664811
H	0.15837585	-2.40097704	-0.79179321
H	2.93943813	0.38598000	2.71911907
H	4.25538023	1.38761692	0.86233947
H	3.54538574	0.90214484	-1.49652816
H	1.55385297	-0.56445187	-1.86274103
H	-2.95152835	0.10695702	-2.73351625
H	-4.29598343	1.20395647	-0.95265946
H	-3.57469502	0.91056900	1.43435069
H	-1.54382942	-0.47028148	1.90348571

E= -534.3189772 a.u.

Optimized geometry and its energy for system pp at M05/6-31G(2d,p) level of theory.

TS form

N	-1.22855800	0.73877900	0.00000000
C	-1.23440400	-0.63276900	0.00000000
C	-0.00041100	-1.30696800	0.00000000
C	1.23431900	-0.63401500	0.00000000
N	1.22900200	0.73743700	0.00000000
C	2.36803800	1.44173600	0.00000000
C	3.60819700	0.85139600	0.00000000
C	3.65418400	-0.55894600	0.00000000
C	2.49705700	-1.29158100	0.00000000
C	-2.36763600	1.44322800	0.00000000
C	-3.60785500	0.85326300	0.00000000
C	-3.65440100	-0.55714600	0.00000000
C	-2.49746100	-1.28993800	0.00000000
H	-0.00122500	-2.38884400	0.00000000
H	2.25331700	2.52221000	0.00000000
H	4.50837500	1.45193800	0.00000000
H	4.61341800	-1.06670100	0.00000000
H	2.51922200	-2.37521800	0.00000000
H	-2.25274800	2.52368300	0.00000000
H	-4.50771300	1.45429000	0.00000000
H	-4.61377500	-1.06461600	0.00000000
H	-2.51973700	-2.37357400	0.00000000
H	0.00000000	1.07376500	0.00000000

E= -534.298164 a.u.

Optimized geometry and its energy for system pq at M05/6-31G(2d,p) level of theory.

E2 form

N	-0.38840238	1.78050298	0.00000000
C	-0.46291843	3.15920631	0.00000000
C	-1.68469258	3.80688036	0.00000000
C	-2.97034046	3.18158395	0.00000000
N	-3.08171771	1.84599316	0.00000000
C	-4.31443474	1.27584083	0.00000000
C	-5.51564523	2.03764135	0.00000000
C	-5.37750327	3.45250248	0.00000000
C	-4.14028562	4.01426363	0.00000000
C	0.76969889	1.08356780	0.00000000
C	1.97616596	1.71375227	0.00000000
C	1.97262749	3.13752519	0.00000000
C	0.80207725	3.83351936	0.00000000
H	-1.65651706	4.88919052	0.00000000
C	-4.41845003	-0.13579937	0.00000000
H	-4.01604668	5.09148894	0.00000000
H	0.66370422	0.00523563	0.00000000
H	0.79512033	4.91674436	0.00000000
H	-1.30878214	1.32653576	0.00000000
H	2.89551896	1.14474424	0.00000000
C	-6.76270770	1.38150132	0.00000000
C	-6.83407150	0.00735320	0.00000000
C	-5.64770640	-0.75168611	0.00000000
H	-6.27025681	4.07164431	0.00000000
H	2.91634019	3.67273954	0.00000000
H	-3.50130884	-0.71506230	0.00000000
H	-7.66865606	1.98100547	0.00000000
H	-7.79656988	-0.49195485	0.00000000
H	-5.70655641	-1.83530400	0.00000000

E= -687.8443507 a.u.

Optimized geometry and its energy for system pq at M05/6-31G(2d,p) level of theory.

E2' form

N	-0.38739830	1.74346515	0.00000000
C	-0.41189479	3.09909157	0.00000000
C	-1.67182366	3.79215581	0.00000000
C	-2.92696941	3.22882656	0.00000000
N	-3.12184610	1.86838773	0.00000000
C	-4.34281002	1.24654523	0.00000000
C	-5.51624524	2.03138845	0.00000000
C	-5.35436951	3.46128067	0.00000000
C	-4.12839658	4.02863485	0.00000000
C	0.79206262	1.12477106	0.00000000
C	2.01673676	1.77239032	0.00000000
C	2.00362952	3.16897964	0.00000000
C	0.79595099	3.83392303	0.00000000
H	-1.63244468	4.87445794	0.00000000
C	-4.43876600	-0.15123715	0.00000000
H	-4.01009324	5.10542061	0.00000000
H	0.75298155	0.03690125	0.00000000
H	0.75871459	4.91776659	0.00000000
H	-2.25730346	1.32762054	0.00000000
H	2.94215472	1.20941259	0.00000000
C	-6.76186997	1.39242428	0.00000000
C	-6.85363992	0.01095621	0.00000000
C	-5.68421408	-0.75526700	0.00000000
H	-6.24520091	4.08209479	0.00000000
H	2.93402695	3.72800616	0.00000000
H	-3.53234934	-0.74794459	0.00000000
H	-7.66012001	2.00273112	0.00000000
H	-7.82318825	-0.47338090	0.00000000
H	-5.74849423	-1.83801252	0.00000000

E= -687.8517311 a.u.

Optimized geometry and its energy for system pq at M05/6-31G(2d,p) level of theory.

M form

N	-0.01173152	3.88449092	1.17639513
C	-0.41964407	3.36093549	0.01674096
C	-1.63551710	3.98405450	-0.62507885
C	-2.88280352	3.19915202	-0.29468384
N	-3.37519188	2.42645005	-1.23653699
C	-4.48626100	1.69219001	-0.95262073
C	-5.13116811	1.72990653	0.31488694
C	-4.56373130	2.57065319	1.30149254
C	-3.44688797	3.30008719	1.00583567
C	1.04735543	3.33008794	1.76725715
C	1.74739756	2.24681029	1.25202267
C	1.31079246	1.70294441	0.04927459
C	0.21034070	2.26517693	-0.57865603
H	-1.72682152	5.00722925	-0.25639982
C	-5.02075403	0.85898830	-1.96410430
H	-2.97601199	3.94313399	1.74050369
H	1.35587380	3.78038172	2.70890276
H	-0.17100631	1.86569991	-1.51178494
H	-1.52668052	4.00096789	-1.70951635
H	2.60489090	1.84347877	1.77804704
C	-6.28381368	0.94072420	0.53414216
C	-6.77914583	0.14165398	-0.46585281
C	-6.14039195	0.10199015	-1.72445527
H	-5.02310626	2.62536206	2.28423994
H	1.82160161	0.85353504	-0.39271318
H	-4.51633270	0.84445384	-2.92331565
H	-6.76837016	0.97697626	1.50524891
H	-7.66344910	-0.46231197	-0.29298439
H	-6.54174856	-0.53404651	-2.50628700

E= -687. 8534833 a.u.

Optimized geometry and its energy for system pq at M05/6-31G(2d,p) level of theory.

TS form

N	-0.71396200	-1.99832200	0.00000000
C	0.59612000	-2.40090900	0.00000000
C	1.59224000	-1.41136700	0.00000000
C	1.29460000	-0.03570100	0.00000000
N	0.00000000	0.36265000	0.00000000
C	-0.33899700	1.68037400	0.00000000
C	0.65192100	2.69680100	0.00000000
C	2.01662000	2.27597900	0.00000000
C	2.33302000	0.95749700	0.00000000
C	-1.72778000	-2.87503800	0.00000000
C	-1.52462600	-4.23171400	0.00000000
C	-0.18866500	-4.69032200	0.00000000
C	0.85229100	-3.80098600	0.00000000
H	2.62854200	-1.72169900	0.00000000
C	-1.69750500	2.05918600	0.00000000
H	3.36515000	0.62587000	0.00000000
H	-2.72403100	-2.44325700	0.00000000
H	1.88139900	-4.14082300	0.00000000
H	-0.70681900	-0.79202800	0.00000000
H	-2.36234000	-4.91623900	0.00000000
C	0.26237400	4.04713200	0.00000000
C	-1.07132500	4.39793600	0.00000000
C	-2.05142700	3.39130400	0.00000000
H	2.79685600	3.03133200	0.00000000
H	0.01311300	-5.75663600	0.00000000
H	-2.45459100	1.28249600	0.00000000
H	1.03293500	4.81237100	0.00000000
H	-1.36423000	5.44178500	0.00000000
H	-3.10141000	3.66550200	0.00000000

E= -687.8375803 a.u.

Optimized geometry and its energy for system p1izo at M05/6-31G(2d,p) level of theory.

E2 form

N	-0.43098196	1.75180797	0.00000000
C	-0.46920244	3.13117941	0.00000000
C	-1.66921617	3.82291281	0.00000000
C	-2.97741137	3.24713320	0.00000000
N	-3.09091811	1.90757771	0.00000000
C	-4.31192342	1.33672421	0.00000000
C	-5.48909319	2.02881944	0.00000000
C	-5.43848289	3.44594101	0.00000000
C	-4.16770841	4.08404675	0.00000000
C	0.70687214	1.02318455	0.00000000
C	1.93055217	1.61961380	0.00000000
C	1.96573046	3.04228589	0.00000000
C	0.81419177	3.76979773	0.00000000
H	-1.57159197	4.89823139	0.00000000
H	-4.31570329	0.24862554	0.00000000
C	-4.13239440	5.49567473	0.00000000
H	0.57141184	-0.05196144	0.00000000
H	0.83860747	4.85280062	0.00000000
H	-1.36833503	1.33105768	0.00000000
H	2.83356934	1.02533519	0.00000000
H	-6.44252961	1.51412635	0.00000000
C	-6.61242600	4.23373203	0.00000000
H	2.92300856	3.55218065	0.00000000
C	-6.54161367	5.60490932	0.00000000
C	-5.28828606	6.24267064	0.00000000
H	-3.18203673	6.01360770	0.00000000
H	-7.57446122	3.73118369	0.00000000
H	-7.45025567	6.19814913	0.00000000
H	-5.23231387	7.32587147	0.00000000

E= -687.8392922 a.u.

Optimized geometry and its energy for system p1izo at M05/6-31G(2d,p) level of theory.

E2' form

N	-0.44326968	1.70407413	0.00000000
C	-0.43271684	3.05989596	0.00000000
C	-1.66642912	3.80019794	0.00000000
C	-2.94419257	3.28942678	0.00000000
N	-3.13939621	1.92613689	0.00000000
C	-4.35428068	1.31688954	0.00000000
C	-5.50313915	2.02571948	0.00000000
C	-5.43116267	3.46094099	0.00000000
C	-4.16594013	4.10274054	0.00000000
C	0.71856691	1.05133477	0.00000000
C	1.96027119	1.66439447	0.00000000
C	1.98511985	3.06129438	0.00000000
C	0.79687560	3.75874358	0.00000000
H	-1.55593284	4.87477393	0.00000000
H	-4.32649590	0.23380913	0.00000000
C	-4.12873358	5.50571233	0.00000000
H	0.64789011	-0.03486051	0.00000000
H	0.79124312	4.84311618	0.00000000
H	-2.27082838	1.38826378	0.00000000
H	2.86957154	1.07602378	0.00000000
H	-6.46207197	1.52476940	0.00000000
C	-6.59864079	4.24444619	0.00000000
H	2.93052159	3.59486243	0.00000000
C	-6.53305369	5.62283588	0.00000000
C	-5.28805688	6.25827082	0.00000000
H	-3.17579809	6.01978894	0.00000000
H	-7.56103735	3.74240739	0.00000000
H	-7.44457411	6.21096889	0.00000000
H	-5.22812931	7.34088198	0.00000000

E= -687.846198 a.u.

Optimized geometry and its energy for system p1izo at M05/6-31G(2d,p) level of theory.

M form

N	2.77030985	-0.16319936	1.42025215
C	2.17464097	-0.57536547	0.29927168
C	0.75455090	-1.05130694	0.43456474
C	-0.29487848	-0.06706909	-0.04071172
N	0.12090691	1.05733096	-0.57424899
C	-0.79826048	1.95532607	-1.00284285
C	-2.14914232	1.76637302	-0.92007159
C	-2.63547307	0.56332451	-0.35642242
C	-1.68537491	-0.39035352	0.10091438
C	4.03413555	0.25348034	1.33448694
C	4.76712987	0.27697942	0.15575751
C	4.14138951	-0.15972017	-1.00663291
C	2.82700385	-0.59153832	-0.93543723
H	0.62473391	-1.99012659	-0.11633369
H	-0.39193772	2.86846936	-1.43089635
C	-2.15502160	-1.60122344	0.66480131
H	4.48877615	0.58475597	2.26620815
H	2.30293850	-0.93017209	-1.82223941
H	0.58086585	-1.27832157	1.48944840
H	5.79431683	0.62272249	0.15080484
H	-2.84246339	2.51977103	-1.27818600
C	-4.01677675	0.27940923	-0.23497461
H	4.67076980	-0.16208737	-1.95399295
C	-4.43982978	-0.90348535	0.31552749
C	-3.50080809	-1.85286290	0.76898093
H	-1.44602580	-2.33967962	1.01947472
H	-4.73472550	1.01411714	-0.58529593
H	-5.50043518	-1.11345405	0.40454567
H	-3.84666537	-2.78482768	1.20277170

E= -687.8457764 a.u.

Optimized geometry and its energy for system p1izo at M05/6-31G(2d,p) level of theory.

TS form

N	0.86408400	-2.39779700	0.00000000
C	-0.47902000	-2.12753600	0.00000000
C	-0.89734000	-0.78683500	0.00000000
C	0.00000000	0.29942000	0.00000000
N	1.32822900	0.02033400	0.00000000
C	2.25514000	1.00243300	0.00000000
C	1.94397100	2.32743400	0.00000000
C	0.57012100	2.70539900	0.00000000
C	-0.42512200	1.69218300	0.00000000
C	1.34247900	-3.65038600	0.00000000
C	0.52019300	-4.74762200	0.00000000
C	-0.87386200	-4.51644100	0.00000000
C	-1.36785100	-3.23993000	0.00000000
H	-1.96219300	-0.60972400	0.00000000
H	3.28845400	0.66615300	0.00000000
C	-1.77895400	2.07839600	0.00000000
H	2.42425600	-3.74183400	0.00000000
H	-2.43509300	-3.05124200	0.00000000
H	1.41486500	-1.33842100	0.00000000
H	0.93208200	-5.74784300	0.00000000
H	2.72009300	3.08281000	0.00000000
C	0.17325300	4.05940100	0.00000000
H	-1.55785900	-5.35892100	0.00000000
C	-1.15815800	4.40647200	0.00000000
C	-2.14427900	3.40750200	0.00000000
H	-2.55410100	1.32228300	0.00000000
H	0.94115800	4.82635800	0.00000000
H	-1.44747800	5.45225600	0.00000000
H	-3.19378400	3.68102300	0.00000000

E= -687.833518 a.u.

Optimized geometry and its energy for system p3izo at M05/6-31G(2d,p) level of theory.

E2 form

N	-0.41420087	1.74507576	0.00000000
C	-0.50334149	3.12777136	0.00000000
C	-1.71546640	3.78282016	0.00000000
C	-3.02570401	3.19909199	0.00000000
N	-3.14422370	1.82387713	0.00000000
C	-4.33911678	1.28774789	0.00000000
C	-5.55160227	2.01144487	0.00000000
C	-5.44885784	3.43238181	0.00000000
C	-4.16774847	4.00025626	0.00000000
C	0.75171267	1.05756231	0.00000000
C	1.95232567	1.69461273	0.00000000
C	1.93729039	3.12150592	0.00000000
C	0.76364291	3.80746385	0.00000000
H	-1.66814357	4.86508705	0.00000000
H	-4.38286496	0.19789983	0.00000000
H	-4.06170365	5.08028249	0.00000000
H	0.65357302	-0.02145242	0.00000000
H	0.75001091	4.89054024	0.00000000
H	-1.32037447	1.27617239	0.00000000
H	2.87520990	1.13229243	0.00000000
C	-6.82162823	1.39074477	0.00000000
H	-6.87693886	0.30610108	0.00000000
C	-6.65089058	4.19145120	0.00000000
H	2.87656703	3.66429870	0.00000000
C	-7.96328430	2.15022254	0.00000000
H	-8.93872603	1.67692492	0.00000000
H	-6.58794770	5.27496429	0.00000000
C	-7.86847634	3.56367556	0.00000000
H	-8.77850198	4.15520287	0.00000000

E= -687.8378101 a.u.

Optimized geometry and its energy for system p3izo at M05/6-31G(2d,p) level of theory.

E2' form

N	-0.47967942	1.74199005	0.00000000
C	-0.46718744	3.10351373	0.00000000
C	-1.69623209	3.83287428	0.00000000
C	-2.97509369	3.29955509	0.00000000
N	-3.15005214	1.91651400	0.00000000
C	-4.33104191	1.30043178	0.00000000
C	-5.51892899	2.00587370	0.00000000
C	-5.42312032	3.44789646	0.00000000
C	-4.18044728	4.05087873	0.00000000
C	0.68039328	1.08439798	0.00000000
C	1.92397276	1.69003035	0.00000000
C	1.95289986	3.08958890	0.00000000
C	0.77130475	3.79415014	0.00000000
H	-1.62935902	4.91373291	0.00000000
H	-4.30487955	0.21590064	0.00000000
H	-4.10424804	5.13218193	0.00000000
H	0.60449758	-0.00176361	0.00000000
H	0.77125461	4.87866845	0.00000000
H	-2.25543476	1.40433853	0.00000000
H	2.83074108	1.09818536	0.00000000
C	-6.79339485	1.36887981	0.00000000
H	-6.83450780	0.28392581	0.00000000
C	-6.65360878	4.18431246	0.00000000
H	2.90125303	3.61843667	0.00000000
C	-7.93435500	2.11177710	0.00000000
H	-8.90616012	1.63178854	0.00000000
H	-6.60876721	5.26836119	0.00000000
C	-7.85238917	3.53911665	0.00000000
H	-8.77135936	4.11609237	0.00000000

E= -687.8295486 a.u.

Optimized geometry and its energy for system p3izo at M05/6-31G(2d,p) level of theory.

M form

N	-0.16183697	3.76733255	1.28184757
C	-0.55459332	3.54221383	0.02530990
C	-1.62832986	4.45528446	-0.52063598
C	-2.96077491	3.75632148	-0.61637468
N	-3.15064575	2.99484224	-1.72997232
C	-4.28571976	2.35239901	-1.84832991
C	-5.33770353	2.38920831	-0.90038876
C	-5.13464927	3.17880479	0.26147609
C	-3.90537367	3.86536787	0.37672990
C	0.77699922	2.96787847	1.79001179
C	1.36509686	1.91893538	1.09569578
C	0.94428366	1.68747250	-0.20934592
C	-0.02874550	2.50922165	-0.75612247
H	-1.69865022	5.32003509	0.13874653
H	-4.41658733	1.75211700	-2.74966510
H	-3.70834964	4.47471457	1.25275108
H	1.07828969	3.18090237	2.81408224
H	-0.39691369	2.35818267	-1.76427478
H	-1.34959328	4.79444034	-1.52091751
H	2.12632153	1.30498403	1.56338085
C	-6.55095156	1.68373975	-1.06974931
H	-6.69192446	1.08475564	-1.96440063
C	-6.16377628	3.23795009	1.23286172
H	1.37053010	0.87792946	-0.79314820
C	-7.53129502	1.75843913	-0.11332956
H	-8.46267190	1.21758371	-0.24006543
H	-6.01411116	3.83913977	2.12402395
C	-7.33181340	2.54262413	1.04580332
H	-8.11592058	2.59319972	1.79399983

E= -687.8507142 a.u.

Optimized geometry and its energy for system p3izo at M05/6-31G(2d,p) level of theory.

TS form

N	2.46933500	0.76627900	0.00000000
C	2.51826100	-0.60380600	0.00000000
C	1.30862200	-1.32859900	0.00000000
C	0.04196900	-0.72334500	0.00000000
N	0.00000000	0.66458800	0.00000000
C	-1.12994500	1.34617800	0.00000000
C	-2.38080700	0.73041600	0.00000000
C	-2.39799700	-0.70716000	0.00000000
C	-1.19338000	-1.40083700	0.00000000
C	3.59223000	1.49322000	0.00000000
C	4.85135200	0.93858300	0.00000000
C	4.93583400	-0.46784800	0.00000000
C	3.79665000	-1.22963800	0.00000000
H	1.35657300	-2.40952100	0.00000000
H	-1.04230800	2.42990700	0.00000000
H	-1.19262800	-2.48519700	0.00000000
H	3.45413600	2.57169500	0.00000000
H	3.84739600	-2.31249100	0.00000000
H	1.13306500	1.04827300	0.00000000
H	5.73430900	1.56447700	0.00000000
C	-3.59679300	1.46325900	0.00000000
H	-3.55336000	2.54825800	0.00000000
C	-3.67541300	-1.34837200	0.00000000
H	5.90786100	-0.95081200	0.00000000
C	-4.79638300	0.81115400	0.00000000
H	-5.72712800	1.36671300	0.00000000
H	-3.71341500	-2.43276100	0.00000000
C	-4.82501800	-0.61251900	0.00000000
H	-5.78494600	-1.11873800	0.00000000

E= -687.8239928 a.u.

Optimized geometry and its energy for system pf at M05/6-31G(2d,p) level of theory.

E2 form

N	-0.50839888	1.78445369	0.00000000
C	-0.47603679	3.11300079	0.00000000
C	-1.70957764	3.83352271	0.00000000
C	-2.98005234	3.27847189	0.00000000
N	-3.17040580	1.91400990	0.00000000
C	-4.38194276	1.31585103	0.00000000
C	-5.53133938	2.04545799	0.00000000
C	-5.40803211	3.46271629	0.00000000
C	-4.18239617	4.05729150	0.00000000
C	0.64482868	1.05227642	0.00000000
C	1.93435241	1.63473323	0.00000000
C	2.00878745	3.08377781	0.00000000
C	0.80547582	3.83063789	0.00000000
H	-1.69252659	4.91216023	0.00000000
H	-4.36662979	0.23227089	0.00000000
H	-4.08543750	5.13607148	0.00000000
C	0.52789456	-0.35445693	0.00000000
C	0.88439706	5.23627365	0.00000000
H	-2.28324441	1.39403336	0.00000000
C	1.64363252	-1.16084523	0.00000000
C	2.92212232	-0.58600162	0.00000000
C	3.05684751	0.78775030	0.00000000
H	-6.49529110	1.55606509	0.00000000
H	-6.30273814	4.07580741	0.00000000
C	3.23532011	3.77662870	0.00000000
H	-0.46986203	-0.77998995	0.00000000
H	1.53383586	-2.24018102	0.00000000
H	3.80412750	-1.21713300	0.00000000
H	4.05421706	1.21185370	0.00000000
C	3.28350741	5.15349582	0.00000000
C	2.09649163	5.89277787	0.00000000
H	-0.02003482	5.82959350	0.00000000
H	4.16510152	3.22172795	0.00000000
H	4.24218224	5.66138871	0.00000000
H	2.12685457	6.97688795	0.00000000

E= -841.3761192 a.u.

Optimized geometry and its energy for system pf at M05/6-31G(2d,p) level of theory.

E2' form

N	-0.45992996	1.78337137	0.00000000
C	-0.50805454	3.15062374	0.00000000
C	-1.72064573	3.79839535	0.00000000
C	-3.03251076	3.20107693	0.00000000
N	-3.17552831	1.85384845	0.00000000
C	-4.40326209	1.33712600	0.00000000
C	-5.56729810	2.08795452	0.00000000
C	-5.43354692	3.47789749	0.00000000
C	-4.17288910	4.03570585	0.00000000
C	0.67172884	1.01085173	0.00000000
C	1.93925076	1.62131544	0.00000000
C	1.99245176	3.08408780	0.00000000
C	0.79335487	3.83717270	0.00000000
H	-1.71595051	4.87803832	0.00000000
H	-4.45647538	0.24999155	0.00000000
H	-4.04418733	5.11233048	0.00000000
C	0.55111731	-0.38619417	0.00000000
C	0.87499437	5.23844859	0.00000000
H	-1.37866108	1.34002315	0.00000000
C	1.68269441	-1.17872324	0.00000000
C	2.94978566	-0.59225746	0.00000000
C	3.06571958	0.78747069	0.00000000
H	-6.53796413	1.60726433	0.00000000
H	-6.31204417	4.11539773	0.00000000
C	3.21590643	3.77439682	0.00000000
H	-0.43898755	-0.83011087	0.00000000
H	1.58116362	-2.25846266	0.00000000
H	3.83988703	-1.21101724	0.00000000
H	4.05735123	1.22350597	0.00000000
C	3.27177357	5.15411997	0.00000000
C	2.09021845	5.89444058	0.00000000
H	-0.03066209	5.83043181	0.00000000
H	4.14489784	3.21865829	0.00000000
H	4.23317881	5.65623893	0.00000000
H	2.12003320	6.97831105	0.00000000

E= -841.3866827 a.u.

Optimized geometry and its energy for system pf at M05/6-31G(2d,p) level of theory.

M form

N	-0.61456111	2.01981213	-0.17204064
C	-0.46628801	3.28851438	0.04915267
C	-1.71349115	4.13851661	0.18057739
C	-3.01627166	3.38830012	0.23293424
N	-3.65838417	3.42033473	1.40297000
C	-4.83318127	2.79439490	1.48658791
C	-5.42918580	2.11877366	0.43128406
C	-4.75502110	2.09045503	-0.78473614
C	-3.53126138	2.73180098	-0.88759396
C	0.49475837	1.21596356	-0.29622680
C	1.81842858	1.70256116	-0.19297701
C	1.99127312	3.11833235	0.04976005
C	0.83349194	3.92525246	0.16855785
H	-1.65045118	4.73288766	1.09428323
H	-5.32777460	2.84124737	2.45493920
H	-2.97149369	2.72204175	-1.81522354
C	0.27061775	-0.15344971	-0.53652988
C	0.97868544	5.30895093	0.39528724
H	-1.72964066	4.85011759	-0.65433069
C	1.32742078	-1.02509359	-0.67290156
C	2.64265588	-0.54763455	-0.57028602
C	2.88129554	0.78963585	-0.33451231
H	-6.38997708	1.63295861	0.55746391
H	-5.17855328	1.57452124	-1.64042900
C	3.25443449	3.73019241	0.17081181
H	-0.75844488	-0.48598352	-0.60706909
H	1.14618490	-2.07839300	-0.85794519
H	3.47683724	-1.23274068	-0.67657987
H	3.90652653	1.13231052	-0.25942498
C	3.37121950	5.08426611	0.39534962
C	2.22569394	5.88346781	0.50713747
H	0.09990048	5.93531926	0.48522313
H	4.15396305	3.13301382	0.08675581
H	4.35483723	5.53250671	0.48644442
H	2.32038426	6.94922437	0.68328668

E= -841.382831 a.u.

Optimized geometry and its energy for system pf at M05/6-31G(2d,p) level of theory.

TS form

N	0.00000000	0.69960700	0.00000000
C	0.45125200	-0.56547800	0.00000000
C	1.84604500	-0.77150100	0.00000000
C	2.77596800	0.28175600	0.00000000
N	2.30923800	1.56837200	0.00000000
C	3.12532400	2.63199400	0.00000000
C	4.48987600	2.50194000	0.00000000
C	5.01948700	1.19172900	0.00000000
C	4.18833400	0.10368600	0.00000000
C	-1.33087700	1.00687200	0.00000000
C	-2.33182500	0.00854600	0.00000000
C	-1.89617800	-1.37984800	0.00000000
C	-0.51115700	-1.67187100	0.00000000
H	2.25102600	-1.77138300	0.00000000
H	2.63651600	3.60119600	0.00000000
H	4.58431100	-0.90501800	0.00000000
C	-1.70638500	2.36462000	0.00000000
C	-0.09856800	-3.01543100	0.00000000
H	1.13584400	1.49728700	0.00000000
C	-3.03574100	2.72883500	0.00000000
C	-4.03274100	1.74559400	0.00000000
C	-3.67753400	0.41047500	0.00000000
H	5.12883000	3.37496400	0.00000000
H	6.09506000	1.04797600	0.00000000
C	-2.80767400	-2.45209700	0.00000000
H	-0.92395200	3.11596300	0.00000000
H	-3.30837800	3.77905600	0.00000000
H	-5.07944600	2.02859700	0.00000000
H	-4.46341700	-0.33545000	0.00000000
C	-2.37885800	-3.76267400	0.00000000
C	-1.01117300	-4.04990200	0.00000000
H	0.95724600	-3.25328400	0.00000000
H	-3.87190100	-2.25246200	0.00000000
H	-3.10498800	-4.56851700	0.00000000
H	-0.66686500	-5.07825200	0.00000000

E= -841.3713981 a.u.

Optimized geometry and its energy for system pq at M05/6-311++G(d,p) level of theory.

E2 form

N	-0.38364300	1.77841300	0.00000000
C	-0.46170200	3.15646000	0.00000000
C	-1.68424200	3.80288000	0.00000000
C	-2.97066600	3.17807900	0.00000000
N	-3.08404600	1.84434000	0.00000000
C	-4.31667000	1.27316800	0.00000000
C	-5.51567200	2.03686100	0.00000000
C	-5.37628900	3.45161600	0.00000000
C	-4.13989100	4.01243000	0.00000000
C	0.77706100	1.08405100	0.00000000
C	1.98020200	1.71861200	0.00000000
C	1.97319500	3.14245400	0.00000000
C	0.80182300	3.83475000	0.00000000
H	-1.65608300	4.88564500	0.00000000
C	-4.42390900	-0.13836800	0.00000000
H	-4.01646900	5.08996800	0.00000000
H	0.67718400	0.00517900	0.00000000
H	0.79411200	4.91813500	0.00000000
H	-1.30166400	1.31809200	0.00000000
H	2.90139100	1.15228500	0.00000000
C	-6.76407500	1.38351100	0.00000000
C	-6.83861000	0.01018300	0.00000000
C	-5.65429900	-0.75130000	0.00000000
H	-6.26778900	4.07288200	0.00000000
H	2.91527200	3.68063000	0.00000000
H	-3.50909700	-0.72198500	0.00000000
H	-7.66995300	1.98377300	0.00000000
H	-7.80267300	-0.48665600	0.00000000
H	-5.71513100	-1.83493600	0.00000000

E= -687.9391886 a.u.

Optimized geometry and its energy for system pq at M05/6-311++G(d,p) level of theory.

E2' form

N	-0.38163500	1.74350400	0.00000000
C	-0.40995200	3.09759000	0.00000000
C	-1.67092000	3.78807700	0.00000000
C	-2.92574300	3.22339100	0.00000000
N	-3.12179400	1.86346400	0.00000000
C	-4.34525600	1.24322100	0.00000000
C	-5.51576000	2.03055400	0.00000000
C	-5.35186300	3.46037500	0.00000000
C	-4.12602900	4.02532600	0.00000000
C	0.79879200	1.12604200	0.00000000
C	2.02100900	1.77780500	0.00000000
C	2.00440300	3.17445800	0.00000000
C	0.79614900	3.83586500	0.00000000
H	-1.63398100	4.87088200	0.00000000
C	-4.44493300	-0.15409500	0.00000000
H	-4.00814200	5.10233900	0.00000000
H	0.76284300	0.03805100	0.00000100
H	0.75756500	4.91980700	0.00000000
H	-2.25802200	1.31914800	0.00000000
H	2.94843100	1.21754500	0.00000000
C	-6.76293200	1.39432900	0.00000000
C	-6.85827700	0.01410300	0.00000000
C	-5.69115200	-0.75519000	0.00000000
H	-6.24080300	4.08392900	0.00000000
H	2.93373500	3.73553200	0.00000000
H	-3.54037500	-0.75395100	0.00000000
H	-7.66085300	2.00546000	0.00000000
H	-7.82926900	-0.46777100	0.00000000
H	-5.75841600	-1.83797800	0.00000000

E= -687.9460255 a.u.

Optimized geometry and its energy for system pq at M05/6-311++G(d,p) level of theory.

M form

C	0.16621500	0.50004300	0.33895400
C	0.20688600	-0.02726300	1.62320500
C	1.41600900	-0.53944700	2.07699900
C	2.51697000	-0.50595500	1.23558900
C	2.37386700	0.03966700	-0.04281900
N	1.21515300	0.53797300	-0.48104600
H	1.49921800	-0.96099600	3.07360800
H	-0.76135200	0.91170000	-0.05433600
H	-0.68135100	-0.03485400	2.24474900
H	3.47896900	-0.89046700	1.55629600
C	3.55312400	0.11619800	-0.98085100
H	4.21684500	-0.73483100	-0.82742500
H	3.17407400	0.09012500	-2.00480100
C	4.35850900	1.37608700	-0.76672700
C	3.82797000	2.62632500	-1.18680700
C	6.26458100	2.37677000	0.04052800
C	4.55965800	3.75995900	-0.97673600
H	2.85221500	2.66037500	-1.65756900
C	5.82347600	3.67179500	-0.34709500
C	7.52397400	2.24723400	0.67438300
H	4.18409700	4.73065900	-1.28806600
C	6.64682500	4.79296400	-0.09249100
C	8.30217900	3.35225700	0.90995800
H	7.84574100	1.25266600	0.96226200
C	7.86243300	4.63696500	0.52398000
H	6.30193200	5.77830400	-0.39255900
H	9.26581000	3.24173400	1.39651000
H	8.49009600	5.50029900	0.71707800
N	5.52401200	1.25626000	-0.17570900

E= -687.9484222 a.u.

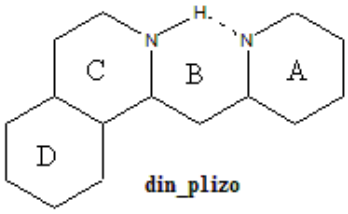
Optimized geometry and its energy for system pq at M05/6-311++G(d,p) level of theory.

TS form

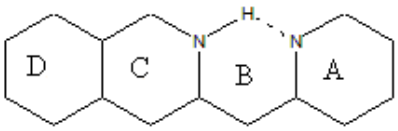
N	-0.70714600	-2.00139000	0.00000000
C	0.60316900	-2.39882000	0.00000000
C	1.59662600	-1.40558900	0.00000000
C	1.29463200	-0.03089400	0.00000000
N	0.00000000	0.36324600	0.00000000
C	-0.34558700	1.68002300	0.00000000
C	0.64151000	2.69874700	0.00000000
C	2.00835700	2.28273200	0.00000000
C	2.32982900	0.96645700	0.00000000
C	-1.71799000	-2.88259300	0.00000000
C	-1.50766600	-4.23781600	0.00000000
C	-0.16992600	-4.69111600	0.00000000
C	0.86647100	-3.79792400	0.00000000
H	2.63439000	-1.71238000	0.00000000
C	-1.70535400	2.05400900	0.00000000
H	3.36379600	0.64026200	0.00000000
H	-2.71718300	-2.45741800	0.00000000
H	1.89671700	-4.13490200	0.00000000
H	-0.70334600	-0.78801700	0.00000000
H	-2.34233000	-4.92669700	0.00000000
C	0.24709100	4.04757500	0.00000000
C	-1.08724000	4.39387700	0.00000000
C	-2.06384600	3.38434500	0.00000000
H	2.78680300	3.04013900	0.00000000
H	0.03647500	-5.75660900	0.00000000
H	-2.46139500	1.27577300	0.00000000
H	1.01402700	4.81685300	0.00000000
H	-1.38359400	5.43689200	0.00000000
H	-3.11480400	3.65504400	0.00000000

E= -687.9318737 a.u.

Scheme of ring notation



din_p1izo



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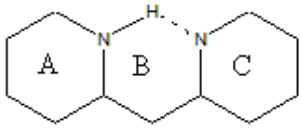
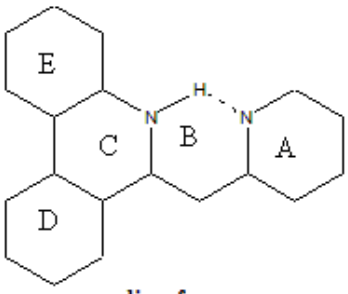
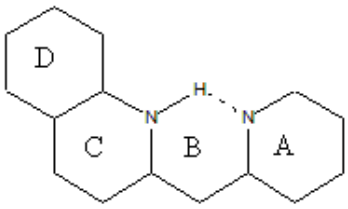


din_pp



din_pf



din_pq

Aromaticity indices (HOMA, PDI, FLU, NICS, NICS(1), $NICS(1)_{zz}$) and the densities of total electron energy at the ring critical point (H_{RCP}) collected for all the systems under consideration.

		ring no	HOMA	PDI	FLU	NICS	NICS(1)	$NICS(1)_{zz}$	$H_{RCP}\times10^3$
pp	E2	A	0.73	0.0602	0.0260	-0.0789	-2.3747	-4.2403	8.455
		B	0.79	0.0182	-	1.6466	-0.8816	1.7634	5.131
		C	0.95	0.0843	0.0042	-5.2722	-8.2919	-22.0050	7.863
	TS	A	0.88	0.0724	0.0117	-3.6265	-6.0553	-15.2060	8.120
		B	0.89	0.0218	-	2.0924	-1.4432	-0.5572	7.359
		C	0.88	0.0724	0.0117	-3.6354	-6.0637	-15.2314	8.120
pq	E2	A	0.76	0.0617	0.0244	-0.7334	-3.1333	-6.3731	8.468
		B	0.83	0.0214	-	1.8921	-0.7588	2.3577	5.312
		C	0.76	0.0566	0.0170	-4.5001	-7.8484	-19.2259	7.699
		D	0.87	0.0760	0.0094	-8.3864	-10.4646	-27.6265	8.280
	TS	A	0.87	0.0716	0.0130	-3.3672	-5.8508	-14.4169	8.202
		B	0.92	0.0239	-	2.2977	-1.1850	0.3723	7.359
		C	0.72	0.0477	0.0225	-2.5917	-5.8238	-13.0716	7.850
		D	0.9	0.0780	0.0076	-7.9357	-10.0633	-26.3177	8.313
	E2'	A	0.96	0.0860	0.0036	-5.4814	-8.5449	-22.6586	7.864
		B	0.78	0.0183	-	1.8688	-0.6130	2.8069	4.901
		C	0.63	0.0350	0.0369	0.9567	-2.0493	-1.7375	8.225
		D	0.96	0.0818	0.0048	-7.6922	-9.4160	-24.0925	8.384
p1izo	E2	A	0.76	0.0622	0.0240	-0.7757	-3.2139	-6.6409	8.469
		B	0.84	0.0214	-	2.0479	-0.8392	2.0432	5.453
		C	0.69	0.0569	0.0139	-4.5880	-7.8998	-19.5957	7.642
		D	0.87	0.0801	0.0067	-8.7516	-10.7564	-28.0102	8.297
	TS	A	0.87	0.0711	0.0134	-3.2865	-5.7324	-14.1718	8.219
		B	0.91	0.0238	-	2.4879	-1.1423	0.4950	7.358
		C	0.65	0.0485	0.0185	-2.9384	-5.9831	-13.7484	7.793
		D	0.89	0.0820	0.0054	-8.2194	-10.5646	-27.6259	8.324
	E2'	A	0.96	0.0857	0.0038	-5.4644	-8.4987	-22.5411	7.876
		B	0.77	0.0189	-	2.0636	-0.6560	2.6548	5.288
		C	0.49	0.0356	0.0328	0.6225	-2.3108	-2.7765	8.127
		D	0.93	0.0853	0.0034	-7.5531	-9.7209	-25.1656	8.357
p3izo	E2	A	0.71	0.0590	0.0272	0.5619	-1.9576	-2.9255	8.452
		B	0.74	0.0143	-	2.1873	-0.4845	3.2637	4.867
		C	0.87	0.0643	0.0122	-6.2365	-9.4138	-23.9354	7.715
		D	0.8	0.0713	0.0115	-7.2286	-9.5766	-24.3945	8.260
	TS	A	0.89	0.0738	0.0101	-3.6866	-6.2205	-15.6981	8.050
		B	0.85	0.0187	-	2.4443	-1.2012	0.4750	7.225
		C	0.82	0.0593	0.0163	-4.2272	-6.8004	-16.0918	8.064
		D	0.68	0.0638	0.0170	-4.0058	-6.9257	-16.5051	8.203
	E2'	A	0.94	0.0822	0.0050	-4.9554	-7.8794	-20.7610	7.871
		B	0.79	0.0167	-	1.8061	-1.0278	1.5031	5.447
		C	0.76	0.0562	0.0230	-0.7741	-3.6261	-6.7454	8.320
		D	0.58	0.0588	0.0215	-1.0378	-4.3253	-8.7120	8.162
pf	E2	A	0.76	0.0629	0.0235	-0.9148	-3.3153	-6.8684	8.480
		B	0.85	0.0235	-	2.1676	-0.6039	2.9285	5.481
		C	0.47	0.0350	0.0242	-1.5243	-5.9194	-12.1647	7.391

		D	0.92	0.0861	0.0037	-8.6820	-10.8415	-28.1471	8.336
		E	0.92	0.0804	0.0064	-7.9780	-10.1842	-26.6303	8.332
	TS	A	0.87	0.0714	0.0136	-3.2342	-5.6819	-13.8386	8.251
		B	0.92	0.0253	-	2.6889	-0.8707	1.5368	7.353
		C	0.46	0.0301	0.0269	-0.1920	-4.3250	-7.3597	7.498
		D	0.93	0.0868	0.0033	-8.0962	-10.4870	-27.2555	8.355
		E	0.93	0.0814	0.0057	-7.5312	-9.7052	-25.0915	8.347
	E2'	A	0.96	0.0865	0.0035	-5.3952	-8.4347	-22.2808	7.879
		B	0.76	0.0190	-	2.4740	-0.2353	4.1392	5.226
		C	0.37	0.0218	0.0387	2.2380	-1.5177	1.0357	7.827
		D	0.94	0.0885	0.0025	-7.2047	-9.5948	-24.6707	8.372
		E	0.96	0.0841	0.0042	-7.2985	-9.1383	-23.1092	8.403

	E2	**E2'**
pp	7.97	7.97
pq	8.42	7.21
p1izo	9.23	8.30
p3izo	7.38	9.27
pf	9.19	8.04

Values of H-bonding energy estimated according to relation proposed by Espinosa et al. The relation is as follows: $E_{\text{H-bond}} = 0.5\ V_{\text{H-BCP}}$, where $V_{\text{H-BCP}}$ is the density of potential electron energy estimated in H-bond critical point.

To describe the aromaticity in a different way two aromaticity indices (PDI and FLU) based on two-center electron delcalization index were used. Delocalization index $\delta(A,B)$ [1,2] of atoms *A* and *B* can be defined by the following expression:

$$\delta(A,B) = 4\sum_{i,j}^{N/2} S_{ij}(A)S_{ij}(B)$$

The sum in the preceding equation run over N/2 occupied molecular orbitals. $S_{ij}(A)$ is the overlap between orbitals *i* and *j* within the basin of an atom *A*. The delocalization index can be explained as a number of electron pairs shared by atoms *A* and *B*. Delocalization indices used in this work were computed using AIMAll[3] program.

The PDI index (*para*- delocalization index)[4] is an arithmetic mean of all delocalization indices of *para*-related atoms in a six-membered ring. The aromatic fluctuation index (FLU).[5,6] FLU is defined as:

$$FLU = \frac{1}{n}\sum_{A-B}^{RING}\left[\left(\frac{V(B)}{V(A)}\right)^{\alpha}\left(\frac{\delta(A,B)-\delta_{ref}(A,B)}{\delta_{ref}(A,B)}\right)\right]^2,$$

with the sum running over all adjacent pairs of atoms being members of the given ring, *n*- being its number, $\delta_{ref}(C,C)$ being the delocalization index for two adjacent C atoms in benzene and $\delta_{ref}(C,N)$ –the delocalization index for adjacent C and N atoms in pyridine both computed on the same level of theory as the systems described in this study. *V(A)* is the global delocalization of an atom *A*, given by the equation:

$$V(A) = \sum_{B\neq A}\delta(A,B).$$

And finally, α is a function defined as:

$$\alpha = \begin{cases} 1 & V(B) > V(A) \\ -1 & V(B) \leq V(A) \end{cases},$$

which makes the value of the term $\frac{V(B)}{V(A)}$ equal or greater than 1. FLU describes the fluctuation of electronic charge between adjacent atoms in the given ring. FLU is close to 0 for aromatic systems and differs from it in non-aromatic ones.

Finally, to describe the aromaticity of the systems, nucleus-independent chemical shifts (NICS)[7] were applied. NICS(0) is defined as a negative value of absolute shielding computed at a ring center determined as an arithmetic mean of coordinates of atoms forming

the ring (or *pseudo*- ring). The more negative the NICS value, the more aromatic the ring is. As was shown in works by Aihara[8] and Lazzeretti[9] NICS(0) values contain a significant contribution from the in-plane tensor that are not related to the aromaticity. Thus, to exlude this effect, NICS(1) (1Å above the ring center) were computed. Shleyer *et al.*[10] showed that the shielding tensor component corresponding to the principal axis perpendicular to the ring plane (usually *zz* direction) better desribes the π system of the ring than the isotropic NICS value that contains an influence from σ-electrons. Therefore, in our work we also used $NICS(1)_{zz}$ index.

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