

Supplementary Data

Effects of End-Caps on the Atropisomerization, Polymerization and Thermal Properties of *Ortho*-Imide Functional Benzoxazines

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2D NMR Spectra

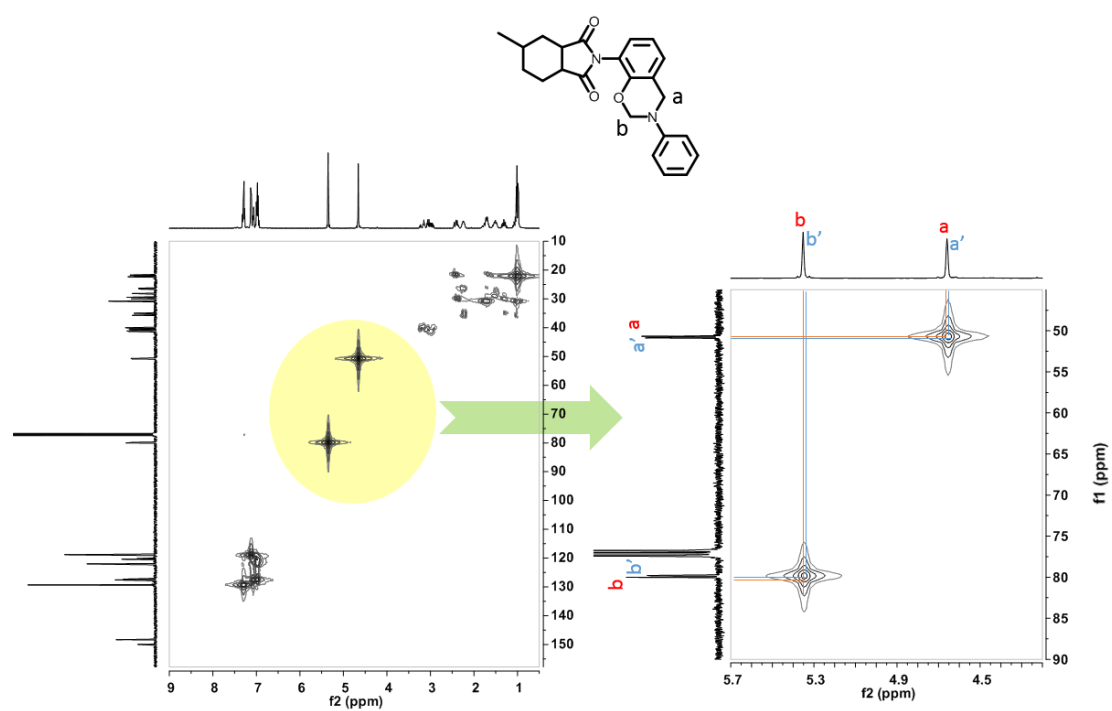


Figure S1. ^1H - ^{13}C HMQC 2D NMR spectrum of oMHI-a.

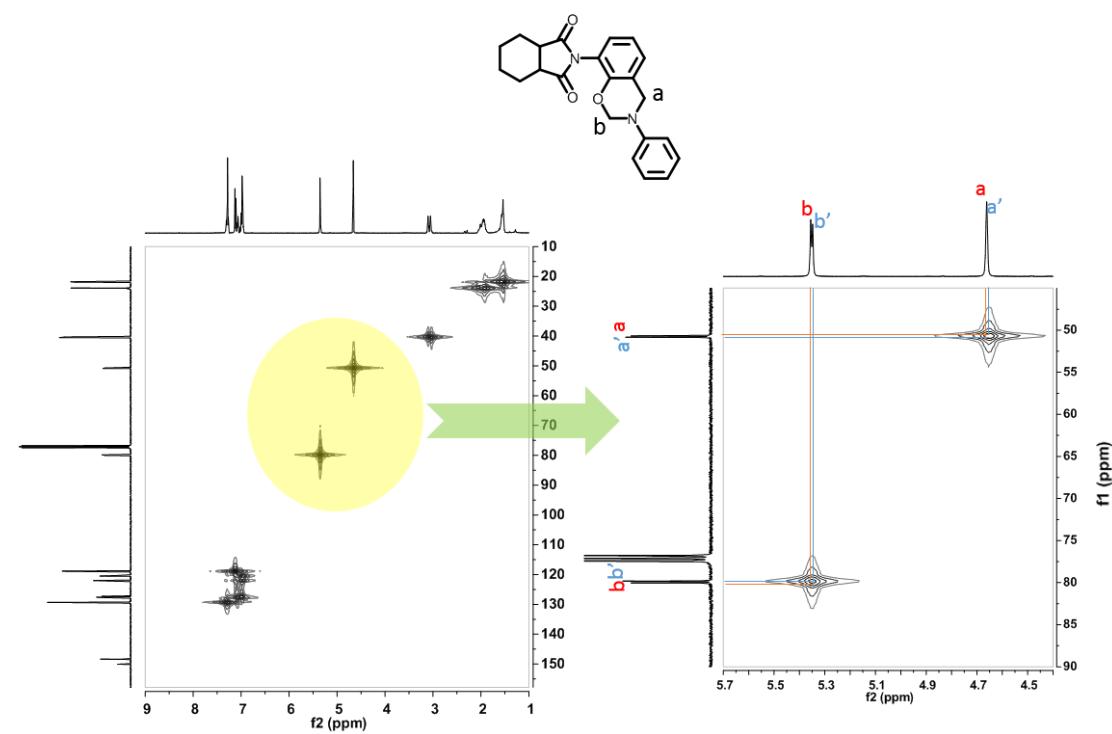


Figure S2. ^1H - ^{13}C HMQC 2D NMR spectrum of oHHI-a.

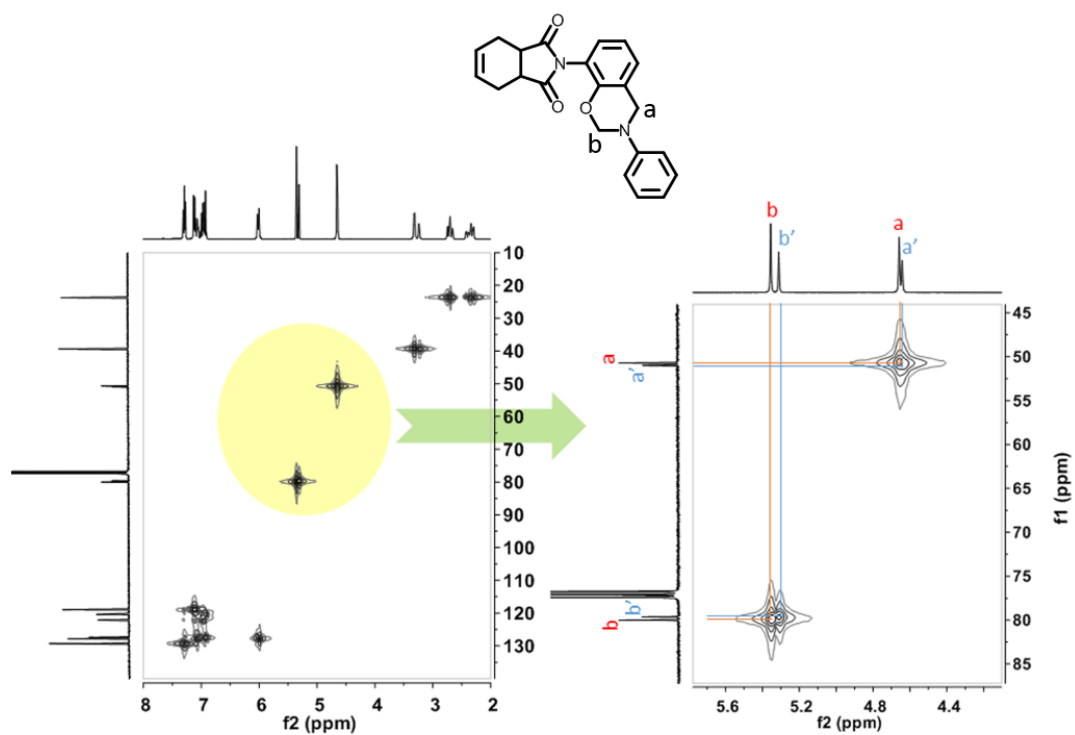


Figure S3. ^1H - ^{13}C HMQC 2D NMR spectrum of oHTI-a.

FT-IR Spectra

In Figure S4, the characteristic doublet at 1779-1772 cm^{-1} and 1720-1708 cm^{-1} are the typical bands for imide, which are attributed to the imide C-C(=O)-C antisymmetric and symmetric stretching, respectively.¹ Besides, the presence of imide is also seen by the other characteristic bands at 1389-1376 cm^{-1} , which is due to the axial stretching of C-N bonding.¹ The bands characteristic of antisymmetric trisubstituted benzene that appear between 1498 and 1488 cm^{-1} confirm the incorporation of imide group into benzoxazine moieties. In addition, the existence of the benzoxazine ring aromatic ether in the monomers is supported by the bands centered in the range of 1236-1228 cm^{-1} due to the C-O-C antisymmetric stretching modes.² Furthermore, the characteristic bands at 950, 925, 924 and 939 cm^{-1} for the oMHI-a, oHHI-a, oHTI-a and oPP-a, respectively, which are mainly related to the oxazine ring, the vibration of O-C₂ vibration with a minor contribution from the phenolic ring (C-H out of plane bending, C-C-C-C torsion).³

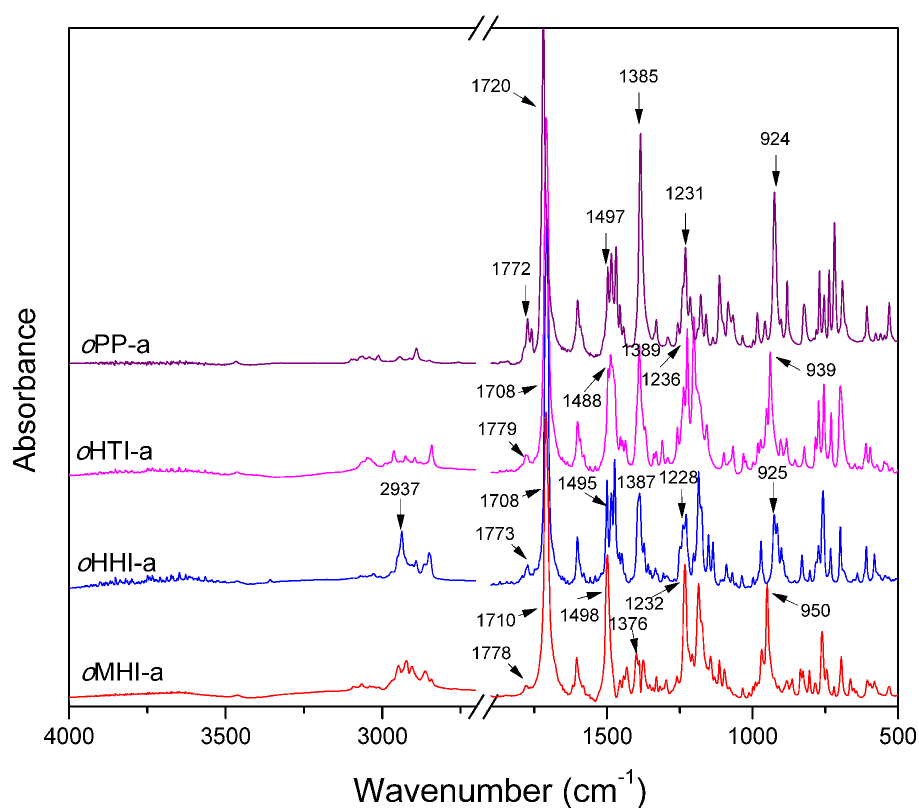
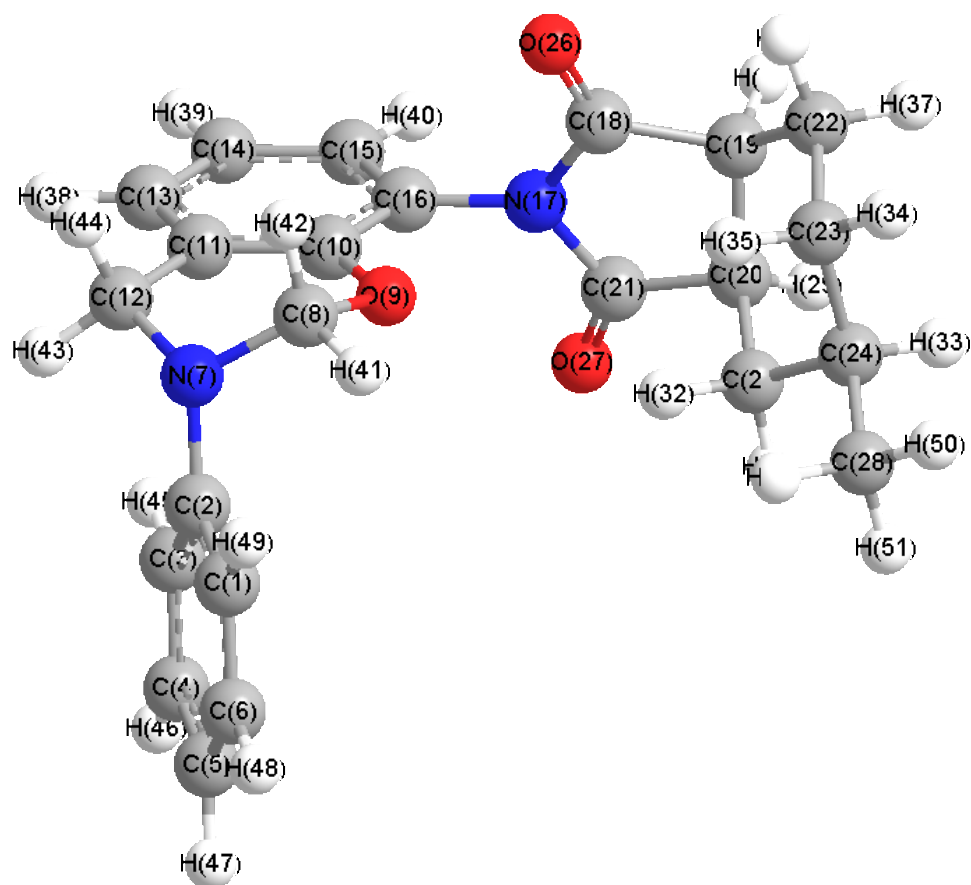


Figure S4. FTIR spectra of benzoxazine monomers.

Atomic Coordinates of the Atoms in Calculated Equilibrium Structures

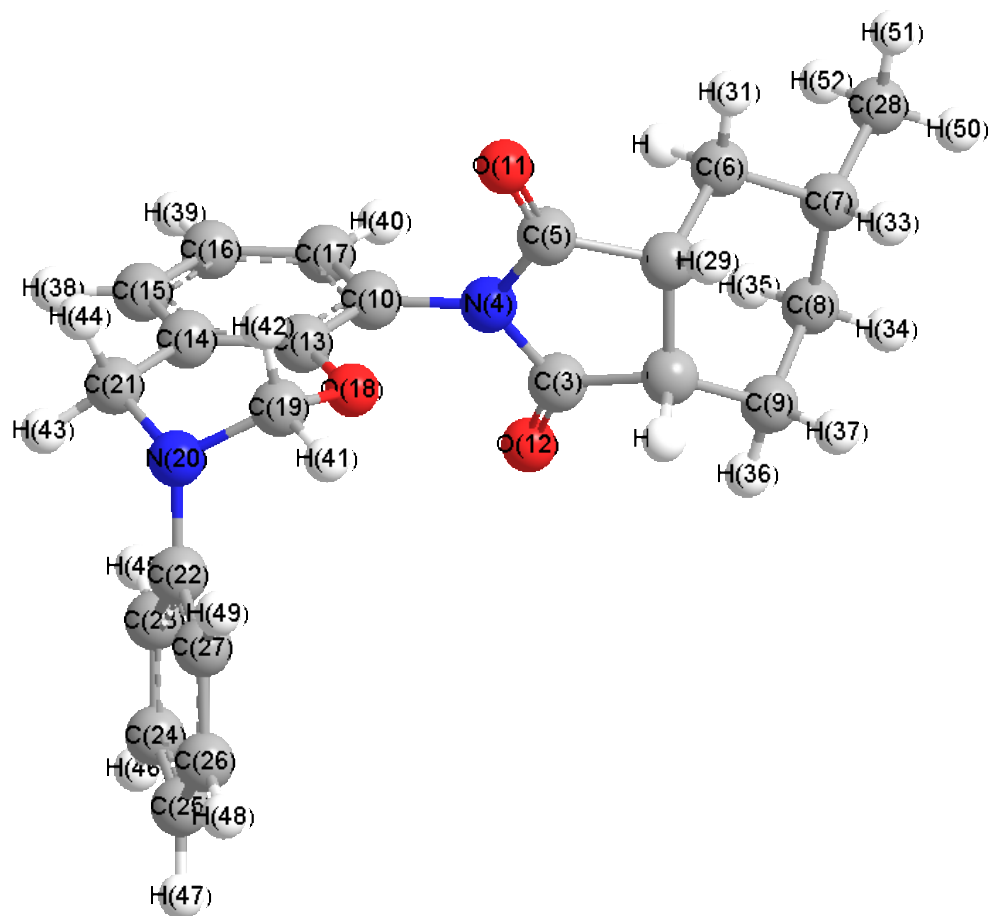
oHMI-a-A



C(1)	3.5264	-2.3442	-0.8760
C(2)	3.3715	-0.9989	-0.4987
C(3)	3.7638	-0.6113	0.7913
C(4)	4.3036	-1.5492	1.6771
C(5)	4.4425	-2.8862	1.3016
C(6)	4.0450	-3.2788	0.0189
N(7)	2.8469	-0.0827	-1.4630
C(8)	1.4891	-0.2832	-1.8762
O(9)	0.5208	0.1722	-0.8934
C(10)	0.7648	1.4158	-0.3870
C(11)	2.0097	2.0542	-0.5248
C(12)	3.1117	1.3512	-1.2985
C(13)	2.1872	3.3173	0.0484
C(14)	1.1600	3.9435	0.7554
C(15)	-0.0736	3.3022	0.8885
C(16)	-0.2733	2.0473	0.3191
N(17)	-1.5308	1.3817	0.4437
C(18)	-2.4467	1.2489	-0.6140
C(19)	-3.6984	0.5808	-0.0418

C(20)	-3.1819	-0.1095	1.2402
C(21)	-1.9436	0.7005	1.6054
C(22)	-4.4942	-0.2858	-1.0280
C(23)	-3.9369	-1.7073	-1.1814
C(24)	-3.7422	-2.3932	0.1817
C(25)	-2.7392	-1.5811	1.0166
O(26)	-2.2734	1.6621	-1.7416
O(27)	-1.3624	0.7302	2.6702
C(28)	-3.2799	-3.8480	0.0312
H(29)	-3.9070	-0.0650	2.0591
H(30)	-4.3356	1.4274	0.2575
H(31)	-2.5708	-2.0443	1.9958
H(32)	-1.7706	-1.5944	0.4955
H(33)	-4.7129	-2.3944	0.7053
H(34)	-4.6186	-2.2967	-1.8090
H(35)	-2.9715	-1.6786	-1.7089
H(36)	-4.5281	0.2262	-1.9966
H(37)	-5.5295	-0.3505	-0.6660
H(38)	3.1519	3.8116	-0.0545
H(39)	1.3172	4.9210	1.2015
H(40)	-0.8885	3.7678	1.4345
H(41)	1.2637	-1.3388	-2.0143
H(42)	1.3027	0.2730	-2.8025
H(43)	4.0827	1.4824	-0.8139
H(44)	3.2023	1.7885	-2.3038
H(45)	3.6284	0.4136	1.1218
H(46)	4.5982	-1.2289	2.6734
H(47)	4.8566	-3.6126	1.9956
H(48)	4.1590	-4.3134	-0.2953
H(49)	3.2613	-2.6462	-1.8861
H(50)	-4.0037	-4.4348	-0.5479
H(51)	-3.1589	-4.3324	1.0081
H(52)	-2.3143	-3.9013	-0.4891

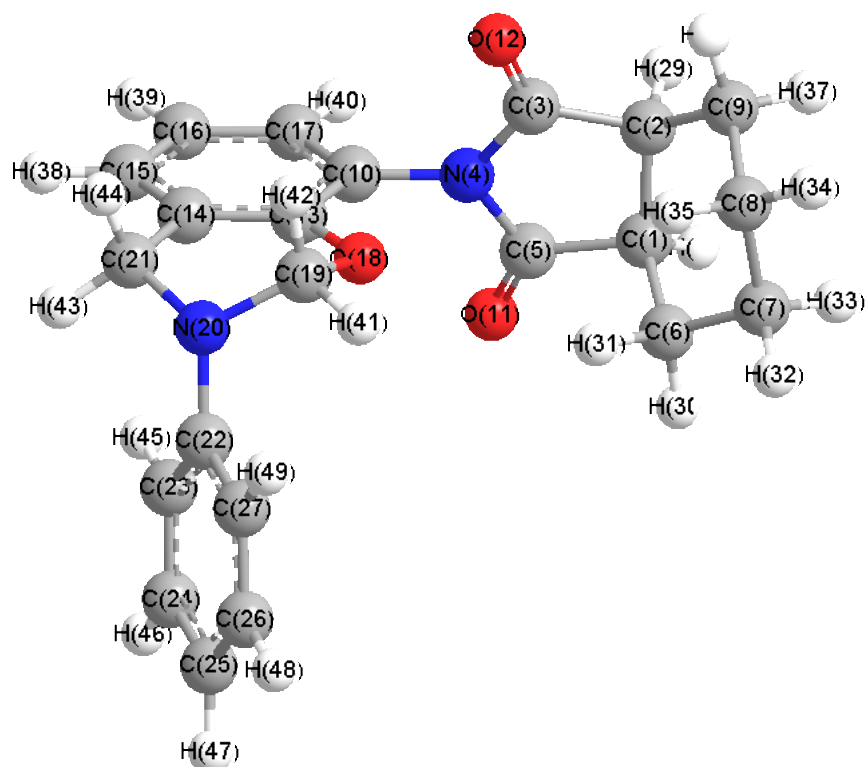
oHMI-a-B



C(1)	-3.1051	-0.5577	-1.1442
C(2)	-2.6468	-1.5257	-0.0308
C(3)	-1.7381	-0.6601	0.8423
N(4)	-1.3244	0.4294	0.0539
C(5)	-2.0000	0.4926	-1.1781
C(6)	-4.4479	0.1564	-0.8345
C(7)	-5.5268	-0.7929	-0.2891
C(8)	-5.0031	-1.4733	0.9872
C(9)	-3.7413	-2.3028	0.7136
C(10)	-0.2736	1.3238	0.4224
O(11)	-1.7696	1.2978	-2.0565
O(12)	-1.3785	-0.8707	1.9816
C(13)	0.9835	1.1816	-0.1895
C(14)	2.0326	2.0533	0.1511
C(15)	1.7981	3.0522	1.1012
C(16)	0.5528	3.1903	1.7157
C(17)	-0.4846	2.3208	1.3712
O(18)	1.1397	0.1637	-1.0840
C(19)	2.3260	0.2626	-1.9163
N(20)	3.5123	0.5664	-1.1707

C(21)	3.3778	1.8812	-0.5329
C(22)	4.1033	-0.5047	-0.4307
C(23)	4.1905	-0.5110	0.9696
C(24)	4.8134	-1.5724	1.6338
C(25)	5.3396	-2.6495	0.9192
C(26)	5.2474	-2.6514	-0.4770
C(27)	4.6470	-1.5859	-1.1459
C(28)	-6.8433	-0.0452	-0.0425
H(29)	-3.1707	-1.0490	-2.1202
H(30)	-1.9530	-2.2543	-0.4777
H(31)	-4.7888	0.6651	-1.7438
H(32)	-4.2795	0.9445	-0.0847
H(33)	-5.7135	-1.5767	-1.0420
H(34)	-5.7774	-2.1236	1.4153
H(35)	-4.7915	-0.7020	1.7436
H(36)	-3.3213	-2.6929	1.6478
H(37)	-4.0179	-3.1725	0.1021
H(38)	2.6105	3.7257	1.3691
H(39)	0.3900	3.9662	2.4578
H(40)	-1.4624	2.4079	1.8349
H(41)	2.3977	-0.7059	-2.4073
H(42)	2.1447	1.0537	-2.6535
H(43)	4.2022	2.0235	0.1708
H(44)	3.5006	2.6432	-1.3166
H(45)	3.7531	0.2947	1.5505
H(46)	4.8675	-1.5595	2.7195
H(47)	5.8170	-3.4750	1.4400
H(48)	5.6641	-3.4758	-1.0505
H(49)	4.6183	-1.5719	-2.2325
H(50)	-7.6209	-0.7256	0.3262
H(51)	-7.2154	0.4240	-0.9617
H(52)	-6.7113	0.7467	0.7068

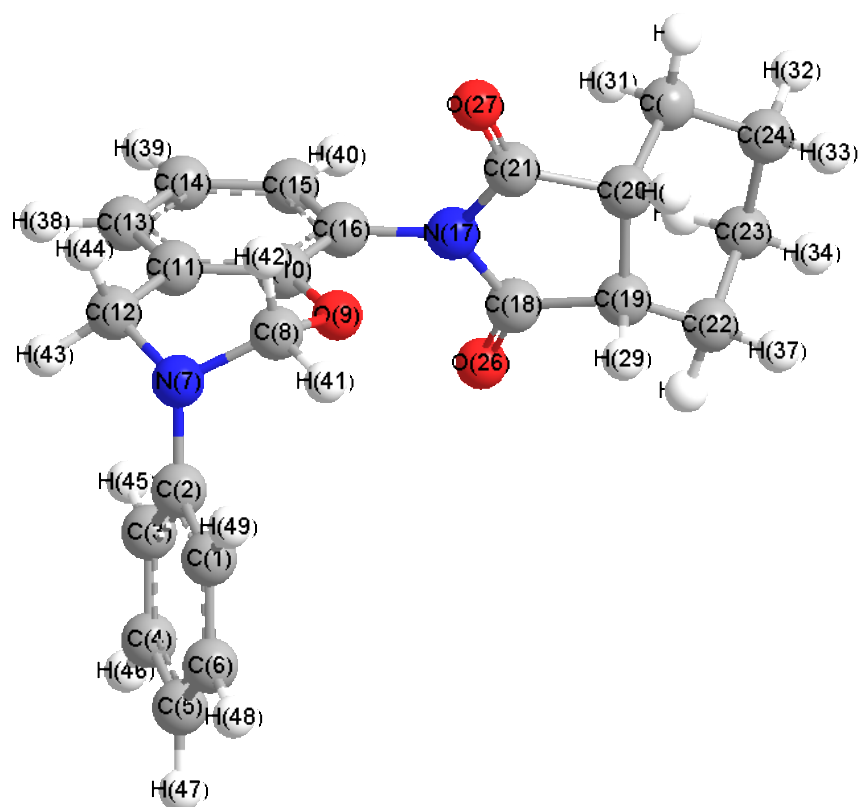
oHHI-a-A



C(1)	3.2649	-0.6499	-1.2432
C(2)	3.8520	-0.0348	0.0482
C(3)	2.6834	0.7697	0.6204
N(4)	1.7946	1.0166	-0.4402
C(5)	2.1317	0.3020	-1.6060
C(6)	2.6534	-2.0632	-1.0361
C(7)	3.5573	-2.9725	-0.1946
C(8)	3.8225	-2.3410	1.1792
C(9)	4.5398	-0.9917	1.0338
C(10)	0.6217	1.8218	-0.3145
O(11)	1.5633	0.4077	-2.6730
O(12)	2.5534	1.1916	1.7505
C(13)	-0.4826	1.3110	0.3888
C(14)	-1.6461	2.0875	0.5287
C(15)	-1.6775	3.3642	-0.0409
C(16)	-0.5849	3.8706	-0.7460
C(17)	0.5674	3.0929	-0.8805
O(18)	-0.3835	0.0456	0.8902
C(19)	-1.3966	-0.2982	1.8730
N(20)	-2.7228	0.0579	1.4618
C(21)	-2.8215	1.5132	1.3007
C(22)	-3.3497	-0.7898	0.4959
C(23)	-3.6931	-0.3577	-0.7939
C(24)	-4.3370	-1.2256	-1.6815

C(25)	-4.6302	-2.5380	-1.3080
C(26)	-4.2822	-2.9757	-0.0254
C(27)	-3.6598	-2.1085	0.8712
H(28)	3.9954	-0.6830	-2.0579
H(29)	4.5837	0.7349	-0.2425
H(30)	2.4444	-2.4991	-2.0191
H(31)	1.6854	-1.9670	-0.5247
H(32)	3.0793	-3.9539	-0.0809
H(33)	4.5121	-3.1448	-0.7146
H(34)	4.4302	-3.0100	1.8017
H(35)	2.8671	-2.2027	1.7058
H(36)	4.6298	-0.4892	2.0037
H(37)	5.5616	-1.1744	0.6733
H(38)	-2.5792	3.9655	0.0632
H(39)	-0.6291	4.8608	-1.1895
H(40)	1.4305	3.4638	-1.4248
H(41)	-1.2940	-1.3732	2.0081
H(42)	-1.1468	0.2303	2.8006
H(43)	-3.7710	1.7558	0.8164
H(44)	-2.8616	1.9557	2.3070
H(45)	-3.4394	0.6451	-1.1226
H(46)	-4.5915	-0.8720	-2.6775
H(47)	-5.1249	-3.2106	-2.0033
H(48)	-4.5156	-3.9905	0.2871
H(49)	-3.4324	-2.4405	1.8811

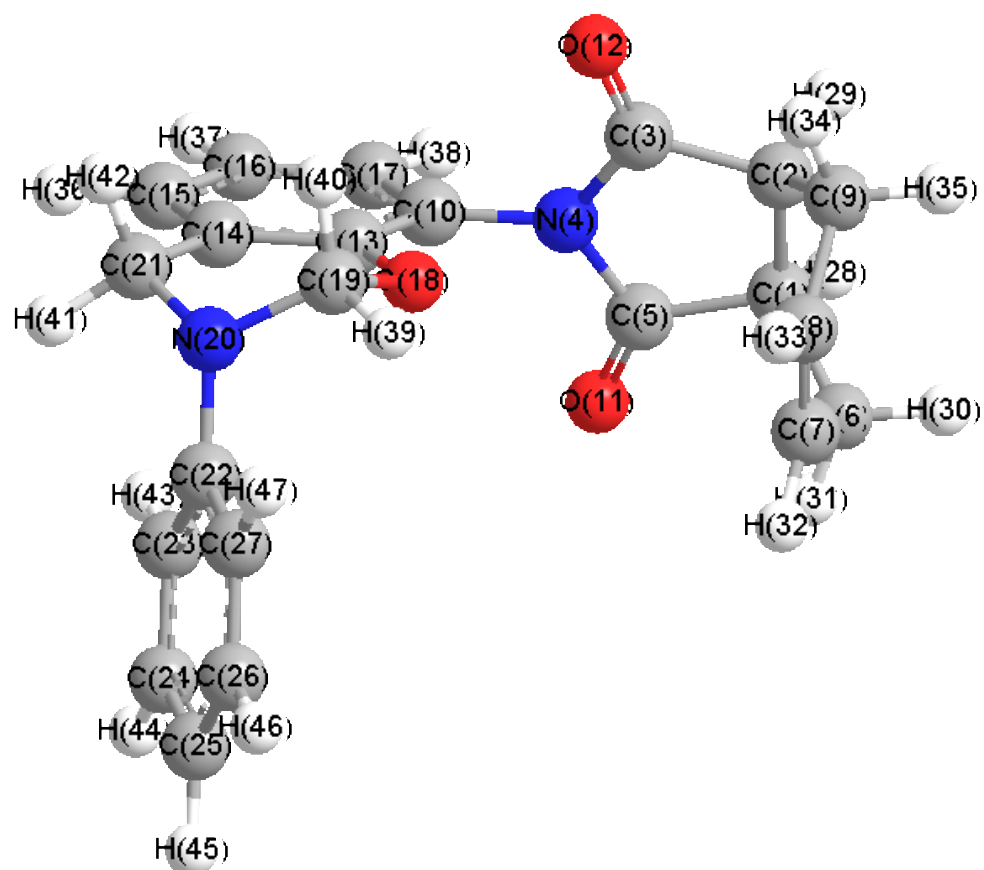
oHHI-a-B



C(1)	-4.3501	-1.5920	1.1447
C(2)	-3.8088	-0.5098	0.4293
C(3)	-3.8951	-0.5170	-0.9710
C(4)	-4.5150	-1.5803	-1.6351
C(5)	-5.0389	-2.6584	-0.9202
C(6)	-4.9475	-2.6593	0.4760
N(7)	-3.2208	0.5631	1.1692
C(8)	-2.0341	0.2625	1.9155
O(9)	-0.8472	0.1660	1.0837
C(10)	-0.6929	1.1843	0.1893
C(11)	-1.7439	2.0533	-0.1521
C(12)	-3.0892	1.8779	0.5310
C(13)	-1.5111	3.0527	-1.1020
C(14)	-0.2657	3.1938	-1.7157
C(15)	0.7735	2.3269	-1.3704
C(16)	0.5643	1.3295	-0.4217
N(17)	1.6169	0.4374	-0.0525
C(18)	2.0330	-0.6514	-0.8405
C(19)	2.9415	-1.5163	0.0333
C(20)	3.3975	-0.5467	1.1481
C(21)	2.2910	0.5016	1.1803
C(22)	4.0338	-2.2976	-0.7122
C(23)	5.2977	-1.4716	-0.9896

C(24)	5.8026	-0.7925	0.2912
C(25)	4.7415	0.1683	0.8417
O(26)	1.6749	-0.8620	-1.9804
O(27)	2.0588	1.3069	2.0581
H(28)	3.4622	-1.0389	2.1239
H(29)	2.2469	-2.2438	0.4807
H(30)	5.0848	0.6720	1.7520
H(31)	4.5720	0.9581	0.0954
H(32)	6.7283	-0.2372	0.0933
H(33)	6.0479	-1.5567	1.0445
H(34)	6.0724	-2.1234	-1.4125
H(35)	5.0860	-0.7042	-1.7487
H(36)	3.6096	-2.6894	-1.6439
H(37)	4.3102	-3.1659	-0.0983
H(38)	-2.3250	3.7242	-1.3706
H(39)	-0.1043	3.9701	-2.4577
H(40)	1.7515	2.4164	-1.8335
H(41)	-2.1037	-0.7060	2.4069
H(42)	-1.8551	1.0543	2.6524
H(43)	-3.9134	2.0179	-0.1734
H(44)	-3.2145	2.6399	1.3143
H(45)	-3.4594	0.2894	-1.5522
H(46)	-4.5686	-1.5680	-2.7208
H(47)	-5.5140	-3.4853	-1.4409
H(48)	-5.3624	-3.4845	1.0497
H(49)	-4.3220	-1.5774	2.2313

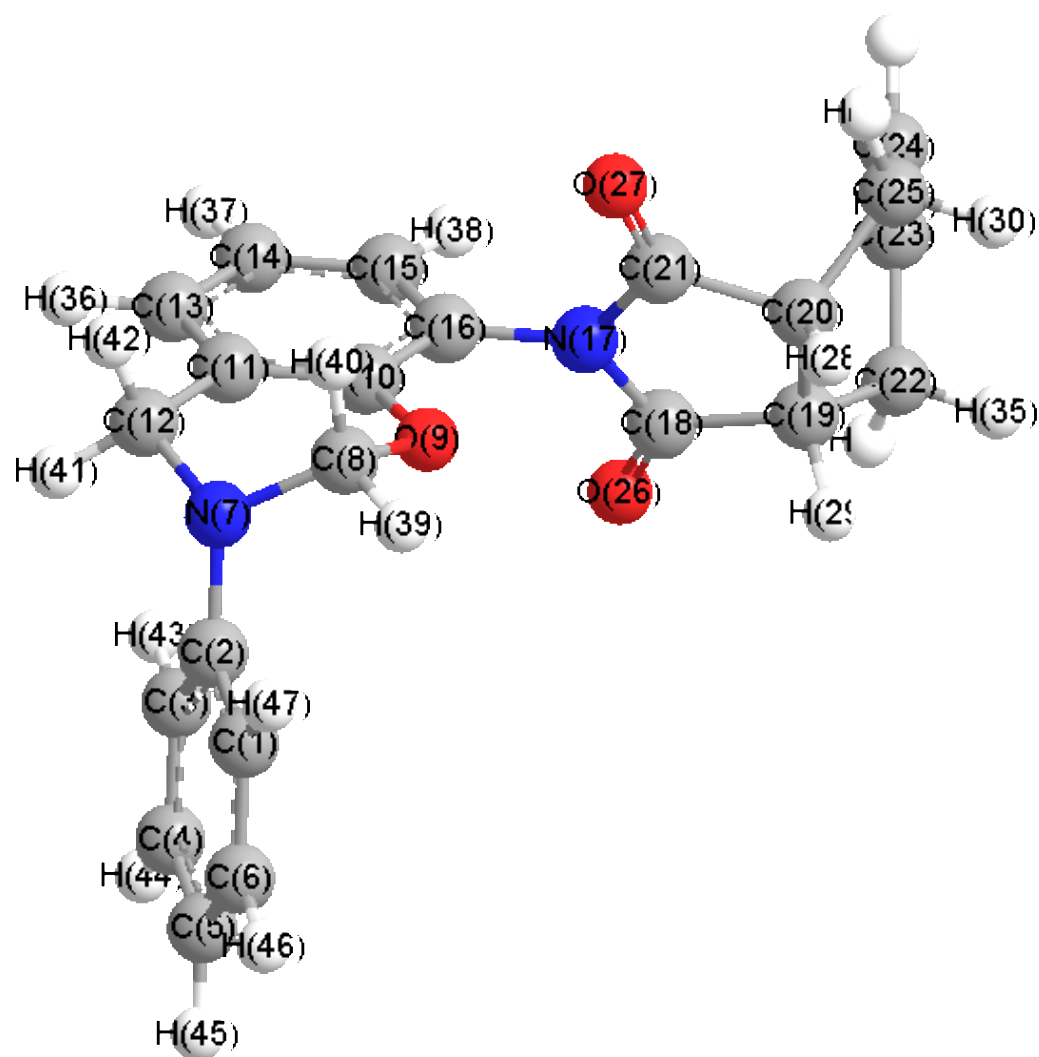
oHTI-a-A



C(1)	-3.5548	-0.8007	1.2147
C(2)	-3.8741	-0.3954	-0.2445
C(3)	-2.8009	0.6314	-0.6122
N(4)	-1.9628	0.8179	0.4954
C(5)	-2.3045	0.0017	1.5820
C(6)	-3.3204	-2.3160	1.4387
C(7)	-2.5446	-2.9321	0.2998
C(8)	-2.8113	-2.5799	-0.9641
C(9)	-3.8909	-1.5673	-1.2598
C(10)	-0.8359	1.6967	0.4887
O(11)	-1.7063	-0.0349	2.6376
O(12)	-2.6910	1.2147	-1.6708
C(13)	0.2848	1.3700	-0.2936
C(14)	1.3976	2.2297	-0.3168
C(15)	1.3636	3.3998	0.4473
C(16)	0.2548	3.7214	1.2317
C(17)	-0.8468	2.8638	1.2487
O(18)	0.2544	0.1960	-0.9843
C(19)	1.2733	0.0643	-2.0098
N(20)	2.5812	0.4373	-1.5550

C(21)	2.5915	1.8553	-1.1779
C(22)	3.2733	-0.5035	-0.7310
C(23)	3.6208	-0.2426	0.6030
C(24)	4.3318	-1.1902	1.3463
C(25)	4.6894	-2.4157	0.7827
C(26)	4.3376	-2.6836	-0.5448
C(27)	3.6481	-1.7344	-1.2975
H(28)	-4.3446	-0.4665	1.8986
H(29)	-4.8339	0.1311	-0.3086
H(30)	-4.3013	-2.8066	1.5304
H(31)	-2.8102	-2.4555	2.3969
H(32)	-1.7710	-3.6623	0.5276
H(33)	-2.2621	-3.0170	-1.7955
H(34)	-3.7966	-1.1584	-2.2708
H(35)	-4.8780	-2.0513	-1.2087
H(36)	2.2266	4.0636	0.4334
H(37)	0.2474	4.6301	1.8260
H(38)	-1.7212	3.0925	1.8506
H(39)	1.2336	-0.9833	-2.3016
H(40)	0.9809	0.7071	-2.8485
H(41)	3.5332	2.0848	-0.6724
H(42)	2.5837	2.4444	-2.1068
H(43)	3.3187	0.6854	1.0778
H(44)	4.5883	-0.9692	2.3794
H(45)	5.2363	-3.1514	1.3660
H(46)	4.6200	-3.6275	-1.0046
H(47)	3.4173	-1.9308	-2.3415

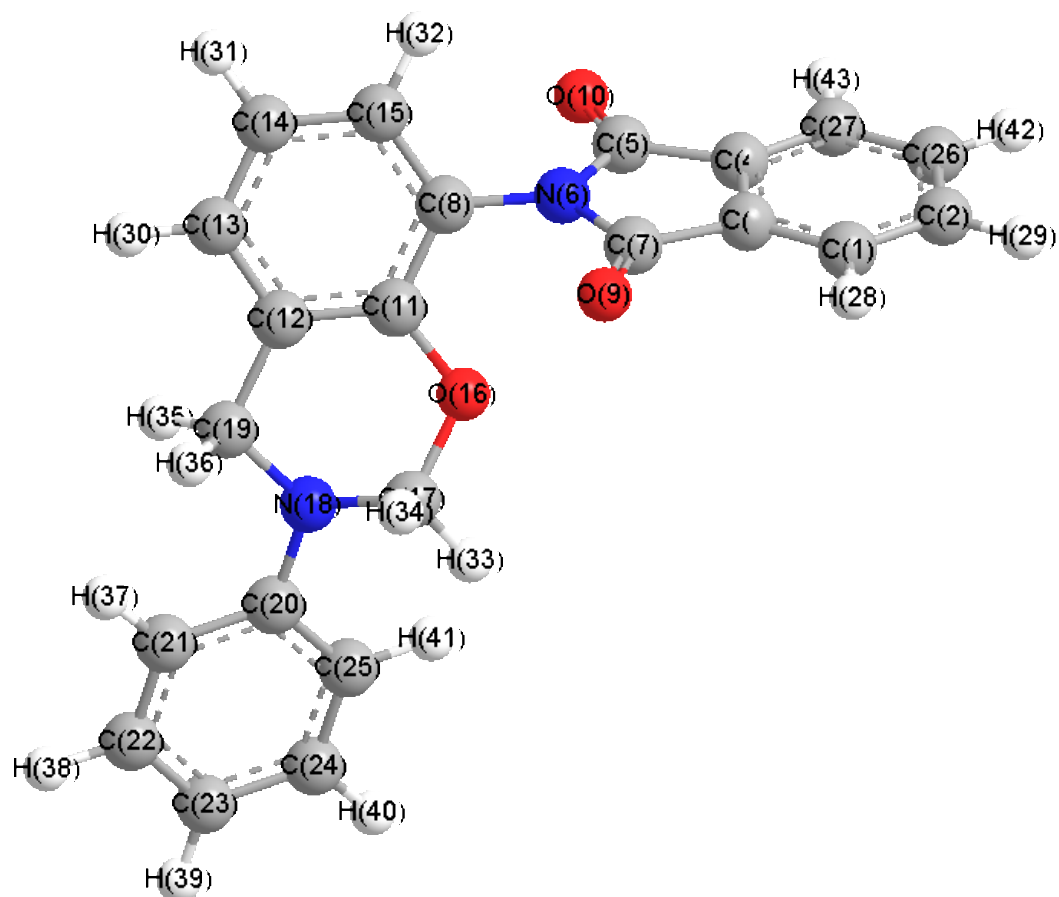
oHTI-a-B



C(1)	0.0747	3.8567	-0.8803
C(2)	0.5355	2.5289	-0.8516
C(3)	0.9008	1.9164	-2.0598
C(4)	0.8121	2.6213	-3.2644
C(5)	0.3413	3.9349	-3.2883
C(6)	-0.0321	4.5468	-2.0867
N(7)	0.6383	1.8762	0.4161
C(8)	-0.5852	1.6356	1.1237
O(9)	-1.3392	0.5136	0.5920
C(10)	-0.6032	-0.6120	0.3638
C(11)	0.8013	-0.5953	0.3051
C(12)	1.5275	0.7163	0.5485
C(13)	1.4790	-1.7875	0.0326
C(14)	0.7884	-2.9803	-0.1868
C(15)	-0.6066	-2.9898	-0.1249
C(16)	-1.2995	-1.8141	0.1523

N(17)	-2.7257	-1.8062	0.2263
C(18)	-3.5646	-1.9663	-0.8839
C(19)	-5.0156	-1.8097	-0.4246
C(20)	-4.9269	-1.5695	1.1020
C(21)	-3.4314	-1.6112	1.4209
C(22)	-5.8635	-3.0368	-0.8451
C(23)	-5.6603	-4.2004	0.0952
C(24)	-5.5845	-3.9918	1.4163
C(25)	-5.7019	-2.5922	1.9704
O(26)	-3.1847	-2.1912	-2.0148
O(27)	-2.9218	-1.5034	2.5171
H(28)	-5.2665	-0.5599	1.3630
H(29)	-5.4028	-0.9241	-0.9425
H(30)	-6.7602	-2.2915	1.9979
H(31)	-5.3328	-2.5325	2.9991
H(32)	-5.4466	-4.8200	2.1084
H(33)	-5.5869	-5.2037	-0.3196
H(34)	-5.6128	-3.3015	-1.8771
H(35)	-6.9234	-2.7405	-0.8456
H(36)	2.5666	-1.7757	-0.0177
H(37)	1.3300	-3.8958	-0.4054
H(38)	-1.1667	-3.9049	-0.2900
H(39)	-1.2650	2.4821	1.0494
H(40)	-0.3628	1.4134	2.1740
H(41)	2.3737	0.8344	-0.1334
H(42)	1.9422	0.7322	1.5671
H(43)	1.2312	0.8826	-2.0735
H(44)	1.0975	2.1271	-4.1898
H(45)	0.2682	4.4765	-4.2274
H(46)	-0.3880	5.5742	-2.0849
H(47)	-0.1744	4.3528	0.0543

oPP-a



C(1)	4.7973	-1.6546	1.3526
C(2)	5.7853	-2.3506	0.6406
C(3)	4.0113	-0.7556	0.6436
C(4)	4.1963	-0.5456	-0.7244
C(5)	3.2063	0.4714	-1.1854
N(6)	2.4733	0.8374	-0.0324
C(7)	2.9003	0.1234	1.1116
C(8)	1.3653	1.7344	-0.0384
O(9)	2.4443	0.2414	2.2296
O(10)	3.0403	0.9204	-2.3014
C(11)	0.0673	1.2164	0.1176
C(12)	-1.0407	2.0744	0.1276
C(13)	-0.8257	3.4494	-0.0184
C(14)	0.4583	3.9684	-0.1844
C(15)	1.5563	3.1044	-0.1944
O(16)	-0.0647	-0.1366	0.2436
C(17)	-1.3177	-0.5346	0.8016
N(18)	-2.4167	0.0664	0.0836
C(19)	-2.4447	1.5124	0.2606
C(20)	-3.6257	-0.6456	-0.0654
C(21)	-4.8737	-0.0316	0.1436

C(22)	-6.0607	-0.7436	-0.0544
C(23)	-6.0347	-2.0816	-0.4474
C(24)	-4.7957	-2.6986	-0.6564
C(25)	-3.6087	-1.9946	-0.4784
C(26)	5.9693	-2.1406	-0.7344
C(27)	5.1723	-1.2276	-1.4394
H(28)	4.6473	-1.8096	2.4166
H(29)	6.4183	-3.0636	1.1606
H(30)	-1.6827	4.1194	-0.0164
H(31)	0.6053	5.0374	-0.3064
H(32)	2.5653	3.4854	-0.3184
H(33)	-1.3487	-1.6186	0.7326
H(34)	-1.3167	-0.2316	1.8636
H(35)	-3.0837	1.9444	-0.5164
H(36)	-2.8767	1.8014	1.2386
H(37)	-4.9297	1.0024	0.4676
H(38)	-7.0117	-0.2426	0.1126
H(39)	-6.9587	-2.6336	-0.5954
H(40)	-4.7517	-3.7356	-0.9804
H(41)	-2.6627	-2.4826	-0.6954
H(42)	6.7433	-2.6946	-1.2594
H(43)	5.3073	-1.0566	-2.5034

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