Supporting Information

Two-electron/24-center (2e/24c) bonding in novel radical π-dimers

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Computational methods

In this work, selecting a suitable and reliable method is important for calculating the long range intermolecular interactions. As proposed in several works, coupled-cluster with singles, doubles, and perturbative triples (CCSD(T))[1] calculation stands as the "golden-standard" in quantum chemical calculations[2-4] of relatively weak interactions but the large computational cost renders them unsuitable for large molecules. In recent few years, much progress has been made in developing density functional theory (DFT) methods that can effectively describe such radical dimers.[5-10] According to previously investigations, the hybrid meta exchange correlation functional (M06-2X)[5, 6] density function theory (DFT) are adapted to studying such π-dimer systems. In order to verify the accuracy of calculated results, the DFT methods with additional dispersion (M06-D3, B3LYP-D3 and B97D) were also employed. It was found that different functional obtained same trend in the structure parameters and interaction energies. Thus, we selected the M06-2X functional for further discussion in present work, the geometry optimizations of radical **1** and π-dimers $\mathbf{2_{180}}$, $\mathbf{2_{60\text{-}R}}$ and $\mathbf{2_{60\text{-}S}}$ with all real frequencies are obtained with a spin-unrestricted broken-symmetry (BS)[11] UM06-2X/6-31+G** method. Spin density distributions on the carbon atoms of π-dimers ($\mathbf{2_{60\text{-}R}}$, $\mathbf{2_{60\text{-}S}}$, $\mathbf{2_{180}}$) are studied. Further, the diradical character (y) was estimated by a complete active space with two electrons and two orbitals CAS (2, 2) method on the basis of ab initio configuration interaction (CI) calculations.[12-14]

In order to the systematically understand bond character of the system, the M06-2X method was employed to calculate the Wiberg bond indices (WBI)[15] and the energy difference of singlet state and the triplet states ($E_{T\text{-}S}$) in this work. Further, the interaction energy (E_{int}) was also calculated at the M06-2X/6-31+G** level, to correct the basis set superposition error, the counterpoise (CP) procedure was used in calculations of interaction energy.[16, 17] The E_{int} can be expressed as the difference between the energy of dimer and the sum of energies of monomers by the following Equation:

$$\Delta E_{int}(AB) = E(AB)_{AB} - [E(A)_{AB} + E(B)_{AB}] \quad (1)$$

All of the above calculations were performed with the Gaussian 09W program package.[18]

In addition, the energy decomposition analysis (EDA) was performed at the M062X-D3/TZ2P and M06-D3/TZ2P level of theory by using the energy decomposition scheme of the Amsterdam density functional (ADF) 2012.01 program.[19-21]

References

1. J. Čížek, *J. Chem. Phys.*, 1966, **45**, 4256-4266.
2. K. E. Riley, M. Pitoňák, P. Jurečka and P. Hobza, *Chem. Rev.*, 2010, **110**, 5023-5063.
3. P. Hobza, *Acc. Chem. Res.*, 2012, **45**, 663-672.
4. M. P. Waller, H. Kruse, C. Muck-Lichtenfeld and S. Grimme, *Chem. Soc. Rev.*, 2012, **41**, 3119-3128.
5. Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215-241.
6. Y. Zhao, N. E. Schultz and D. G. Truhlar, *J. Chem. Theory Comput.*, 2006, **2**, 364-382.
7. R.-L. Zhong, H.-L. Xu, S.-L. Sun, Y.-Q. Qiu, L. Zhao and Z.-M. Su, *J. Chem. Phys.*, 2013, **139**, 124314.
8. Z.-h. Cui, A. Gupta, H. Lischka and M. Kertesz, *Phys. Chem. Chem. Phys.*, 2015, **17**, 23963-23969.
9. M. Capdevila-Cortada, J. Ribas-Arino and J. J. Novoa, *J. Chem. Theory Comput.*, 2014, **10**, 650-658.
10. H. Z. Beneberu, Y.-H. Tian and M. Kertesz, *Phys. Chem. Chem. Phys.*, 2012, **14**, 10713-10725.
11. A. Yu, X. Xue, J. Wang, H. Wang and Y. Wang, *J. Phys. Org. Chem.*, 2012, **25**, 92-100.
12. D. Herebian, K. E. Wieghardt and F. Neese, *J. Am. Chem. Soc.*, 2003, **125**, 10997-11005.
13. K. Yamaguchi, *Chem. Phys. Lett.*, 1975, **33**, 330-335.
14. S. Yamanaka, M. Okumura, M. Nakano and K. Yamaguchi, *J. Mol. Struct.: THEOCHEM*, 1994, **310**, 205-218.
15. K. B. Wiberg, *Tetrahedron*, 1968, **24**, 1083-1096.
16. S. F. Boys and F. Bernardi, *Mol. Phys.*, 1970, **19**, 553-566.
17. I. Alkorta and J. Elguero, *J. Phys. Chem. A*, 1999, **103**, 272-279.
18. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. Peralta, J. E , F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision A. 02. Gaussian, Inc.: Wallingford, CT, 2009.
19. M. v. Hopffgarten and G. Frenking, *WIREs Comput. Mol. Sci.*, 2012, **2**, 43-62.
20. C. Fonseca Guerra, G. J. Snijders, G. te Velde and J. E. Baerends, *Theor. Chem. Acc.*, 1998, **99**, 391-403.
21. ADF 2012. 01, SCM, Theoretical Chemistry; Vrije Universiteit: Amsterdam, http://www.scm.com.

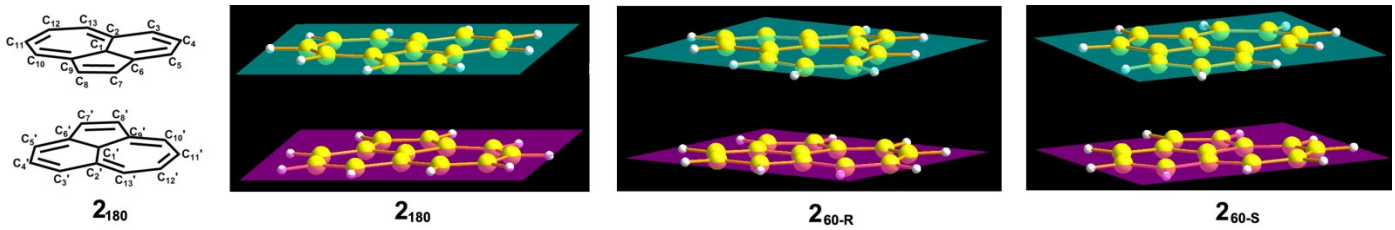

Figure S1. The schematic diagrams of layers structures of π-dimers ($\mathbf{2_{60\text{-}R}}$, $\mathbf{2_{60\text{-}S}}$, $\mathbf{2_{180}}$) by Diamond software.

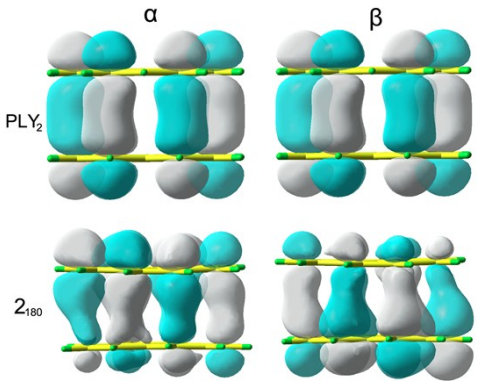

Figure S2. The isosurface for α and β spin electron density in the HOMO of the $\mathbf{PLY_2}$ and $\mathbf{2_{180}}$.

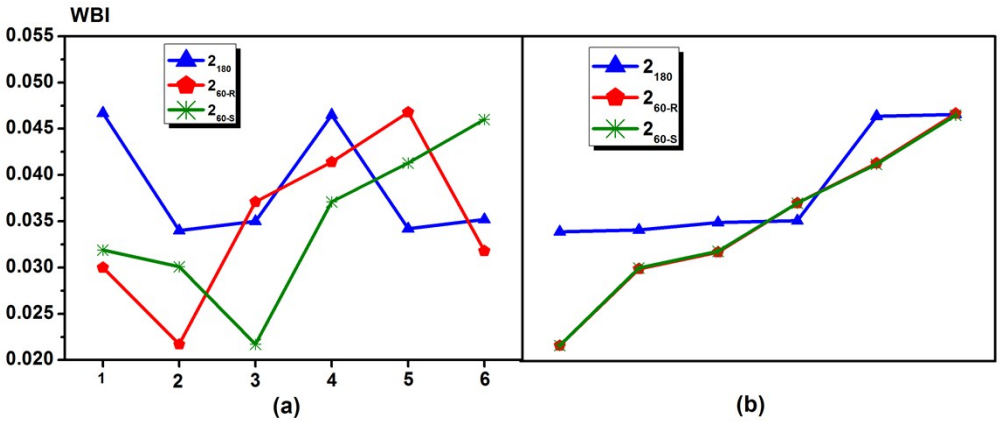

Figure S3 (a) Detailed comparison of WBI component in related carbon set (see **Table S2**). Not easily read the information in the table due to these points are confusing, so we will data in ascending order. (b) shows data ordering from small to big, for WBI component in $\mathbf{2}_{\mathbf{180}}$, there are two largest values (0.0465 and 0.0467) compared with a pair enantiomer ($\mathbf{2}_{\mathbf{60\text{-}R}}$ and $\mathbf{2}_{\mathbf{60\text{-}S}}$). Besides, there is also a smallest WBI value. The total WBI value of the $\mathbf{2}_{\mathbf{180}}$ is largest, which shows that $\mathbf{2}_{\mathbf{180}}$ has a stronger covalent interaction than $\mathbf{2}_{\mathbf{60\text{-}R}}$ and $\mathbf{2}_{\mathbf{60\text{-}S}}$.

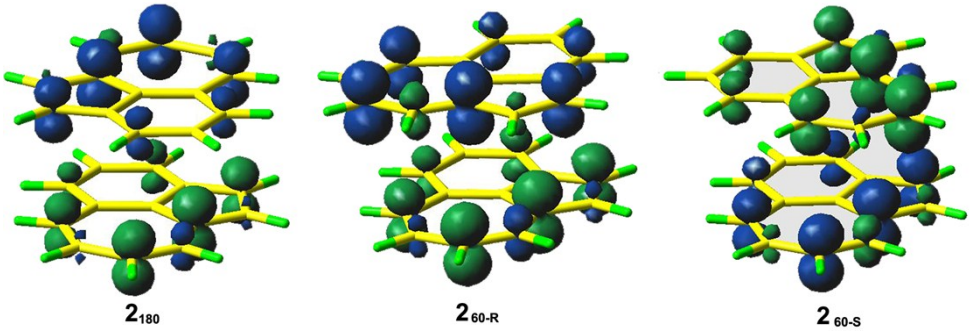

Figure S4. DFT-calculated spin density distributions. For the two-electron forms, the spin density of $\mathbf{2}_{180}$, $\mathbf{2}_{60\text{-}R}$ and $\mathbf{2}_{60\text{-}S}$ are predominantly localized on heptagon of up-layer and down-layer. Corresponding analysis of spin density on the carbon atoms is presented in Table S3.

Table S1. The distances between the up-layer and the down-layer, the average Layer distance [Å] of π-dimers (**$2_{60\text{-}R}$**, **$2_{60\text{-}S}$**, **2_{180}**) at UM06-2X/6-31+G** level of theory.

	C_1*	C_2*	C_3*	C_4*	C_5*	C_6*	C_7*	C_8*	C_9*	C_{10}*	C_{11}*	C_{12}*	C_{13}*	Layer distance
2_{180}	3.149	3.145	3.157	3.186	3.167	3.148	3.132	3.149	3.151	3.187	3.177	3.148	3.117	3.155
$2_{60\text{-}R}$	3.289	3.291	3.306	3.308	3.290	3.288	3.286	3.308	3.302	3.313	3.286	3.259	3.257	3.291
$2_{60\text{-}S}$	3.292	3.290	3.273	3.265	3.278	3.295	3.30	3.314	3.298	3.282	3.274	3.302	3.304	3.290

*The distances between the atoms C_n (n=1-13) in up-layer and the down-layer.

Table S2. The WBI components of π-dimers (**$2_{60\text{-}R}$**, **$2_{60\text{-}S}$**, **2_{180}**) at M06-2X/6-31+G** level of theory.

The total wiberg bond index (WBI) values of these dimers include seven WBI components by six sets peripheral carbon atoms (1, 2, 3, 4, 5 and 6) and the one pair center atoms (C_1 and C_1').

		up-layer	down-layer	WBI
2_{180}	1	C_2/C_3	C_8'/C_9'	0.0340
	2	C_4/C_5	C_{10}'/C_{11}'	0.0350
	3	C_6/C_7	C_{12}'/C_{13}'	0.0465
	4	C_8/C_9	C_2'/C_3'	0.0342
	5	C_{10}/C_{11}	C_4'/C_5'	0.0352
	6	C_{12}/C_{13}	C_6'/C_7'	0.0467
		C_1	C_1'	0.0074
$2_{60\text{-}R}$	1	C_2/C_3	C_4'/C_5'	0.0301
	2	C_4/C_5	C_6'/C_7'	0.0407
	3	C_6/C_7	C_8'/C_9'	0.0339
	4	C_8/C_9	C_{10}'/C_{11}'	0.0372
	5	C_{10}/C_{11}	C_{12}'/C_{13}'	0.0432
	6	C_{12}/C_{13}	C_2'/C_3'	0.0463
		C_1	C_1'	0.0040
$2_{60\text{-}S}$	1	C_2/C_3	C_{12}'/C_{13}'	0.0301
	2	C_4/C_5	C_2'/C_3'	0.0217
	3	C_6/C_7	C_4'/C_5'	0.0371
	4	C_8/C_9	C_6'/C_7'	0.0413
	5	C_{10}/C_{11}	C_8'/C_9'	0.0466
	6	C_{12}/C_{13}	C_{10}'/C_{11}'	0.0319
		C_1	C_1'	0.0040

Table S3. Spin density on the carbon atoms of π-dimers (**$2_{60\text{-}R}$**, **$2_{60\text{-}S}$**, **2_{180}**) at UM06-2X/6-31+G** level of theory.

From the Table S3, Spin density for up-layer are localized on C_9 and C_{11} of heptagon, corresponding Spin density for down-layer are localized on $C_{9'}$ and $C_{11'}$ of heptagon. We find that the spin density is related to WBI, since the largest WBI component value of is presents carbon atoms of heptagon.

		2_{180}	**$2_{60\text{-}R}$**	**$2_{60\text{-}S}$**
up-layer	**C_9**	0.2269	0.2716	-0.3519
	C_{11}	0.2279	0.3607	-0.3680
down-layer	**$C_{9'}$**	-0.2271	-0.3517	0.2712
	$C_{11'}$	-0.2278	-0.3683	0.3610

Table S4. The layer distances [Å] of studied π-dimers ($\mathbf{2_{180}}$, $\mathbf{2_{60\text{-}R}}$ and $\mathbf{2_{60\text{-}S}}$) at different methods.

	Layer distance			
	M06-2X	**M06-D3**	**B97-D2**	**B3LYP-D3**
$\mathbf{2_{180}}$	3.155	3.191	3.065	3.159
$\mathbf{2_{60\text{-}R}}$	3.291	3.418	3.104	3.324
$\mathbf{2_{60\text{-}S}}$	3.290	3.421	3.105	3.318

The geometry structures were optimized using the DFT methods without/with additional dispersion (M06-2X, B3LYP-D3, M06-D3 and B97D) in π-dimers ($\mathbf{2_{180}}$, $\mathbf{2_{60\text{-}R}}$ and $\mathbf{2_{60\text{-}S}}$). It is found that different methods obtained same trend in the structure parameters.

Table S5. The EDA results (ΔE_{int}, kcal mol^{-1}) of studied π-dimers (**2$_{60\text{-}R}$**, **2$_{60\text{-}S}$**, **2$_{180}$**) by M06-D3/TZ2P method. It is found that two functional (M062X-D3/TZ2P and M06-D3/TZ2P) obtained same trend in The EDA results. The ΔE_{orb} value makes a major contribution to ΔE_{int}.

	ΔE_{elstat}	ΔE_{Pauli}	ΔE_{disp}	ΔE_{orb}	ΔE_{int}
2$_{180}$	-15.06	22.78	-13.62	-44.85	-50.76
2$_{60\text{-}R}$	-9.22	10.42	-12.52	-29.88	-41.20
2$_{60\text{-}S}$	-9.23	10.45	-12.53	-29.92	-41.22

Cartesian coordinates of the optimized structures of **2**

(1) $\mathbf{2_0}$ π-dimer.

$\mathbf{2_0}$	frequency=-44.95	The total energy = -1001.149	
Atom	X	Y	Z
C	-2.475025	1.667828	-1.331587
C	-1.221759	1.675961	-1.874800
C	0.067659	1.693225	-1.216104
C	0.235793	1.691606	0.176337
C	-0.727561	1.669562	1.266646
C	-2.121252	1.667038	1.176448
C	1.237704	1.709285	-2.009396
C	1.528542	1.707268	0.756460
C	2.665607	1.719984	-0.049155
C	2.505706	1.723327	-1.438616
H	1.133074	1.705938	-3.091164
H	-3.289803	1.654641	-2.053180
H	-1.173786	1.675868	-2.962579
H	-2.657606	1.657261	2.125072
H	3.381011	1.727585	-2.080918
C	-2.898702	1.650586	0.031413
H	-3.974814	1.645699	0.182105
H	3.659253	1.725665	0.390479
C	1.366314	1.702426	2.202915
C	0.030081	1.690288	2.491311
H	2.181225	1.708703	2.916495
H	-0.415883	1.672814	3.478719
C	0.235764	-1.691601	0.176421
C	0.067622	-1.693297	-1.216019
C	-0.727585	-1.669481	1.266735
C	1.528515	-1.707248	0.756538
C	-1.221799	-1.676051	-1.874707
C	1.237663	-1.709419	-2.009316
C	-2.121275	-1.666942	1.176544
C	0.030065	-1.690147	2.491397
C	2.665576	-1.720029	-0.049082
C	1.366296	-1.702308	2.202994

C	-2.475062	-1.667867	-1.331488
H	-1.173832	-1.676021	-2.962487
C	2.505668	-1.723449	-1.438542
H	1.133027	-1.706132	-3.091083
H	-2.657624	-1.657103	2.125172
C	-2.898732	-1.650542	0.031513
H	-0.415894	-1.672610	3.478806
H	3.659224	-1.725695	0.390547
H	2.181211	-1.708548	2.916570
H	-3.289844	-1.654707	-2.053078
H	3.380970	-1.727753	-2.080848
H	-3.974843	-1.645630	0.182210

(2) $\mathbf{2}_{\mathbf{60\text{-}R}}$ π-dimer.

$\mathbf{2}_{\mathbf{60\text{-}R}}$	frequency=18.72	The total energy = -1001.152	
Atom	X	Y	Z
C	-2.173999	2.017468	1.486944
C	-0.906190	1.753815	1.927711
C	-0.167695	0.510576	1.914938
C	-0.658729	-0.688817	1.371414
C	-1.942302	-1.023083	0.766233
C	-3.038060	-0.182150	0.569747
C	1.136019	0.488629	2.457677
C	0.132094	-1.861722	1.359342
C	1.421750	-1.853280	1.890841
C	1.910142	-0.668113	2.447458
H	1.540950	1.405868	2.876123
H	-2.503198	3.046560	1.617732
H	-0.365837	2.594857	2.358893
H	-3.908394	-0.639132	0.099480
H	2.912780	-0.642131	2.863985
C	-3.141294	1.164324	0.879306
H	-4.086561	1.640670	0.632645
H	2.035117	-2.749536	1.874299
C	-0.651482	-2.918210	0.736793
C	-1.879924	-2.414713	0.402559
H	-0.304273	-3.932517	0.579685

H	-2.690332	-2.950637	-0.077631
C	1.040259	0.332512	-1.320052
C	0.336677	1.546351	-1.267353
C	0.676341	-0.976266	-1.839528
C	2.361397	0.229170	-0.811838
C	-1.004180	1.730269	-1.779612
C	0.993569	2.649155	-0.673265
C	-0.536735	-1.353151	-2.421679
C	1.809501	-1.838586	-1.633975
C	2.982768	1.332686	-0.232164
C	2.813119	-1.136043	-1.022176
C	-1.837260	0.823732	-2.369916
H	-1.399562	2.737807	-1.663109
C	2.285017	2.543776	-0.166185
H	0.467876	3.599015	-0.619420
H	-0.614634	-2.397456	-2.721131
C	-1.650333	-0.564047	-2.647803
H	1.831432	-2.884451	-1.916997
H	3.989990	1.254732	0.168246
H	3.785835	-1.516010	-0.733865
H	-2.810665	1.212885	-2.662287
H	2.756061	3.413092	0.282594
H	-2.499400	-1.059315	-3.111743

(3) $\mathbf{2}_{\mathbf{60\text{-}S}}$ π-dimer.

$\mathbf{2}_{\mathbf{60\text{-}S}}$	frequency=18.75	The total energy = -1001.152	
Atom	X	Y	Z
C	1.850981	0.826055	-2.362029
C	1.016927	1.732682	-1.773212
C	-0.326103	1.549749	-1.266326
C	-1.031473	0.337176	-1.324500
C	-0.667600	-0.971019	-1.845365
C	0.547252	-1.348622	-2.423392
C	-0.983551	2.652312	-0.672335
C	-2.354740	0.234843	-0.821649
C	-2.976478	1.338024	-0.241767
C	-2.277055	2.547868	-0.170399

H	-0.456603	3.601234	-0.614448
H	2.826079	1.214354	-2.649868
H	1.413267	2.739468	-1.653409
H	0.624611	-2.392394	-2.724824
H	-2.748407	3.416928	0.278568
C	1.662994	-0.560866	-2.643490
H	2.513125	-1.056520	-3.105062
H	-3.985319	1.260793	0.154695
C	-2.807887	-1.129105	-1.036886
C	-1.802981	-1.831948	-1.646237
H	-3.782465	-1.508055	-0.753561
H	-1.825541	-2.877129	-1.931725
C	0.649036	-0.693016	1.373768
C	0.158455	0.506349	1.917829
C	1.934343	-1.028718	0.772961
C	-0.144328	-1.864068	1.355801
C	0.899530	1.747948	1.936078
C	-1.147397	0.486002	2.455543
C	3.032497	-0.189710	0.582299
C	1.870308	-2.419358	0.405841
C	-1.436160	-1.853927	1.882064
C	0.639363	-2.920822	0.733849
C	2.169608	2.009836	1.500738
H	0.359337	2.589207	2.367028
C	-1.924080	-0.668959	2.439527
H	-1.551919	1.403172	2.874518
H	3.903619	-0.647501	0.114279
C	3.137373	1.155964	0.895026
H	2.681481	-2.955928	-0.072329
H	-2.051437	-2.748776	1.860961
H	0.290485	-3.933954	0.572837
H	2.500450	3.037965	1.634926
H	-2.928267	-0.641742	2.852219
H	4.084502	1.630866	0.652774

(4) $\mathbf{2}_{180}$ π-dimer.

$\mathbf{2}_{180}$	frequency=60.66	The total energy = -1001.159

Atom	X	Y	Z
C	2.582940	-1.982870	0.132615
C	1.326510	-2.401787	-0.220186
C	0.042100	-1.984852	0.290405
C	-0.128636	-0.975282	1.250632
C	0.831413	-0.148359	1.963255
C	2.224752	-0.191907	1.881523
C	-1.129308	-2.611978	-0.202952
C	-1.424835	-0.593668	1.689077
C	-2.557768	-1.233919	1.190736
C	-2.394937	-2.257677	0.248986
H	-1.020582	-3.394990	-0.948832
H	3.395703	-2.475675	-0.397735
H	1.279237	-3.180464	-0.979139
H	2.759529	0.508811	2.521731
H	-3.267620	-2.768265	-0.147019
C	3.002606	-0.996115	1.066486
H	4.078403	-0.867858	1.153696
H	-3.550363	-0.951811	1.531404
C	-1.264800	0.476608	2.656304
C	0.074341	0.720369	2.821633
H	-2.079417	0.972054	3.171020
H	0.519363	1.455615	3.482057
C	0.128483	0.975118	-1.250683
C	-0.041389	1.985243	-0.290859
C	-0.832119	0.148637	-1.963031
C	1.424414	0.592573	-1.689167
C	-1.325466	2.403077	0.219841
C	1.130423	2.611995	0.201966
C	-2.225529	0.192931	-1.880889
C	-0.075777	-0.720474	-2.821547
C	2.557805	1.232382	-1.191267
C	1.263615	-0.477912	-2.655988
C	-2.582118	1.983896	-0.131607
H	-1.277597	3.182082	0.978428
C	2.395771	2.256703	-0.250001
H	1.022253	3.395538	0.947371
H	-2.760850	-0.507395	-2.521073

C	-3.002595	0.997120	-1.065286
H	-0.521257	-1.455450	-3.481965
H	3.550161	0.949502	-1.531993
H	2.077821	-0.973814	-3.170906
H	-3.394493	2.476857	0.399183
H	3.268822	2.766992	0.145582
H	-4.078488	0.869168	-1.151773