The Role of π-linkers in tuning optoelectronic properties of Triphenylamine derivatives for solar cell applications - A DFT/TDDFT study†

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Electronic supporting information (ESI)

SI 1.1 Computational Details

One of the attractive features of these molecules is the presence of weak intramolecular hydrogen bonds. This has been extensively studied through quantum theory of atoms in molecules (QTAIM) analysis using AIM 2000 package.[1] The necessary wave functions for the QTAIM calculations have been generated at M06-2X/6-311++G(d,p) level using G09 program. To understand the effect of polarity of solvent on absorption and emission spectra, a range of solvents such as cyclohexane, tetrahydrofuran (THF), dichloromethane (DCM) and dimethyl sulfoxide (DMSO) have been used.

SI 1.2 Conformation Analysis:

The excellent flexibility nature of organic molecules leads to different conformers. Therefore conformational search has to be carried out to locate the most stable conformer of an organic molecule. Hence, geometry optimization is carried out with different starting geometries and the two competitive conformers are given here for comparison. Especially the conformation problem arises only with the thiophene and furan π-linkers (TPA6-9) and not with other TPA molecules (TPA1-5). The two conformers of TPA6-9 are given in Fig. S1. Among them (A and B conformer), conformer-A is found to show minimum energy and maximum stability. Our results show that all the molecules (TPA6-9) are observed to be at conformer-A. This is due to the possibility of having intramolecular hydrogen bonding. Here, conformer-A of TPA9 is found to show a CH---N hydrogen bond while it was missing in conformer-B (Fig. S2, ESI†). Hence, conformer-A is more stable than conformer-B. For instance, conformer-A of TPA6 is more stable compared to conformer-B of TPA6 by 2.47 KJ/mol. Similarly, conformer-A of TPA7, TPA8 and TPA9 is found to show more stability than conformer-B of TPA7, TPA8 and TPA9 respectively. Thus, conformer-A is found to be more stable. In order to understand the nature of intramolecular hydrogen bonding present in these TPA derivatives, Bader's topological analysis has been performed using quantum theory of atoms in molecules (QTAIM) analysis[2]. It is well known that the QTAIM analysis is based on the electron density obtained at the bond critical point (BCP) existing between the two interacting atoms.[3] This gives an idea about the strength and nature of covalent and non-covalent interactions.[3] Remember, the occurrence of BCP indicates the presence of an interaction. These interactions are characterized by the set of criteria proposed by Bader and Co-workers[3-5]. For example, the calculated electron density $\rho(r)$ is used to analyse the strength of the interactions. At the same time, the nature

of bonding can be studied through the calculated laplacian of electron density at the bond critical point (BCP). Therefore, the QTAIM properties have been calculated and listed in Table. S1 (ESI†). It is seen from the Fig. 2, the $TPA7_A$ (conformer A of TPA7) is stabilized by an intramolecular hydrogen bonding which is confirmed by the presence of (3,-1) bond critical point which is missing in $TPA7_B$. Similar trend is predicted for other molecules. But the N---HC interaction is presented in both the conformations of TPA9. However, the calculated electron density ρ(r) is 0.01168 a.u in $TPA9_A$ while the same for $TPA9_B$ is very less with 0.00057 a.u. This situation is observed for almost all the studied molecules. To gain more insights into the nature of hydrogen bonding in the most stable conformer-A, TPA9 is taken and its QTAIM properties has been explained in Fig. 2. The right hand side panel represents the laplacian of rho graph while the left hand side gives the zero flux surface graph of the identified hydrogen bonds. From the figure, it is clear that valence shell charge concentration of hydrogen (which is involved in the hydrogen bonding) is slightly deform from its position and orient towards the axis of the most electronegative nitrogen atom. This leads to the formation of the strong hydrogen bonding. This has been confirmed by drawing the Zero flux surface of N---H interaction (left panel in Fig. 2) where the trajectories originating from hydrogen atom are marching towards the nitrogen atom. This is an excellent evidence for the presence of strong N---H interactions in this molecule. Thus conformer-A is found to be the most stable conformer where it shows a strong hydrogen bonding compared to conformer-B. The most stable conformers are taken for further calculations.

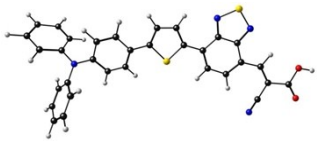
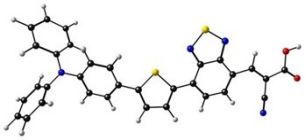
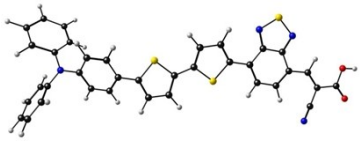
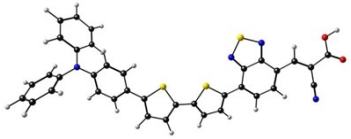
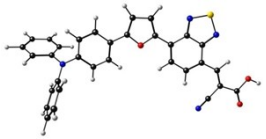
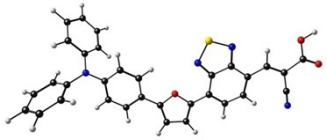
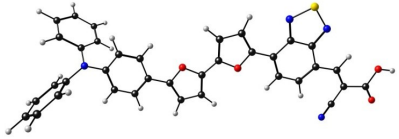
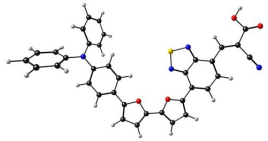
Molecules	Conformer-A	Conformer-B	ΔE (kJ/mol)
TPA 6	 -6293344.29kJ/mol	 -6293341.82kJ/mol	2.47
TPA 7	 -7742057.04kJ/mol	 -7742051.82kJ/mol	5.22
TPA 8	 -5445387.49kJ/mol	 -5445372.57kJ/mol	14.92
TPA 9	 -6046130.63kJ/mol	 -6046104.98kJ/mol	25.65

Fig. S1 Conformational analysis of TPA6-TPA9 molecules the energies of each conformer is given in kJ/mol.

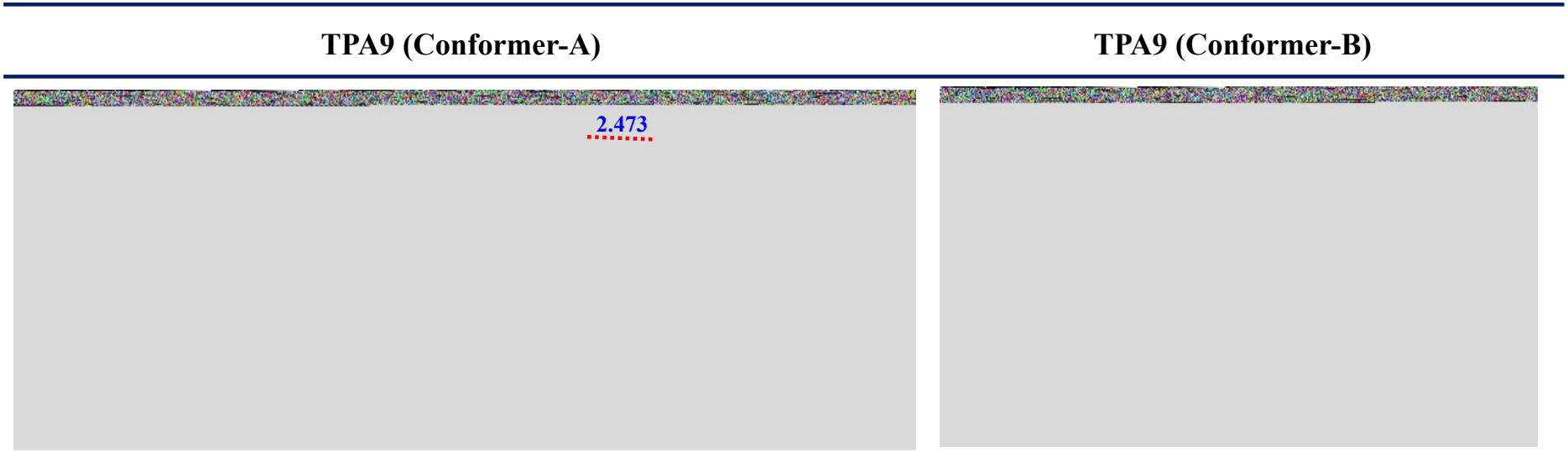


Fig. S2 Optimized conformers (A & B) of TPA9 and the dotted line indicate the intramolecular hydrogen bonding.

SI 1.3 Geometry Optimization

Fig. 4 represents the calculated bond lengths of C–C and C–N bonds in all the nine molecules. From the figure, it is clear that all C–C bond lengths fall between their single and double bond limits. For instance C–C bond length of D4 (connecting BTD and cyanoacrylic acid) in all these molecules is in the range of 1.40 -1.42 (Fig. 3). Similarly C–N bond lengths are also lie in between their single and double bonds limits (Fig. 3). Similar trend is observed for C–N bond lengths and all the calculated C−C, C−N and N−S bond lengths are given in supporting information (Fig. S4,ESI†).

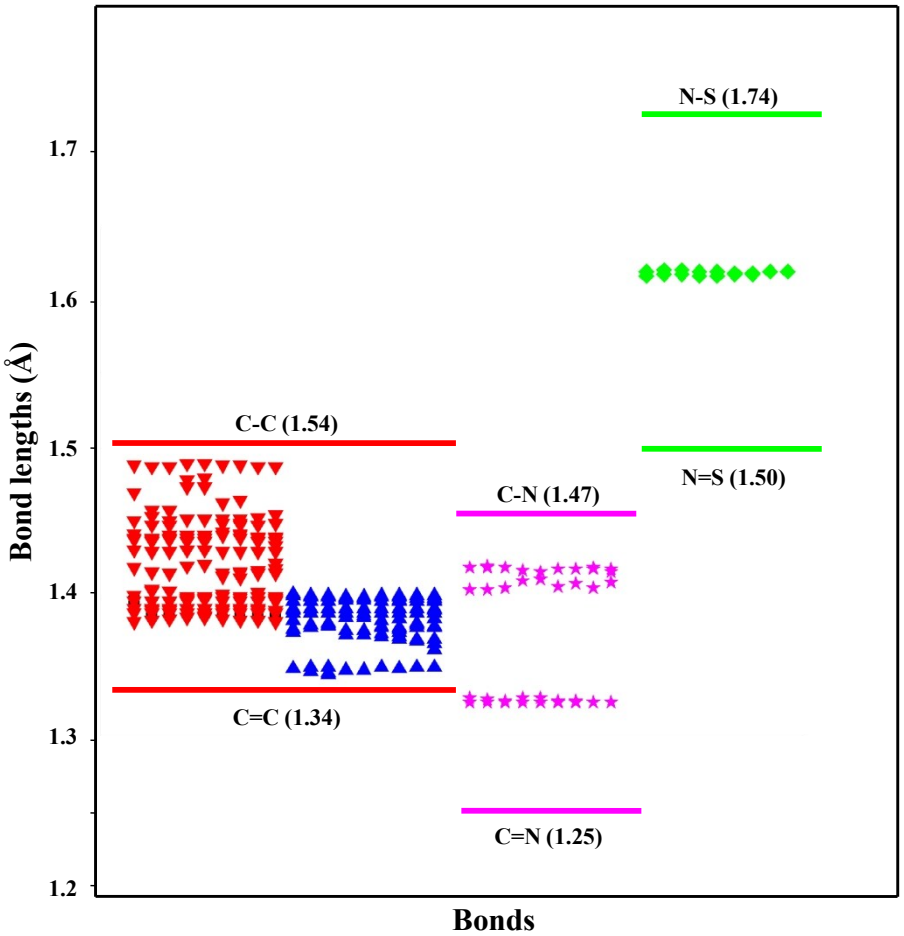
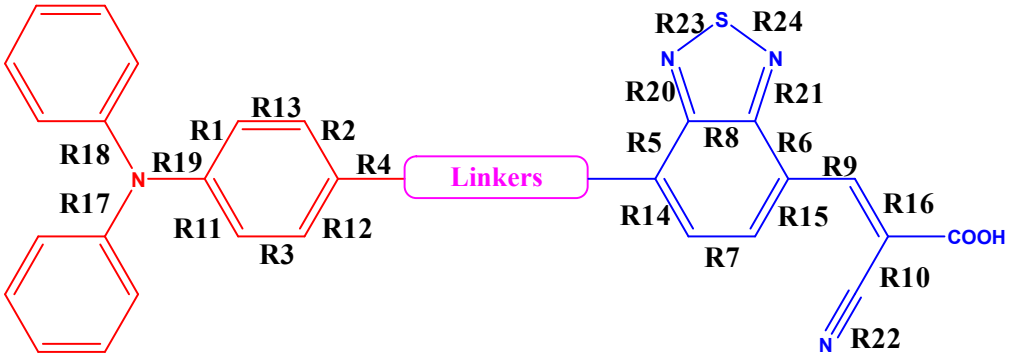


Fig. S3 Illustration of π delocalization from calculated all C−C, C−N and N−S bond lengths at M06-2X/6-311G(d,p) level. It represents the calculated bond lengths of C–C, C-N and N–S bonds in all the nine molecules. The bold straight lines indicate their single and double bond limits.



Molecule	C-C										C=C					
	R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R12	R13	R14	R15	R16
TPA1	1.40	1.40	1.38	1.46	1.45	1.44	1.44	1.44	1.42	1.45	1.40	1.38	1.40	1.38	1.38	1.35
TPA2	1.40	1.40	1.38	1.46	1.44	1.45	1.44	1.44	1.44	1.42	1.40	1.38	1.40	1.38	1.38	1.35
TPA3	1.40	1.40	1.39	1.48	1.40	1.40	1.39	1.47	1.44	1.44	1.40	1.39	1.40	1.37	1.38	1.35
TPA4	1.40	1.40	1.39	1.48	1.40	1.40	1.39	1.48	1.39	1.40	1.40	1.39	1.40	1.37	1.38	1.35
TPA5	1.40	1.40	1.38	1.46	1.41	1.45	1.44	1.44	1.42	1.45	1.40	1.38	1.40	1.38	1.38	1.35
TPA6	1.40	1.40	1.38	1.47	1.42	1.45	1.41	1.45	1.44	1.44	1.40	1.38	1.40	1.38	1.38	1.35
TPA7	1.40	1.40	1.38	1.45	1.42	1.44	1.44	1.44	1.44	1.42	1.40	1.38	1.40	1.38	1.38	1.35
TPA8	1.40	1.40	1.38	1.46	1.42	1.43	1.42	1.44	1.44	1.44	1.40	1.38	1.40	1.38	1.38	1.35
TPA9	1.40	1.40	1.38	1.46	1.45	1.44	1.44	1.44	1.42	1.45	1.40	1.38	1.40	1.38	1.38	1.35

Molecule	C-N			C=N		C≡N	N-S	
	R17	R18	R19	R20	R21	R22	R23	R24
TPA1	1.42	1.42	1.40	1.33	1.33	1.15	1.62	1.62
TPA2	1.42	1.42	1.40	1.33	1.33	1.15	1.62	1.62
TPA3	1.42	1.42	1.41	1.33	1.33	1.15	1.62	1.62
TPA4	1.42	1.42	1.41	1.33	1.33	1.15	1.62	1.62
TPA5	1.42	1.42	1.41	1.33	1.33	1.15	1.62	1.62
TPA6	1.42	1.42	1.41	1.33	1.33	1.15	1.62	1.62
TPA7	1.42	1.42	1.41	1.33	1.33	1.15	1.62	1.62
TPA8	1.42	1.42	1.41	1.33	1.33	1.15	1.62	1.62
TPA9	1.42	1.42	1.41	1.33	1.33	1.15	1.62	1.62

Fig. S4 Calculated all C–C, C–N and N–S bond lengths at M06-2X/6-311G(d,p) level.

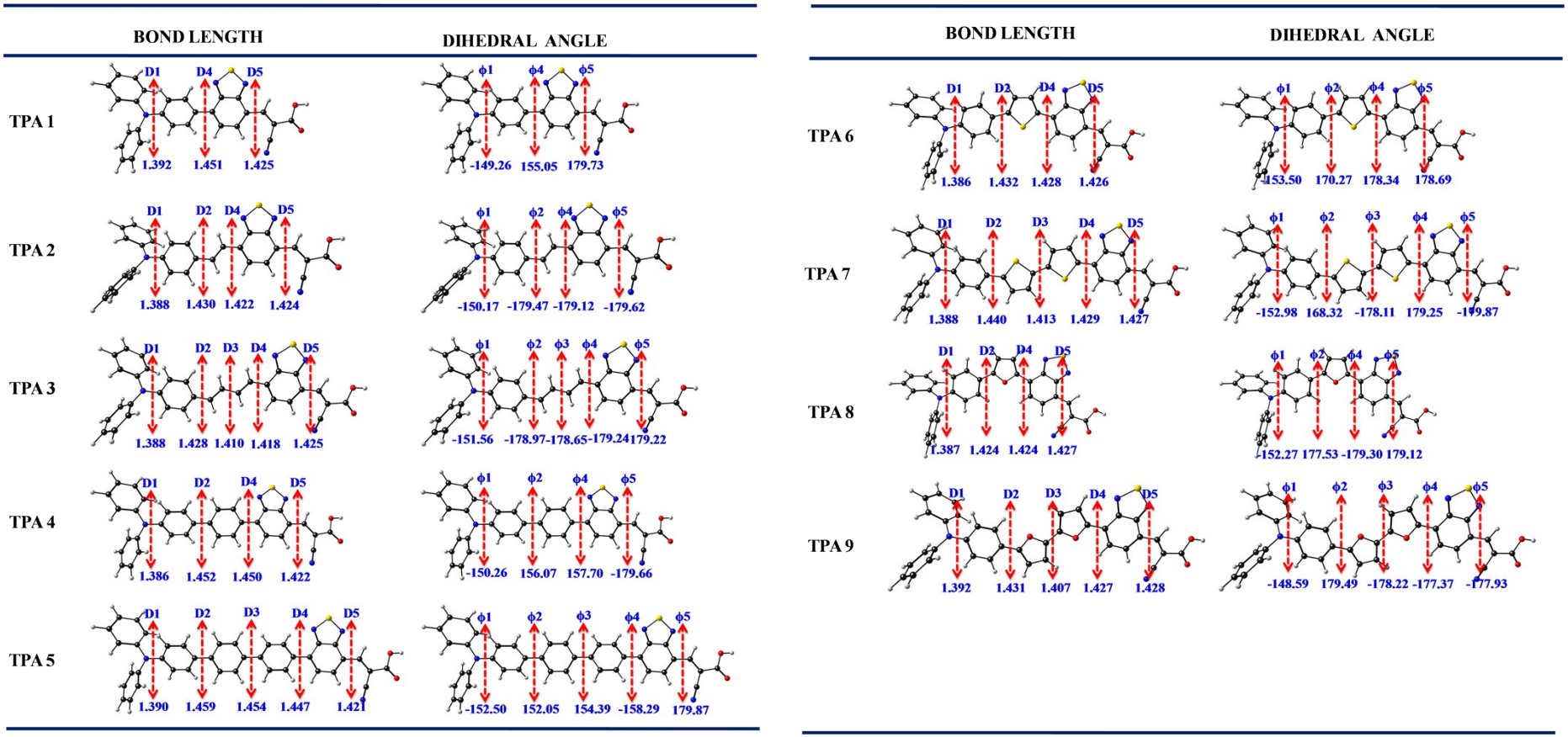


Fig. S5 Selected bond parameters of TPA derivatives in the excited states calculated at M06-2X/6-311G(d,p) level.

Table S1. The calculated QTAIM properties of possible hydrogen bonding in TPA derivatives.

Molecule	BCP	ρ(r)	L(r)	G(r)	V(r)	Lamda-1	Lamda-2	Ellipticity	V/G
TPA1	N---H	0.01217165	-0.011368375	0.009402885	0.007437395	-0.009748421	-0.00771084	0.264248837	0.790969452
TPA4	N---H	0.011673997	-0.010877658	0.008997104	0.00711655	-0.009029505	-0.007023425	0.285627005	0.790982253
TPA5	N---H	0.011686775	-0.010911301	0.009020467	0.007129633	-0.009023542	-0.006961196	0.296263248	0.790384029
TPA6$_A$	N---H	0.014487042	-0.013709311	0.011319017	0.008928722	-0.013454021	-0.011845791	0.13576391	0.788824886
TPA6$_B$	N---S	0.014029074	-0.012171592	0.010808337	0.009445083	-0.00954808	-0.009023232	0.058166353	0.873870105
TPA7$_A$	N---H	0.014409601	-0.013630236	0.011250839	0.008871443	-0.01335233	-0.011699151	0.141307628	0.788513909
TPA7$_B$	N---S	0.01431376	-0.012418687	0.011042444	0.0096662	-0.009793757	-0.009304966	0.05253018	0.875367861
TPA8$_A$	N---H	0.011717197	-0.010781674	0.00886549	0.006949307	-0.009937613	-0.008177311	0.215266624	0.783860415
TPA8$_B$	N---O	0.012708377	-0.013727383	0.011589613	0.009451843	-0.009889238	-0.009332662	0.059637446	0.815544316
TPA9$_A$	N---H	0.011681266	-0.010734638	0.008826698	0.006918758	-0.009902626	-0.008159657	0.213608087	0.78384445
TPA9$_B$	N---H	0.000577488	-0.000641551	0.000430712	0.000219873	-0.000368581	-0.000325776	0.131393617	0.51048679
	N---O	0.012136552	-0.013131771	0.011046796	0.00896182	-0.009370704	-0.008656778	0.082470273	0.811259724

SI 1.4 Frontier Molecular Orbitals (FMO):

The information drawn from these highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) are not only tells about the reactivity of the molecules but also provides clues to design newer molecules with desire HOMO-LUMO gaps.[6] Therefore, the FMOs consists of HOMO-2, HOMO-1, HOMO, LUMO, LUMO+1 and LUMO+2 have been studied for all these nine molecules and HOMOs/LUMOs levels are listed in supporting information (Table. S2, ESI†). Insertion of –CH=CH- alters both the HOMO and LUMO levels of TPA1 by ~0.1eV. Similarly, HOMO of TPA1 is altered to -6.36eV from -6.56eV when –CH=CH–CH=CH– is introduced in TPA3. Hence the π-linkers (ethene and butadiene) tend to affect both HOMO and LUMO levels. From the Fig. 6 it is evident that HOMO is localized on the TPA unit in all the molecules. It is interesting to see that the BTD unit is also contributing to a small extend for the stabilization of HOMO in all the molecules except TPA4 and TPA5. It is important to note that the TPA9, TPA7 and TPA3 have their HOMO all over the donor and π-linkers and have lower HOMO-LUMO gaps. This implies that π-linkers play a crucial role in altering the HOMOs of the TPA molecules.

Table S2. The Calculated frontier molecular orbital energy levels of TPA derivatives.

Molecule	HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1	LUMO+2	E_g (eV)
TPA1	-8.52	-7.91	-6.56	-2.54	-1.13	-0.11	4.02
TPA2	-8.50	-7.55	-6.45	-2.63	-1.11	-0.68	3.81
TPA3	-8.36	-7.30	-6.36	-2.68	-1.11	-0.94	3.67
TPA4	-8.40	-7.64	-6.49	-2.58	-1.16	-0.49	3.91
TPA5	-8.11	-7.46	-6.46	-2.59	-1.17	-0.69	3.87
TPA6	-8.44	-7.37	-6.45	-2.67	-1.16	-0.71	3.77
TPA7	-8.06	-7.07	-6.38	-2.71	-1.17	-1.05	3.66
TPA8	-8.44	-7.30	-6.36	-2.65	-1.15	-0.57	3.71
TPA9	-7.99	-6.97	-6.24	-2.66	-1.15	-0.79	3.58

SI 1.5 Frontier Molecular Orbitals (FMO) Contribution:

To gain more insights into the FMOs, their energetics of FMOs and their corresponding compositions have been calculated using QMForge program [7]. Here, the molecule is segmented into 4 units namely donor (Triphenylmine), π-linker, BTD (benzothiadiazole) and acceptor (cyanoacrylic acid). The different fragments involved in the calculation of percentage contribution to FMOs shown in Fig .7a and the FMO composition (%) of various fragments of the TPA derivatives are shown in Fig .7b. Table S3 (ESI†) lists the individual contribution of these four units towards their respective HOMO and LUMO levels. In all the molecules, donor unit contributes significantly (58-92%) towards the stabilization of HOMO. Especially the HOMO of TPA5 gets 92% contribution from donor unit. It is important to note that TPA9 has the lowest HOMO-LUMO gap gets only 58% contribution from donor and 36 % contribution from π-linker towards stabilization of HOMO. As, expected the donor contributes merely (1-10%) to LUMO. In all the molecules, The BTD unit largely stabilizes the LUMO and its contribution to LUMO varies from 57% to 65%. But the BTD unit contributes to the stabilization of HOMO is only up to 9%. The main contribution (65%) of BTD unit to LUMO is observed for TPA3 while minimum (57%) is obtained for TPA7. The acceptor (CA) unit contributes up to 29% to LUMO whereas its contribution is negligible (maximum of 2%) towards HOMO in all the molecules. Combining together the contributions of BTD and acceptor units, it is seen that about 84-90% of the stabilization of LUMO is done by these two units. HOMO is also stabilized by π-linkers to certain extend (7 to 36%). Especially when the molecules attain planarity, the contribution of π-linkers to HOMO increases. For instance in TPA9, 36% contribution is coming from π-linker while the same is reduced to 9% in TPA5. Greater the planarity of the molecule, greater will be the contribution of π-linkers to HOMO. The larger HOMO – LUMO gap molecules

(TPA4 and TPA5) are getting minimum contribution from π-linkers towards their HOMO and LUMO respectively. Only 7% of contribution is arising from π-linkers to HOMO and LUMO in the case of TPA4. The lower HOMO-LUMO gap molecules enjoy higher percentage (approximately 15%) of contributions from π-linkers for the stabilization of LUMO. Overall, this study shows that, the donor unit is largely stabilizing the HOMO whereas LUMO is stabilized by BTD and acceptor units. Hence, to tune LUMO, suitable substitution should be made on the BTD and acceptor units. Similarly, to alter the HOMO levels, donor unit should be tuned through substitutions along with modification in π-linkers. Thus this study sheds light on the contribution of different units in this class of molecules towards their FMOs. This information is very handy in designing molecules with desired HOMO and LUMO levels for various solar cell applications.

Table S3. The calculated percentage contribution of various fragments of TPA molecules towards HOMO & LUMO levels using QMForge program.

Molecule	FMO	Donor	Bridge	BTD	Acceptor
TPA 1	**HOMO**	89	0	9	2
	LUMO	11	0	61	28
TPA 2	**HOMO**	82	8	8	2
	LUMO	8	8	59	25
TPA 3	**HOMO**	73	17	7	3
	LUMO	5	15	60	20
TPA 4	**HOMO**	91	7	2	0
	LUMO	1	7	65	27
TPA 5	**HOMO**	92	8	0	0
	LUMO	0	8	62	30
TPA 6	**HOMO**	80	14	5	1
	LUMO	2	11	58	29
TPA 7	**HOMO**	70	26	3	1
	LUMO	1	15	57	27
TPA 8	**HOMO**	71	19	8	2
	LUMO	3	10	58	29
TPA 9	**HOMO**	58	36	5	1
	LUMO	1	13	58	28

SI 1.6 Solvent Effect on Absorption Spectra:

To understand the effect of solvent on the absorption spectra, TDDFT calculations have been carried out in solvent medium. Here, SCRF-PCM model is used to incorporate the solvent effects as this model has been identified as one of the most successful models for the accurate predictions of spectra in TDDFT calculations.[8,9] Various solvents including cyclohexane, tetrahydrofuran (THF), dichloromethane (DCM) and dimethyl sulfoxide (DMSO) have been used and the obtained results are given in supporting information (Table S4-S7, ESI†). The result shows that the solvents play a little role in enhancing the absorption maxima of these TPA derivatives. Moreover, the polarity of the solvent does not alter the λ_{max} very much. For instance, the inclusion of solvent is found to increase the λ_{max} only up to 5 nm from their gas phase λ_{max}. Further, the λ_{max} is altered by ~1-2 nm when the polarity of the solvent varies. Thus the role of solvent is minimum in the absorption spectra of these molecules. $S_0 \rightarrow S_1$ transitions are the dominant one in different solvents. Almost all these molecules are found to show HOMO→LUMO transitions with higher percentage of (%) contribution while HOMO-1 to LUMO transitions is found to show 8% to 54% contribution and data is given in supporting information Table S4-S7. The increasing order of λ_{max} in solvent medium is TPA5<TPA4<TPA1<TPA6<TPA7<TPA2< TPA3<TPA8<TPA9 which completely agrees with the gas phase trends. Hence, the polarity of the solvent does not change this trend at all.

Table S4. Computed absorption maxima (λ_{max} in nm), electronic Transitions, oscillator strengths (f_0) and electronic excitation energies (eV) of TPA (1-9) in cyclohexane medium using TDDFT method at M06-2X/6-311++G(d,p) level.

Molecule	State	λ_{max}	eV	f	LHE	Assignment
TPA 1	$S_0 \rightarrow S_1$	474.4	2.613	0.887	0.87	HOMO→LUMO (87%) HOMO-1→LUMO (8%)
TPA 2	$S_0 \rightarrow S_1$	509.5	2.433	1.361	0.96	HOMO→LUMO (81%) HOMO-1→LUMO (12%)
TPA 3	$S_0 \rightarrow S_1$	526.5	2.354	1.690	0.98	HOMO→LUMO (76%) HOMO-1→LUMO (15%)
TPA 4	$S_0 \rightarrow S_1$	435.1	2.849	0.921	0.88	HOMO→LUMO (67%) HOMO-1→LUMO (25%)
TPA 5	$S_0 \rightarrow S_1$	410.7	3.018	1.175	0.93	HOMO→LUMO (49%) HOMO-1→LUMO (43%)
TPA 6	$S_0 \rightarrow S_1$	502.9	2.465	1.167	0.93	HOMO→LUMO (72%) HOMO-1→LUMO (23%)
TPA 7	$S_0 \rightarrow S_1$	511.0	2.426	1.395	0.96	HOMO→LUMO (56%) HOMO-1→LUMO (35%)
TPA 8	$S_0 \rightarrow S_1$	528.9	2.344	1.037	0.91	HOMO→LUMO (79%) HOMO-1→LUMO (15%)
TPA 9	$S_0 \rightarrow S_1$	541.6	2.288	1.237	0.94	HOMO→LUMO (69%) HOMO-1→LUMO (23%)

Table S5. Computed absorption maxima (λ_{max} in nm), electronic Transitions, oscillator strengths (f_0) and electronic excitation energies (eV) of TPA (1-9) in THF medium using TDDFT method at M06-2X/6-311++G(d,p) level.

Molecule	State	λ_{max}	eV	f	LHE	Assignment
TPA 1	$S_0 \rightarrow S_1$	474.5	2.612	0.898	0.87	HOMO→LUMO (87%) HOMO-1→LUMO (8%)
TPA 2	$S_0 \rightarrow S_1$	511.4	2.424	1.371	0.96	HOMO→LUMO (81%) HOMO-1→LUMO (12%)
TPA 3	$S_0 \rightarrow S_1$	528.7	2.345	1.699	0.98	HOMO→LUMO (76%) HOMO-1→LUMO (15%)
TPA 4	$S_0 \rightarrow S_1$	431.9	2.870	0.957	0.89	HOMO→LUMO (67%) HOMO-1→LUMO (27%)
TPA 5	$S_0 \rightarrow S_1$	410.7	3.018	1.163	0.93	HOMO→LUMO (33%) HOMO-1→LUMO (52%) HOMO-2→LUMO (8%)
TPA 6	$S_0 \rightarrow S_1$	501.8	2.470	1.183	0.93	HOMO→LUMO (72%) HOMO-1→LUMO (23%)
TPA 7	$S_0 \rightarrow S_1$	508.2	2.439	1.421	0.96	HOMO→LUMO (56%) HOMO-1→LUMO (35%)
TPA 8	$S_0 \rightarrow S_1$	528.8	2.344	1.053	0.91	HOMO→LUMO (79%) HOMO-1→LUMO (15%)
TPA 9	$S_0 \rightarrow S_1$	539.7	2.297	1.261	0.95	HOMO→LUMO (69%) HOMO-1→LUMO (21%)

Table S6. Computed absorption maxima (λ_{max} in nm), electronic Transitions, oscillator strengths (f_0) and electronic excitation energies (eV) of TPA (1-9) in DCM medium using TDDFT method at M06-2X/6-311++G(d,p) level.

Molecule	State	λ_{max}	eV	f	LHE	Assignment
TPA 1	$S_0 \rightarrow S_1$	474.7	2.611	0.904	0.88	HOMO→LUMO (87%) HOMO-1→LUMO (8%)
TPA 2	$S_0 \rightarrow S_1$	512.0	2.421	1.376	0.96	HOMO→LUMO (81%) HOMO-1→LUMO (12%)
TPA 3	$S_0 \rightarrow S_1$	529.4	2.341	1.704	0.98	HOMO→LUMO (76%) HOMO-1→LUMO (15%)
TPA 4	$S_0 \rightarrow S_1$	431.8	2.871	0.966	0.89	HOMO→LUMO (64%) HOMO-1→LUMO (27%)
TPA 5	$S_0 \rightarrow S_1$	410.7	3.018	1.175	0.93	HOMO→LUMO (33%) HOMO-1→LUMO (52%) HOMO-2→LUMO (8%)
TPA 6	$S_0 \rightarrow S_1$	502.1	2.469	1.188	0.94	HOMO→LUMO (72%) HOMO-1→LUMO (23%)
TPA 7	$S_0 \rightarrow S_1$	508.4	2.438	1.426	0.96	HOMO→LUMO (56%) HOMO-1→LUMO (35%)
TPA 8	$S_0 \rightarrow S_1$	529.3	2.342	1.058	0.91	HOMO→LUMO (79%) HOMO-1→LUMO (15%)
TPA 9	$S_0 \rightarrow S_1$	540.1	2.295	1.266	0.95	HOMO→LUMO (69%) HOMO-1→LUMO (21%)

Table S7. Computed absorption maxima (λ_{max} in nm), electronic Transitions, oscillator strengths (f_0) and electronic excitation energies (eV) of TPA (1-9) in DMSO medium using TDDFT method at M06-2X/6-311++G(d,p) level.

Molecule	State	λ_{max}	eV	f	LHE	Assignment
TPA 1	$S_0 \rightarrow S_1$	473.6	2.617	0.910	0.88	HOMO→LUMO (87%) HOMO-1→LUMO (8%)
TPA 2	$S_0 \rightarrow S_1$	511.6	2.423	1.381	0.96	HOMO→LUMO (81%) HOMO-1→LUMO (12%)
TPA 3	$S_0 \rightarrow S_1$	529.1	2.343	1.709	0.98	HOMO→LUMO (76%) HOMO-1→LUMO (15%)
TPA 4	$S_0 \rightarrow S_1$	429.8	2.884	0.987	0.90	HOMO→LUMO (64%) HOMO-1→LUMO (28%)
TPA 5	$S_0 \rightarrow S_1$	409.1	3.030	1.203	0.94	HOMO→LUMO (30%) HOMO-1→LUMO (54%) HOMO-2→LUMO (8%)
TPA 6	$S_0 \rightarrow S_1$	500.8	2.475	1.196	0.94	HOMO→LUMO (72%) HOMO-1→LUMO (23%)
TPA 7	$S_0 \rightarrow S_1$	648.7	1.911	1.763	0.98	HOMO→LUMO (79%) HOMO-1→LUMO (13%)
TPA 8	$S_0 \rightarrow S_1$	528.2	2.346	1.064	0.91	HOMO→LUMO (79%) HOMO-1→LUMO (15%)
TPA 9	$S_0 \rightarrow S_1$	538.4	2.302	1.276	0.95	HOMO→LUMO (69%) HOMO-1→LUMO (21%)

SI 1.7 Solvent Effect on Emission Spectra:

To gain further insights into the influences of solvent on emission spectra, solvent phase calculations have been carried out using SCRF-PCM. Our results show that the gas phase emission spectra is not much altered by the inclusion of solvents. For instance TPA1 shows emission maxima at 559 nm in DMSO medium which is only 4 nm higher than its gas phase λ_{max} (Table S8-S11, ESI†). Increase the polarity of solvent, increases the emission maxima, however its upto few nanometers only.

Table S8. Computed emission spectra (λ_{max} in nm), electronic Transitions, oscillator strengths (f_0) and electronic excitation energies (eV) of TPA (1-9) in cyclohexane using TDDFT method at the M06-2X/6-311++G(d,p).

Molecule	State	λ_{max}	eV	f	LHE	Assignment
TPA 1	$S_1 \rightarrow S_0$	554.7	2.234	1.089	0.92	HOMO→LUMO (89%) HOMO-1→LUMO (5%)
TPA 2	$S_1 \rightarrow S_0$	602.8	2.056	1.567	0.97	HOMO→LUMO (89%) HOMO-1→LUMO (5%)
TPA 3	$S_1 \rightarrow S_0$	635.7	1.950	1.962	0.99	HOMO→LUMO (89%) HOMO-1→LUMO (5%)
TPA 4	$S_1 \rightarrow S_0$	545.7	2.271	1.335	0.95	HOMO→LUMO (76%) HOMO-1→LUMO (18%)
TPA 5	$S_1 \rightarrow S_0$	525.5	2.359	1.487	0.97	HOMO→LUMO (54%) HOMO-1→LUMO (40%)
TPA 6	$S_1 \rightarrow S_0$	615.8	2.013	1.410	0.96	HOMO→LUMO (87%) HOMO-1→LUMO (8%)
TPA 7	$S_1 \rightarrow S_0$	646.0	1.919	1.724	0.98	HOMO→LUMO (79%) HOMO-1→LUMO (13%)
TPA 8	$S_1 \rightarrow S_0$	618.3	2.005	1.177	0.93	HOMO→LUMO (87%) HOMO-1→LUMO (8%)
TPA 9	$S_1 \rightarrow S_0$	541.6	2.288	1.237	0.94	HOMO→LUMO (69%) HOMO-1→LUMO (23%)

Table S9. Computed emission spectra (λ_{max} in nm), electronic Transitions, oscillator strengths (f_0) and electronic excitation energies (eV) of TPA (1-9) in THF using TDDFT method at the M06-2X/6-311++G(d,p).

Molecule	State	λ_{max}	eV	f	LHE	Assignment
TPA 1	$S_0 \rightarrow S_1$	558.3	2.220	1.109	0.92	HOMO→LUMO (89%) HOMO-1→LUMO (5%)
TPA 2	$S_0 \rightarrow S_1$	610.0	2.032	1.595	0.97	HOMO→LUMO (89%) HOMO-1→LUMO (5%)
TPA 3	$S_0 \rightarrow S_1$	645.0	1.922	1.990	0.99	HOMO→LUMO (89%) HOMO-1→LUMO (6%)
TPA 4	$S_0 \rightarrow S_1$	545.7	2.271	1.353	0.96	HOMO→LUMO (76%) HOMO-1→LUMO (18%)
TPA 5	$S_0 \rightarrow S_1$	522.1	2.374	1.524	0.97	HOMO→LUMO (52%) HOMO-1→LUMO (40%)
TPA 6	$S_0 \rightarrow S_1$	619.9	1.999	1.437	0.96	HOMO→LUMO (84%) HOMO-1→LUMO (9%)
TPA 7	$S_0 \rightarrow S_1$	648.1	1.912	1.749	0.98	HOMO→LUMO (79%) HOMO-1→LUMO (13%)
TPA 8	$S_0 \rightarrow S_1$	622.8	1.990	1.205	0.94	HOMO→LUMO (87%) HOMO-1→LUMO (8%)
TPA 9	$S_0 \rightarrow S_1$	645.9	1.919	1.447	0.96	HOMO→LUMO (81%) HOMO-1→LUMO (12%)

Table S10. Computed emission spectra (λ_{max} in nm), electronic Transitions, oscillator strengths (f_0) and electronic excitation energies (eV) of TPA (1-9) in DCM using TDDFT method at the M06-2X/6-311++G(d,p).

Molecule	State	λ_{max}	eV	f	LHE	Assignment
TPA 1	$S_0 \rightarrow S_1$	559.3	2.216	1.115	0.92	HOMO→LUMO (89%) HOMO-1→LUMO (5%)
TPA 2	$S_0 \rightarrow S_1$	611.7	2.026	1.601	0.97	HOMO→LUMO (89%) HOMO-1→LUMO (5%)
TPA 3	$S_0 \rightarrow S_1$	647.2	1.915	1.996	0.99	HOMO→LUMO (89%) HOMO-1→LUMO (6%)
TPA 4	$S_0 \rightarrow S_1$	546.2	2.269	1.360	0.96	HOMO→LUMO (76%) HOMO-1→LUMO (18%)
TPA 5	$S_0 \rightarrow S_1$	522.3	2.373	1.532	0.97	HOMO→LUMO (52%) HOMO-1→LUMO (40%)
TPA 6	$S_0 \rightarrow S_1$	621.3	1.995	1.444	0.96	HOMO→LUMO (84%) HOMO-1→LUMO (9%)
TPA 7	$S_0 \rightarrow S_1$	649.4	1.909	1.754	0.98	HOMO→LUMO (79%) HOMO-1→LUMO (13%)
TPA 8	$S_0 \rightarrow S_1$	624.2	1.986	1.210	0.94	HOMO→LUMO (87%) HOMO-1→LUMO (8%)
TPA 9	$S_0 \rightarrow S_1$	647.2	1.915	1.452	0.96	HOMO→LUMO (81%) HOMO-1→LUMO (12%)

Table S11. Computed emission spectra (λ_{max} in nm), electronic Transitions, oscillator strengths (f_0) and electronic excitation energies (eV) of TPA (1-9) in DMSO using TDDFT method at the M06-2X/6-311++G(d,p).

Molecule	State	λ_{max}	eV	f	LHE	Assignment
TPA 1	$S_0 \rightarrow S_1$	559.4	2.216	1.122	0.92	HOMO→LUMO (89%) HOMO-1→LUMO (5%)
TPA 2	$S_0 \rightarrow S_1$	613.2	2.021	1.611	0.98	HOMO→LUMO (89%) HOMO-1→LUMO (5%)
TPA 3	$S_0 \rightarrow S_1$	649.4	1.909	2.005	0.99	HOMO→LUMO (89%) HOMO-1→LUMO (6%)
TPA 4	$S_0 \rightarrow S_1$	544.8	2.275	1.369	0.96	HOMO→LUMO (76%) HOMO-1→LUMO (18%)
TPA 5	$S_0 \rightarrow S_1$	520.0	2.384	1.549	0.97	HOMO→LUMO (52%) HOMO-1→LUMO (40%)
TPA 6	$S_0 \rightarrow S_1$	621.5	1.994	1.452	0.96	HOMO→LUMO (84%) HOMO-1→LUMO (9%)
TPA 7	$S_0 \rightarrow S_1$	648.7	1.911	1.763	0.98	HOMO→LUMO (79%) HOMO-1→LUMO (13%)
TPA 8	$S_0 \rightarrow S_1$	624.7	1.984	1.219	0.94	HOMO→LUMO (87%) HOMO-1→LUMO (8%)
TPA 9	$S_0 \rightarrow S_1$	646.8	1.916	1.463	0.97	HOMO→LUMO (81%) HOMO-1→LUMO (12%)

Table S12. The different components of β for the calculation of hyperpolaraizability of the TPA derivatives.

Molecule	β_{xxx}	β_{xyy}	β_{xzz}	β_{yyy}	β_{yzz}	β_{yxx}	β_{zzz}	β_{zxx}	β_{zyy}	β_{xxx}	$\beta_{total}=10^{-28}$
TPA1	-26172.393	784.850	84.676	-0.051	-3.790	-43.537	1.249	38.257	-5.226	-26172.393	2.186
TPA2	46968.533	-863.002	-172.85	72.577	7.959	-487.871	13.526	-46.140	8.974	46968.533	3.968
TPA3	-66223.763	925.457	119.983	141.002	10.290	-1226.362	-5.3190	112.719	22.085	-66223.763	5.631
TPA4	24047.959	-777.033	-146.90	-33.239	-18.340	477.218	7.409	-256.825	24.426	24047.959	1.998
TPA5	21470.134	-853.077	-77.774	63.020	5.858	-648.163	-2.757	-7.555	6.523	21470.134	1.775
TPA6	-39895.467	-35.218	80.832	375.216	-5.961	2296.348	7.653	-201.580	36.129	-39895.467	3.450
TPA7	-52296.148	760.067	-47.720	256.759	16.355	-1148.983	11.683	1485.215	61.197	-52296.148	4.459
TPA8	37385.859	1761.335	-58.243	932.360	14.867	4415.597	8.974	1491.706	7.730	37385.859	3.411
TPA9	-56198.914	291.157	134.073	310.644	30.962	-850.639	-12.278	400.418	61.313	-56198.914	4.818

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Cartesian coordinates of Ground state optimized structures

TPA 1

C	4.49970100	2.52645100	0.77686800
C	4.93960500	1.47291500	-0.02743700
C	6.05213600	1.65474600	-0.85111600
C	6.71476200	2.87500300	-0.86475700
C	6.26970000	3.92886500	-0.07334600
C	5.15801600	3.74850500	0.74338800
H	3.64132200	2.37881800	1.42168200
H	6.39176400	0.83360400	-1.47139400
H	7.57743600	3.00494900	-1.50719100
H	6.78496800	4.88107400	-0.09164400
H	4.80730700	4.55931500	1.37063200
N	4.27192200	0.22005200	0.00068100

C	5.04591400	-0.96931400	0.04164600
C	6.16865700	-1.04443500	0.86833200
C	4.70222800	-2.06555000	-0.75249400
C	6.93671700	-2.20098200	0.89466100
H	6.43323000	-0.19096900	1.48141600
C	5.46632200	-3.22399300	-0.70605600
H	3.83450800	-2.00204400	-1.39858100
C	6.58830200	-3.29760500	0.11322400
H	7.80631800	-2.24746300	1.53922600
H	5.18955600	-4.06872000	-1.32548700
H	7.18594300	-4.20014700	0.14098600
C	2.86911600	0.16159800	-0.00421800
C	2.11649600	1.13196500	-0.67986000
C	2.19062500	-0.86840700	0.66023600
C	0.73510000	1.07573500	-0.67174000

H	2.62511700	1.92084900	-1.21980600
C	0.80845900	-0.92908500	0.64403100
H	2.75736100	-1.62053100	1.19476700
C	0.04897400	0.04840000	-0.01117400
H	0.17690500	1.82020300	-1.22787900
H	0.30972200	-1.73288800	1.16799200
C	-1.42141800	0.03500400	0.00772600
C	-2.18151600	-1.18616700	-0.02455900
C	-2.16071800	1.19413900	0.04727800
C	-3.62380200	-1.15754700	-0.01910800
C	-3.57956000	1.22639200	0.05120300
H	-1.63965900	2.14181600	0.10771600
C	-4.34935300	0.08490500	0.02193600
H	-4.05090000	2.19831100	0.09273700
C	-5.79813700	0.00536200	0.03386000

C	-6.72838200	0.98436600	0.03003000
C	-6.42854500	2.38345000	0.00667100
C	-8.18538700	0.67527800	0.04609000
N	-6.16654600	3.50332700	-0.01176000
O	-8.43567700	-0.64527900	0.06876000
H	-9.39643900	-0.74321600	0.07624900
O	-9.04657600	1.50749100	0.03965100
H	-6.18772300	-1.00743700	0.04361000
N	-4.16910600	-2.36668000	-0.06754800
N	-1.69178500	-2.42132700	-0.08519100
S	-2.95151100	-3.43692400	-0.12021700

TPA 2

C	-5.80411800	-1.99254900	1.51437900
C	-6.19051400	-1.28530600	0.37387400

C	-7.34563000	-1.66433800	-0.31235800
C	-8.10344000	-2.73595200	0.14170300
C	-7.71268700	-3.44868900	1.27044100
C	-6.55859900	-3.07320700	1.95086300
H	-4.91112700	-1.69020900	2.04879300
H	-7.64280500	-1.11098900	-1.19545500
H	-8.99848200	-3.02127600	-0.39800600
H	-8.30267000	-4.28755800	1.61791800
H	-6.24930300	-3.61541800	2.83639500
N	-5.42299700	-0.17936500	-0.07860500
C	-6.09472700	1.00260700	-0.48572800
C	-7.17641400	1.48238700	0.25580600
C	-5.69210000	1.68641100	-1.63515100
C	-7.84566100	2.62839900	-0.15237900
H	-7.48719800	0.94828100	1.14595900

C	-6.35660700	2.84155600	-2.02539100
H	-4.85834900	1.30684200	-2.21412700
C	-7.43777800	3.31688100	-1.29020300
H	-8.68402800	2.99080700	0.43038000
H	-6.03500200	3.36406600	-2.91837600
H	-7.95811500	4.21383100	-1.60200800
C	-4.02193900	-0.25903300	-0.12311900
C	-3.38213600	-1.47372500	-0.39594600
C	-3.23163800	0.87822800	0.11056800
C	-2.00021600	-1.54198600	-0.42375900
H	-3.97608700	-2.35886900	-0.58642700
C	-1.85399600	0.79847100	0.06945300
H	-3.71399800	1.82291100	0.32905400
C	-1.20094200	-0.41536100	-0.19396200
H	-1.52367300	-2.49227300	-0.64041600

H	-1.27722900	1.69583900	0.25828200
C	2.59983500	0.21429300	-0.03285900
C	3.44854800	1.25566900	0.47971500
C	3.25421700	-0.88565300	-0.54404700
C	4.88213300	1.12813700	0.46759000
C	4.66391400	-1.01914800	-0.55251400
H	2.67893800	-1.69499100	-0.97570100
C	5.51602200	-0.05082500	-0.05995900
H	5.06891800	-1.92769600	-0.97581900
C	6.96378500	-0.09539900	-0.02749800
C	7.82092800	-1.06662000	-0.41299600
C	7.42027000	-2.32531500	-0.96279600
C	9.29483200	-0.89968900	-0.28775200
N	7.07721100	-3.33116000	-1.40318800
O	9.64063500	0.29138600	0.23177000

H	10.60539800	0.30318300	0.27308400
O	10.09384600	-1.73114700	-0.61192500
H	7.42644100	0.79887800	0.37762500
N	5.50124400	2.18514500	0.98024000
N	3.03150500	2.40455700	1.00167800
S	4.35208300	3.23806100	1.43130200
C	1.15819600	0.40128600	0.01829500
C	0.25006700	-0.55645000	-0.23457700
H	0.84033700	1.39558800	0.31148200
H	0.59849600	-1.55655000	-0.48126600

TPA 3

C	-7.15466000	-2.10425000	1.31608500
C	-7.45824800	-1.23565500	0.26531000
C	-8.61565800	-1.44524700	-0.48699000
C	-9.45780400	-2.50765200	-0.18614100

C	-9.15039400	-3.37973100	0.85286400
C	-7.99380600	-3.17382500	1.59834600
H	-6.25931100	-1.93436500	1.90255400
H	-8.84869200	-0.76847100	-1.30057700
H	-10.35364900	-2.65998000	-0.77612900
H	-9.80612200	-4.21076800	1.08073800
H	-7.74821400	-3.84149400	2.41552900
N	-6.60542300	-0.14001600	-0.02995900
C	-7.18449500	1.11973100	-0.33264000
C	-8.25500300	1.59692300	0.42675500
C	-6.70219500	1.88488200	-1.39697400
C	-8.83500300	2.82041000	0.11952200
H	-8.62747400	0.99953400	1.25059000
C	-7.27760900	3.11530600	-1.68560200
H	-5.87698400	1.50870100	-1.99018300

C	-8.34798800	3.58824000	-0.93337500
H	-9.66562700	3.17991000	0.71506200
H	-6.89485600	3.70024400	-2.51340400
H	-8.79890500	4.54476200	-1.16628100
C	-5.21090400	-0.30958500	-0.06051400
C	-4.64226000	-1.52358400	-0.46183300
C	-4.35691600	0.73875700	0.31724500
C	-3.26641300	-1.67585600	-0.48133700
H	-5.28565000	-2.34212800	-0.75967100
C	-2.98609000	0.57764700	0.28104500
H	-4.78500900	1.67838500	0.64420600
C	-2.40318500	-0.63378900	-0.12132700
H	-2.84520400	-2.62325300	-0.80075400
H	-2.35912700	1.40497400	0.59134100
C	3.81892100	0.34419300	0.11519800

C	4.74317500	1.41350000	0.38171400
C	4.39223200	-0.87091900	-0.19579100
C	6.16627900	1.20638700	0.32190700
C	5.79070300	-1.07961700	-0.25624800
H	3.75694600	-1.72166500	-0.40766200
C	6.71371500	-0.08253200	-0.00813600
H	6.12867500	-2.07447300	-0.51064000
C	8.15701500	-0.19896500	-0.04585300
C	8.94565000	-1.26225200	-0.31875900
C	8.45737100	-2.56699400	-0.64463300
C	10.43028900	-1.15596400	-0.30088000
N	8.04421000	-3.60868100	-0.90462100
O	10.85912700	0.08046000	0.00828200
H	11.82418500	0.04771800	-0.00535000
O	11.17088900	-2.06783300	-0.53523400

H	8.68247300	0.72246300	0.18379900
N	6.86223900	2.30343300	0.59691500
N	4.41052800	2.66015100	0.69979000
S	5.79067000	3.48314300	0.90197600
C	0.00824900	0.05333300	0.05388300
C	-0.96239400	-0.85010500	-0.17897600
H	-0.23861500	1.07853600	0.31455500
H	-0.65680500	-1.85948600	-0.44855000
C	1.40954600	-0.27203700	-0.03321400
H	1.64882400	-1.29930200	-0.29786500
C	2.39525800	0.61856700	0.19163100
H	2.13314100	1.63875500	0.45410400

TPA 4

C	6.69433400	2.56262100	0.16730100
C	7.13968700	1.32025900	-0.29142500

C	8.28518800	1.25515300	-1.08840800
C	8.97463600	2.41578600	-1.41318900
C	8.52536100	3.65378400	-0.96530500
C	7.38052800	3.71930500	-0.17773800
H	5.80931300	2.61147800	0.79066400
H	8.62903400	0.29099000	-1.44385100
H	9.86225900	2.35130400	-2.03121600
H	9.06182600	4.55739800	-1.22643000
H	7.02433600	4.67649400	0.18414300
N	6.44138700	0.13559200	0.05288200
C	7.17049900	-1.02638000	0.40950900
C	8.30535300	-0.92434500	1.21789000
C	6.76679100	-2.28338100	-0.04804900
C	9.02514300	-2.06278900	1.55508800
H	8.61728200	0.05088900	1.57251600

C	7.48305100	-3.41783300	0.30943700
H	5.89014100	-2.36110500	-0.68023000
C	8.61720100	-3.31540000	1.10842600
H	9.90407300	-1.96941600	2.18180000
H	7.15872500	-4.38659000	-0.05163600
H	9.17723900	-4.20173000	1.37910700
C	5.03146700	0.11511200	0.04398500
C	4.31406500	0.83172000	-0.91996500
C	4.32231500	-0.62175400	0.99869300
C	2.92883700	0.81597800	-0.91836200
H	4.85224500	1.39349200	-1.67381500
C	2.93732900	-0.64525000	0.97914000
H	4.86633700	-1.16832700	1.75948400
C	2.21101100	0.07525100	0.02581400
H	2.39422700	1.35653300	-1.69139900

H	2.40803100	-1.20128500	1.74482200
C	-3.56383700	0.02369400	0.03235900
C	-4.34856800	-1.08707800	-0.43308500
C	-4.27373900	1.10284400	0.49939100
C	-5.78925700	-1.03396500	-0.40281600
C	-5.69311100	1.15936300	0.53114600
H	-3.72964800	1.95353100	0.89166300
C	-6.48634000	0.12300100	0.09435700
H	-6.14286200	2.05753700	0.93057500
C	-7.93786600	0.07239800	0.09078000
C	-8.84480700	1.01574000	0.42112700
C	-8.51284000	2.33690400	0.86014500
C	-10.30930400	0.75064300	0.34428000
N	-8.22548200	3.39356900	1.21199500
O	-10.58919500	-0.49719300	-0.06865800

H	-11.55191900	-0.57194200	-0.08842700
O	-11.15022000	1.55755600	0.61887700
H	-8.34927000	-0.87632200	-0.23826100
N	-6.36135700	-2.13221600	-0.88100900
N	-3.88541900	-2.22562500	-0.94153200
S	-5.16735400	-3.13379400	-1.33002200
C	-2.08960300	0.01268300	0.00466800
C	-1.38695500	1.18539400	-0.29363300
C	-0.00183700	1.20532200	-0.28881900
H	-1.93302200	2.08570800	-0.55113100
C	0.73202800	0.05464100	0.01761000
H	0.52034400	2.12969900	-0.50698000
C	0.02652800	-1.11704400	0.31098700
C	-1.35889900	-1.14347600	0.29966700
H	0.57384600	-2.02768900	0.52537200

H	-1.87977000	-2.06548100	0.51944100

TPA 5

C	-8.85180200	-2.43981800	0.66597900
C	-9.30253100	-1.33379800	-0.05950100
C	-10.45446700	-1.45232200	-0.84153700
C	-11.14431100	-2.65631900	-0.88796100
C	-10.68996700	-3.76008600	-0.17354300
C	-9.53884200	-3.64447100	0.59888400
H	-7.96161900	-2.34617200	1.27668100
H	-10.80273700	-0.59494900	-1.40522300
H	-12.03659300	-2.73396800	-1.49777700
H	-11.22701100	-4.69929700	-0.21792300
H	-9.17790000	-4.49406000	1.16634500
N	-8.60185000	-0.10386200	-0.00033600

C	-9.32245400	1.11364700	0.07133600
C	-10.46832100	1.20975700	0.86531800
C	-8.89744900	2.23020900	-0.65363200
C	-11.17758700	2.40190600	0.92392300
H	-10.79676900	0.34447000	1.42877500
C	-9.60378000	3.42290200	-0.57439600
H	-8.01198400	2.15400400	-1.27355900
C	-10.74891700	3.51609300	0.20989600
H	-12.06484800	2.46201600	1.54297900
H	-9.26269900	4.28081200	-1.14163900
H	-11.30107000	4.44600300	0.26365200
C	-7.19004500	-0.09258500	-0.00533400
C	-6.47367000	-0.99631200	-0.79618700
C	-6.48168300	0.82151000	0.78073100
C	-5.08802600	-0.98785300	-0.78994600

H	-7.01283600	-1.69943500	-1.41968500
C	-5.09605700	0.83214200	0.76633600
H	-7.02674100	1.51696200	1.40769000
C	-4.36992000	-0.07305100	-0.01365800
H	-4.55275100	-1.67935500	-1.43098900
H	-4.56666700	1.53080600	1.40448900
C	5.71019100	-0.04543300	-0.02972000
C	6.50174700	1.15431200	-0.02067900
C	6.41291600	-1.22523700	-0.04443700
C	7.94200400	1.08497000	-0.01964200
C	7.83210600	-1.29822700	-0.04367700
H	5.86348200	-2.15804500	-0.08459300
C	8.63166900	-0.17833100	-0.03173900
H	8.27603800	-2.28357700	-0.06594700
C	10.08378200	-0.13887300	-0.03942200

C	10.98398800	-1.14255500	0.02049300
C	10.64270300	-2.52912500	0.11741300
C	12.45055200	-0.87743900	-0.00279300
N	10.34785100	-3.63819800	0.19431600
O	12.73878500	0.43189500	-0.09387000
H	13.70198700	0.50293400	-0.09998400
O	13.28561800	-1.73358100	0.05324500
H	10.50178400	0.86099200	-0.09544700
N	8.52119200	2.27912400	0.00437900
N	6.04602500	2.40366400	0.00929000
S	7.33379700	3.38352300	0.02716300
C	-0.06516700	-0.04695100	-0.01892100
C	-0.77609100	-1.24935200	-0.06729300
C	-2.16271800	-1.25738300	-0.06602200
H	-0.23523100	-2.18740600	-0.12331100

C	-2.88979100	-0.06388800	-0.01651200
H	-2.69214500	-2.20319600	-0.08555000
C	1.41555000	-0.03812100	-0.01875600
C	2.12892400	0.93030300	-0.73190700
C	3.51463900	0.94915200	-0.72685700
H	1.58861600	1.66380200	-1.31913300
C	4.23576700	-0.01573600	-0.01515400
H	4.04316000	1.70532900	-1.29125700
C	2.13888600	-0.99421600	0.70118500
C	3.52420000	-0.98479700	0.70109100
H	4.06316700	-1.71374900	1.29535000
H	1.60824700	-1.73008500	1.29418100
C	-2.17692600	1.13822000	0.03133100
C	-0.79030700	1.14689000	0.03034600
H	-0.26051600	2.09118700	0.08626100

H	-2.71765200	2.07759600	0.05223300

TPA 6

C	-5.90857800	2.50404800	-1.08629800
C	-6.53898100	1.67617800	-0.15452800
C	-7.58332500	2.18522900	0.62051400
C	-7.99145600	3.50256000	0.45881400
C	-7.35663400	4.33078100	-0.46088800
C	-6.31206800	3.82505600	-1.22811900
H	-5.10332500	2.10503700	-1.69188300
H	-8.07083400	1.54006800	1.34188700
H	-8.80338200	3.88600100	1.06512800
H	-7.67315700	5.35948900	-0.57945000
H	-5.81484900	4.45799900	-1.95341300
N	-6.13246300	0.32530000	-0.00162800

C	-7.12086800	-0.68309900	0.13626300
C	-8.26489400	-0.65734900	-0.66428400
C	-6.96492800	-1.70240800	1.07848800
C	-9.23852500	-1.63651800	-0.51799300
H	-8.38335700	0.13555300	-1.39335500
C	-7.93578700	-2.68700700	1.20524600
H	-6.08029500	-1.71553000	1.70431100
C	-9.07834900	-2.65847100	0.41204800
H	-10.12216400	-1.60560300	-1.14416900
H	-7.80372200	-3.47280700	1.93942000
H	-9.83679200	-3.42388000	0.51892200
C	-4.76687400	-0.01071000	0.01232600
C	-3.82120600	0.85992000	0.56748300
C	-4.32371600	-1.22295900	-0.53258500
C	-2.47796900	0.52632600	0.57375500

H	-4.14991200	1.79554800	1.00271400
C	-2.97996700	-1.55089400	-0.51594900
H	-5.04183400	-1.89805200	-0.98160300
C	-2.02908200	-0.68567400	0.03803300
H	-1.76867500	1.20514300	1.03434700
H	-2.65476500	-2.47759600	-0.97434300
C	3.28765900	-0.65719600	0.04431800
C	4.35555000	-1.60919400	-0.13618100
C	3.68548000	0.65243000	0.21267500
C	5.73245500	-1.17704200	-0.13623100
C	5.03609900	1.07613600	0.20878600
H	2.93169800	1.41552600	0.36574600
C	6.09080000	0.20532300	0.04085600
H	5.22014200	2.13180600	0.35055400
C	7.50286500	0.53206800	0.02468800

C	8.12768200	1.72205900	0.16153400
C	7.45491100	2.96876500	0.36223900
C	9.61187300	1.83291200	0.11237700
N	6.89447800	3.96036700	0.52310300
O	10.21499400	0.64639300	-0.07739000
H	11.16478300	0.82037200	-0.09519500
O	10.21100100	2.86341100	0.22837300
H	8.15569500	-0.32227100	-0.12179600
N	6.58954800	-2.17390900	-0.31740800
N	4.22969000	-2.91886800	-0.32019500
S	5.72067200	-3.53259900	-0.47416200
C	1.89083700	-1.05641100	0.04282500
C	1.34566800	-2.31853700	0.08473800
C	-0.06744500	-2.31660900	0.09421500
H	1.95152800	-3.21042400	0.12142200

C	-0.61352800	-1.05846200	0.05267500
H	-0.66930000	-3.21258800	0.16167300
S	0.62867700	0.14447800	-0.00939600

TPA 7

C	8.78943900	-2.17080800	-0.92880100
C	9.00410600	-1.17384700	0.02601200
C	10.08949500	-1.28251300	0.89846100
C	10.94773900	-2.37034600	0.80990600
C	10.72812900	-3.36868300	-0.13339400
C	9.64320900	-3.26365800	-0.99783100
H	7.95108400	-2.08126800	-1.60963100
H	10.25419900	-0.50827200	1.63844500
H	11.78653700	-2.44253400	1.49191300
H	11.39582600	-4.21889000	-0.19525300
H	9.46590100	-4.03047300	-1.74251300

N	8.13458600	-0.05657100	0.10608400
C	8.68118900	1.23388300	0.32554400
C	9.83277900	1.63213600	-0.35714100
C	8.08218500	2.11267300	1.23132500
C	10.37698200	2.88917900	-0.12989700
H	10.29571100	0.94793700	-1.05846200
C	8.62385600	3.37428400	1.43864600
H	7.19271800	1.79971900	1.76537200
C	9.77466800	3.76871300	0.76388700
H	11.27124900	3.18601700	-0.66477200
H	8.14980200	4.04708700	2.14332100
H	10.19817900	4.75069600	0.93375700
C	6.74093500	-0.22908500	0.00346900
C	6.12165800	-1.37624700	0.51467300
C	5.94496800	0.74757600	-0.60583300

C	4.75055800	-1.53694500	0.41651600
H	6.72361800	-2.13253000	1.00344700
C	4.57343700	0.58136200	-0.69419000
H	6.41233800	1.63446000	-1.01588300
C	3.94810000	-0.56365400	-0.18951500
H	4.28635700	-2.41468000	0.85116100
H	3.98101900	1.33998300	-1.19381100
C	-5.21406000	0.30624400	-0.21334000
C	-6.13066700	1.41895200	-0.21944800
C	-5.79151300	-0.93600000	-0.05668900
C	-7.54893200	1.20221200	-0.06669300
C	-7.18293500	-1.14763400	0.09678800
H	-5.15789100	-1.81494500	-0.05790500
C	-8.09841400	-0.11777900	0.09636600
H	-7.51462000	-2.16994200	0.21188300

C	-9.53706600	-0.22398100	0.24107500
C	-10.32240200	-1.31113500	0.40266900
C	-9.83705900	-2.65571400	0.46380200
C	-11.80123300	-1.19170500	0.53325500
N	-9.42572800	-3.72895300	0.51020600
O	-12.22631600	0.08221500	0.47328100
H	-13.18720900	0.05645100	0.56694000
O	-12.53826900	-2.12469200	0.67643200
H	-10.05846100	0.72724200	0.21362900
N	-8.25151800	2.32784800	-0.08998500
N	-5.81940800	2.70385300	-0.34955100
S	-7.20133600	3.54617200	-0.28621900
C	0.02451700	-0.43318400	-0.40688700
C	0.40005700	-1.75019400	-0.46302100
C	1.80320300	-1.93201800	-0.39407500

H	-0.31040500	-2.55744500	-0.58490400
C	2.49901100	-0.75638500	-0.28602400
H	2.29127900	-2.89471900	-0.46226700
C	-1.30868800	0.13085200	-0.46064900
C	-1.68539300	1.40653500	-0.80053100
C	-3.08144600	1.61187000	-0.73854200
H	-0.97611500	2.16418500	-1.10572800
C	-3.78055900	0.49013900	-0.35830700
H	-3.56796300	2.54519000	-0.97528200
S	1.41267100	0.59574800	-0.24403100
S	-2.68578000	-0.82987400	-0.04212300

TPA 8

C	-5.25921400	2.25015500	-1.54497800
C	-5.84282800	1.74031000	-0.38297400

C	-6.65442800	2.56629900	0.39751900
C	-6.88022400	3.88183500	0.01470600
C	-6.29012700	4.39362600	-1.13619400
C	-5.47663700	3.57200800	-1.90998600
H	-4.63544900	1.60521200	-2.15273900
H	-7.10627300	2.16734900	1.29804200
H	-7.51200200	4.51316800	0.62799100
H	-6.46269900	5.42206000	-1.42778400
H	-5.01742100	3.95697100	-2.81263800
N	-5.62413900	0.39086700	-0.00164700
C	-6.71546400	-0.37585200	0.48238100
C	-7.96014600	-0.29740700	-0.14603900
C	-6.55933700	-1.20471700	1.59579200
C	-9.03166600	-1.03593200	0.33830200
H	-8.07821600	0.34804500	-1.00844700

C	-7.63228100	-1.95270600	2.06205600
H	-5.59493100	-1.25714400	2.08731500
C	-8.87385200	-1.87054500	1.43990100
H	-9.99274100	-0.96604300	-0.15701700
H	-7.49896600	-2.59223400	2.92644200
H	-9.71014900	-2.44969400	1.81099800
C	-4.34022200	-0.17530600	-0.08882700
C	-3.19723200	0.60124200	0.13779200
C	-4.17905300	-1.53137900	-0.40670500
C	-1.93549000	0.04013800	0.04557700
H	-3.30730600	1.64866100	0.39002400
C	-2.91660000	-2.08772300	-0.48610600
H	-5.05422100	-2.14096500	-0.59434000
C	-1.77191200	-1.31412100	-0.26300200
H	-1.06250500	0.65311300	0.23089400

H	-2.81836200	-3.13593000	-0.74327300
C	3.00234800	-1.15224500	-0.17212400
C	4.25587500	-1.85007300	-0.26348600
C	3.07426800	0.20620000	0.05045900
C	5.49951300	-1.13613400	-0.12395400
C	4.29785200	0.90443300	0.18636200
H	2.15265700	0.76822900	0.12483700
C	5.52844000	0.28477200	0.10790300
H	4.23926600	1.96993100	0.35903600
C	6.83037400	0.90749400	0.23366400
C	7.16861300	2.19867300	0.44650000
C	6.22752600	3.26564700	0.59700000
C	8.59159700	2.62504000	0.54367200
N	5.45459400	4.10939000	0.71541500
O	9.45184900	1.60168900	0.39860300

H	10.33886000	1.97559100	0.47622700
O	8.94176700	3.75516100	0.73073300
H	7.66352700	0.21847000	0.14031600
N	6.56201400	-1.92428000	-0.23218200
N	4.42322500	-3.15049100	-0.47217300
S	6.02017300	-3.43081900	-0.48747900
C	1.74738600	-1.84468400	-0.30620300
C	1.40315300	-3.15098100	-0.53141800
C	-0.01357800	-3.19386000	-0.55869200
H	2.09623900	-3.96479700	-0.65700200
C	-0.44929300	-1.91178200	-0.34972400
H	-0.63236600	-4.06310200	-0.70699000
O	0.61592000	-1.09144100	-0.19597900

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C	8.18231800	-1.71937200	-1.62332800
C	8.47394800	-1.01492800	-0.45310800
C	9.65299900	-1.29497600	0.24064800
C	10.52659700	-2.26389600	-0.23578200
C	10.23063300	-2.97388600	-1.39461500
C	9.05301500	-2.69841200	-2.08225400
H	7.26912300	-1.49570800	-2.16248700
H	9.87782100	-0.74798400	1.14880100
H	11.43854200	-2.47296200	0.31072100
H	10.91139900	-3.73302000	-1.75924500
H	8.81474300	-3.23958900	-2.99018500
N	7.57432600	-0.02715600	0.02476500
C	8.08198300	1.19164700	0.53791400
C	9.15452600	1.82578600	-0.09493600
C	7.52931000	1.76590600	1.68569600

C	9.66788900	3.00820400	0.42072800
H	9.58226400	1.38272700	-0.98647200
C	8.03807500	2.95863900	2.18231200
H	6.70243100	1.27270000	2.18303800
C	9.11182900	3.58458600	1.55799900
H	10.50112700	3.48791300	-0.07910700
H	7.59968300	3.39239700	3.07322600
H	9.51059600	4.51063900	1.95316600
C	6.19240800	-0.30099600	0.06302700
C	5.73038500	-1.59266400	0.34566600
C	5.25573700	0.70951800	-0.17942500
C	4.37451200	-1.86071200	0.37929100
H	6.44595300	-2.38277500	0.53781300
C	3.89871000	0.43811300	-0.13113500
H	5.60202900	1.71099000	-0.40455400

C	3.43432100	-0.85135300	0.14658200
H	4.04203600	-2.86758800	0.60324200
H	3.18538300	1.23018600	-0.32123200
C	-4.70539100	0.54928500	-0.23650500
C	-5.70361300	1.54670900	-0.50909600
C	-5.16864800	-0.69583400	0.13084600
C	-7.10345300	1.22711900	-0.38975600
C	-6.54451800	-1.00560100	0.24815500
H	-4.44759100	-1.47483300	0.34128800
C	-7.54380800	-0.08620400	0.00318600
H	-6.79845600	-2.01453400	0.54192300
C	-8.97356500	-0.30433000	0.09368800
C	-9.67071300	-1.39715000	0.47553200
C	-9.07606700	-2.62813400	0.89732700
C	-11.15955800	-1.40492700	0.49242900

N	-8.57913000	-3.60977800	1.23294000
O	-11.68998400	-0.23706900	0.08922000
H	-12.64899500	-0.34107200	0.13463900
O	-11.82099300	-2.34576000	0.82703400
H	-9.57314900	0.55524100	-0.18835300
N	-7.89344300	2.25480100	-0.67538200
N	-5.48652500	2.80257900	-0.88058900
S	-6.93644100	3.50559600	-1.05968500
C	-0.10911900	-0.61297100	0.03997300
C	-0.07766900	-1.93489100	0.37265600
C	1.29818600	-2.28019200	0.47408700
H	-0.93457800	-2.57017000	0.52298500
C	2.01004100	-1.14597000	0.19752500
H	1.70581400	-3.24569600	0.72302200
C	-1.18389400	0.30552000	-0.20570600

C	-1.21591400	1.62296900	-0.57206600
C	-2.58805600	1.97209900	-0.65972600
H	-0.35820200	2.24802000	-0.75498000
C	-3.30043100	0.84609200	-0.34088100
H	-3.01680000	2.92388500	-0.92218000
O	1.15208600	-0.12592300	-0.06884000
O	-2.43770200	-0.17502100	-0.06290600