Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Structure-dependent luminescence of tetra-(4-pyridylphenyl)ethylene: a first-principles study

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S1. Comparison of geometry

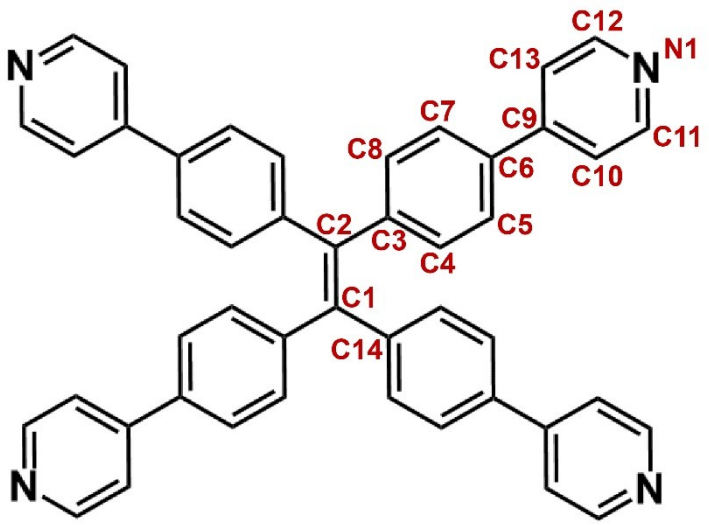


Table S1. A comparison of calculated geometry of TPPE with the experiment.[a]

	Cal.	Exp.
	Bond lengths (angstrom)	
C1-C2	1.367	1.352
C2-C3	1.493	1.480-1.498
C3-C4/C3-C8	1.406	1.387-1.403
C4-C5/C7-C8	1.391	1.368-1.387
C5-C6/C6-C7	1.405	1.387-1.402
C6-C9	1.482	1.478-1.491
C9-C10/C9-C13	1.404	1.371-1.393
C10-C11/C12-C13	1.393	1.374-1.393
C11-N1/C12-N1	1.341	1.311-1.339
	Dihedral Angles (degree)	
C14-C1-C2-C3 (β)	12.8	5.6
C1-C2-C3-C4 (α)	49.9,50.0	50.7-57.3
C5-C6-C9-C10	33.3-33.9	21.9-32.2

[a] Selected bond lengths and dihedral angles of the B3LYP/6-31G(d) equilibrium geometry in comparison to experimental data.[1]

As shown in Table S1, the differences between computational and experimental bond lengths are all less than 0.02 Å which are very consistent. In the case of dihedral angle, the computational values of C1-C2-C3-C4 and C5-C6-C9-C10 are closed to that

in experiment, but the value of C14-C1-C2-C3 is larger than experiment because the molecular structure measured in experiment is in solid state which would reduce the planarity of TPPE due to the molecular stacking. In general, the calculated geometry of TPPE is consistent with the experimental result.

S2. Emission wavelength

Table S2. The emission wavelength of TPPE with α and β varying from 0° to 80° calculated at B3LYP/6-31G(d) level.

α (degree)	Emission Wavelength (nm)	β (degree)	Emission Wavelength (nm)
0	727.68	0	466.88
10	731.37	10	466.18
20	690.95	20	472.64
30	602.16	30	488.75
40	525.66	40	516.49
50	467.18	50	563.30
60	418.42	60	645.57
70	380.59	70	807.86
80	351.73	80	1252.08

S3. Energy surface

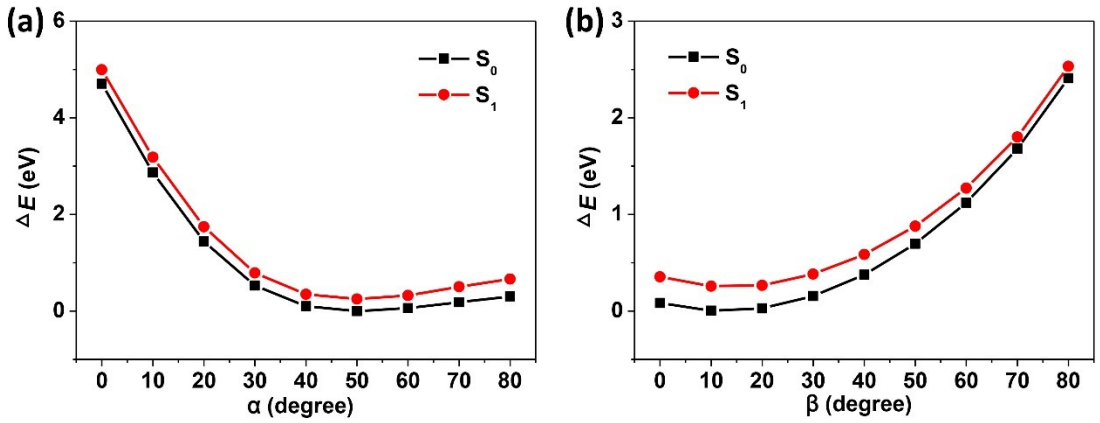
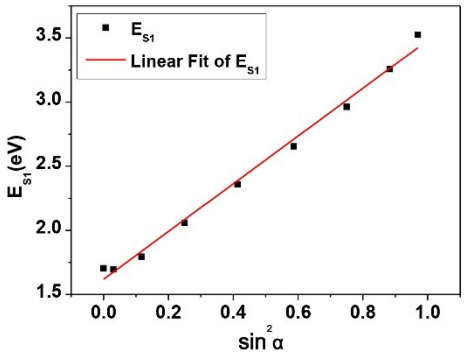


Fig. S1 Energy surfaces of TPPE at S_0 and S_1 respectively with α (β is fixed in 12.8°) (a) or β (α is fixed in 50.0°) (b) varying from 0° to 80°. All the energies have subtracted the reference energy of the equilibrium geometry of TPPE at S_0. These optimizations are all performed at B3LYP/6-31G(d) level.

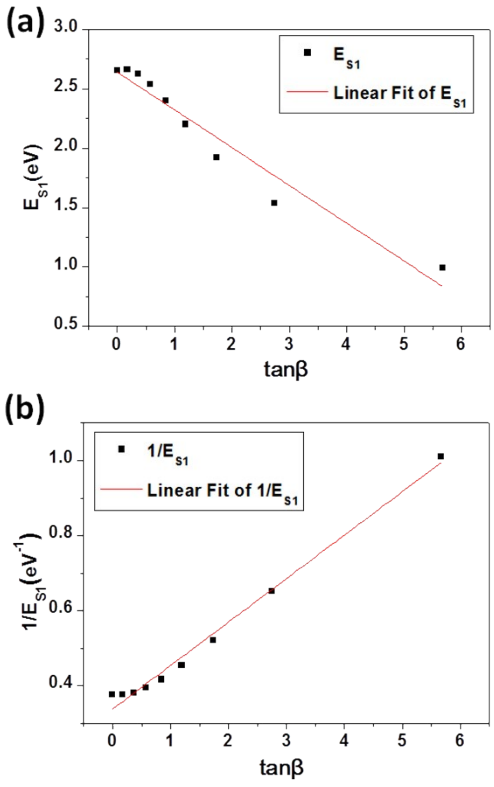
As shown in Fig. S1, the trend of energy surfaces of S_0 and S_1 are exactly the same. The energy varies with α and β reaches a minimum at α=50° and β=13° respectively, consistent with the equilibrium geometry of TPPE at S_0 (Table S1). The molecular energy is low when α is in the 30° to 80° range (ΔE < 1 eV), and it rises dramatically when α is less than 20° due to the enhanced steric hindrance effect (Fig. S1a). In the case of β, the molecular energy is increased gradually with the twisting of the ethylenic C=C bond (the increasing β) (Fig. S1b).

S4. Fitting details



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0.0269		
Adj. R-Square	0.99197		
		Value	Standard Error
E_{S1}	Intercept	1.61827	0.03345
	Slope	1.86191	0.05918

Fig. S2 Linear fit of the emission energy (E_{S1}) to $\sin^2\alpha$ and the fitting details.



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0.1322		
Adj. R-Square	0.9446		
		Value	Standard Error
E_{S1}	Intercept	2.63891	0.06087
	Slope	-0.31796	0.02713

Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0.0033		
Adj. R-Square	0.98915		
		Value	Standard Error
$1/E_{S1}$	Intercept	0.33788	0.00962
	Slope	0.11582	0.00429

Fig. S3 Linear fit of E_{S1} (a) and its reciprocal (b) to tanβ with the fitting details.

S5. Comparison of emission energy

Table S3. A comparison of emission energies of TPPE calculated by Eq. (3) with the values calculated by TDDFT at B3LYP/6-31G(d) level. The energy difference is defined as $\Delta E = E_{\text{Eq.3}} - E_{\text{TDDFT}}$.

α (degree)	β (degree)	Emission energy (eV)		ΔE (eV)
		Eq. 3	TDDFT	
0	50	0.992	1.003	-0.011
10	30	1.418	1.431	-0.013
20	0	2.068	1.971	0.097
30	20	1.988	2.055	-0.067
40	60	1.517	1.771	-0.254
50	80	0.989	0.994	-0.005
60	20	2.919	2.919	-0.00015
70	70	2.059	1.782	0.277
80	40	2.995	3.042	-0.047
90	10	3.544	3.632	-0.088

As shown in Table S3, all the energy differences are within 0.3 eV, most of them are within 0.1 eV. Only two values calculated by Eq. (3) have a sizable difference ($|\Delta E| > 0.25$ eV) with TDDFT calculation, and they appear when β is 60° and 70° which indicate that Eq. (3) is not so accurate for the configuration with a large β. This error can be attributed to the lack of the fitting that the trigonometric function can not exactly describe the emission energy when α and β change in the whole range. However, the error of Eq. (3) is within acceptable range and it can give an accurate result when β is relatively small (less than 60°) and when either α or β is near the fitting value (their respective value in the equilibrium geometry of TPPE at S_0), such as when α=50° and β=80° (Table S3). Therefore, Eq. (3) is desirable as a quick and convenient way to predict the approximate emission energy (or wavelength) of TPPE.

S6. Absorption property

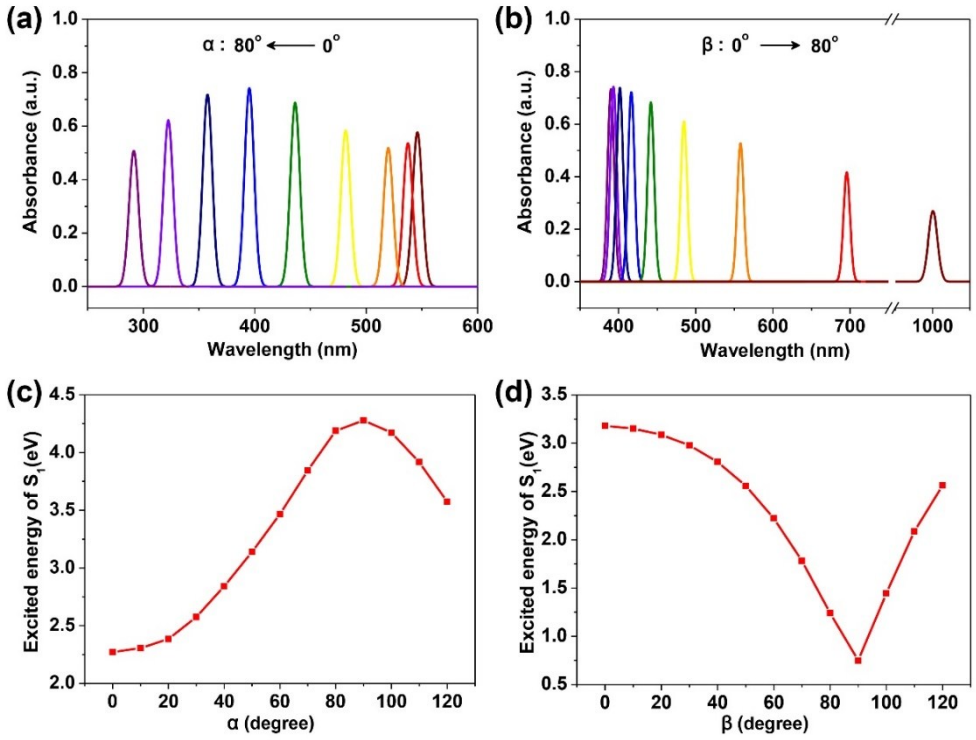


Fig. S4 Maximum absorption ability (reflected by transition oscillator strength) versus wavelength for TPPE with α (a) and β (b) varying from 0° to 80° respectively. Plots of excited energy from the S_0 to the S_1 of TPPE versus α (c) and β (d) varying from 0° to 120°.

As shown in Fig. S4, the maximum absorption wavelength is blue-shifted from 550 nm to 290 nm with increasing α, and red-shifted from 390 nm to 1000 nm with increasing β, which shows the same trend with emission properties (Fig. 2).

S7. Hole-electron distribution

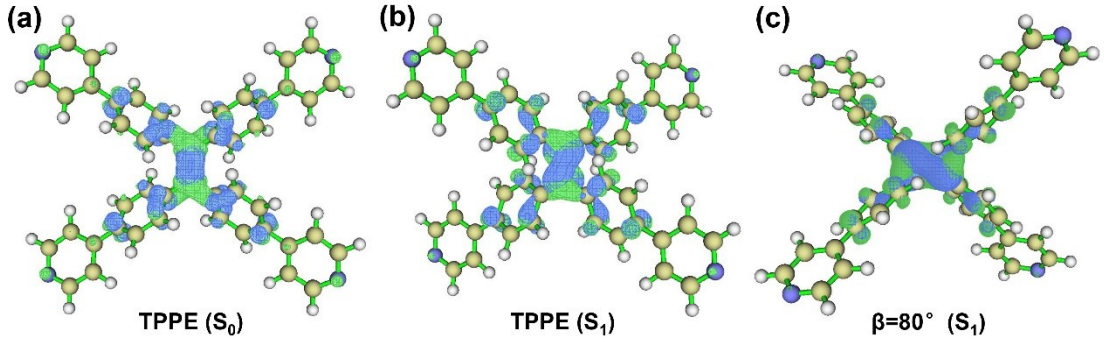


Fig. S5 Hole-electron distributions of TPPE for the lowest excited state based on the equilibrium geometries at S_0 (a) and S_1 (b) respectively, and the S_1 geometry when β is 80° (α is 50°) (c). The blue and green isosurfaces represent hole and electron distributions, respectively. The analyses are performed by the Multiwfn software[2] based on the TDDFT calculations at B3LYP/6-31G(d) level.

As shown in Fig. S5, the distributions of hole and electron for the lowest excited state of TPPE are not separated from each other whether in the S_0 or S_1 geometries, and the same in an extremely twisted geometry (β=80°). Therefore, there no appreciable charge transfer property was found in the lowest excited state of TPPE.

S8. Molecular orbital energy

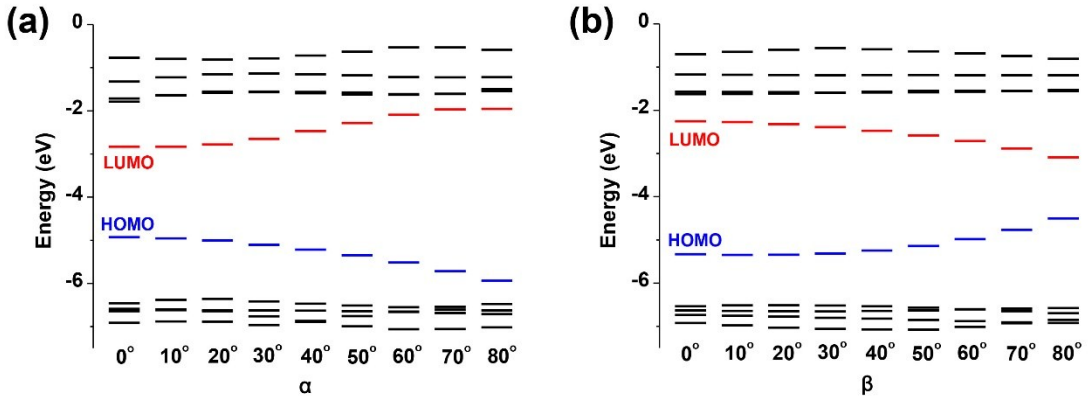


Fig. S6 Molecular orbital energies of TPPE at successively increasing values of α (a) or β (b) based on the optimization geometries of the S_1 which are calculated at B3LYP/6-31G(d) level. Here HOMO (LUMO) represents the highest occupied molecular orbital (lowest unoccupied molecular orbital).

As shown in Fig. S6, the energy of HOMO is increased and the energy of LUMO is decreased with the decreasing α and increasing β respectively, and leading to the reduction of energy gap. The energy changes of other molecular orbitals are all small.

S9. Solvent effect

Table S4. The values of α, β and the maximum absorption wavelength of TPPE in each solvent based on the optimized geometries at S_0 calculated at B3LYP/6-31G(d) level.

Solvent (Dielectric constant)	α (degree)	β (degree)	Maximum absorption wavelength (nm)
Hexane (1.88)	48.80	12.73	395.54
Toluene (2.37)	48.92	12.73	396.90
$CHCl_3$ (4.71)	49.61	12.82	395.59
THF (7.52)	49.81	12.82	395.02
CH_2Cl_2 (8.93)	49.89	12.81	395.16
MeOH (32.6)	50.15	12.85	393.81
H_2O (78.4)	50.23	12.86	393.72

Table S5. The values of α, β and the emission wavelength of TPPE in each solvent based on the optimized geometries at S_1 calculated at B3LYP/6-31G(d) level.

Solvent (Dielectric constant)	α (degree)	β (degree)	Emission wavelength (nm)
Hexane (1.88)	24.05	54.97	763.51
Toluene (2.37)	24.04	55.39	767.96
$CHCl_3$ (4.71)	23.56	57.16	799.10
THF (7.52)	23.57	57.40	795.41
CH_2Cl_2 (8.93)	23.57	57.48	802.70
MeOH (32.6)	23.59	57.73	800.07
H_2O (78.4)	23.60	57.80	801.00

S10. Results calculated at PBE0 level

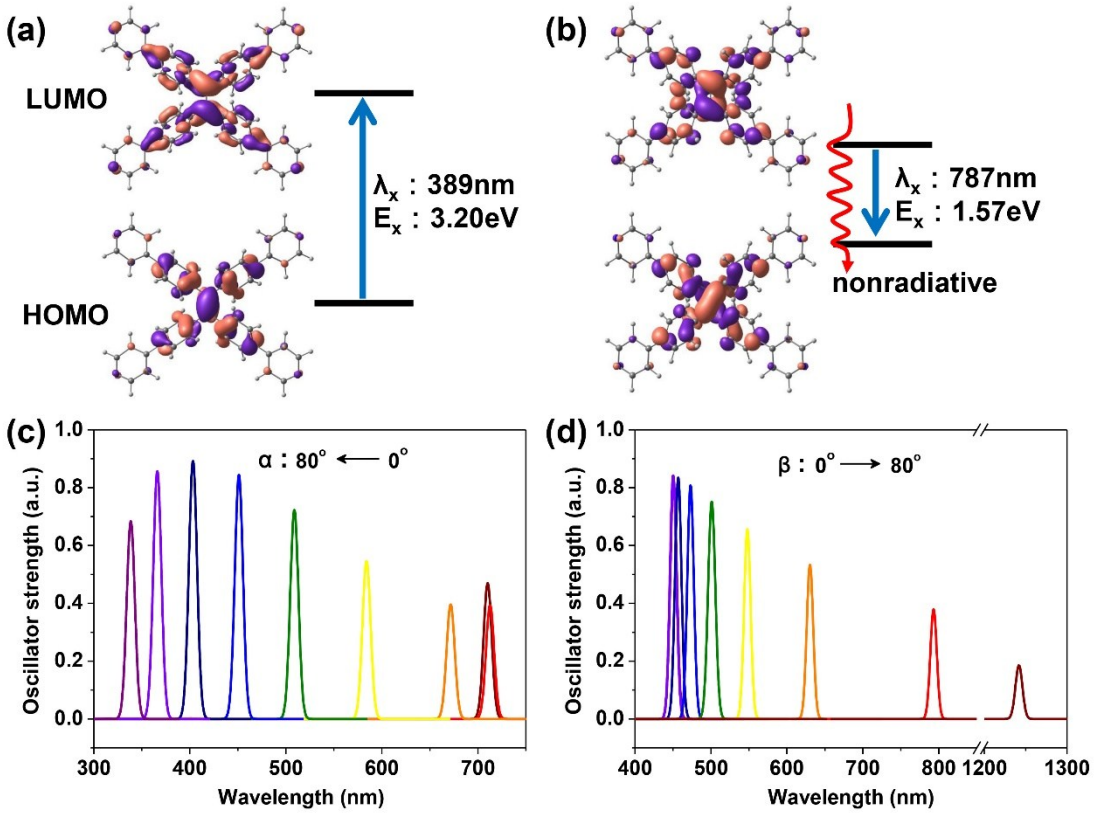


Fig. S7 Transition orbital energies with wavefunctions of the lowest excited state based on the equilibrium geometries of S_0 (a) and S_1 (b) respectively, and emission ability (reflected by transition oscillator strength) versus wavelength for TPPE with α (c) and β (d) varying from 0° to 80° respectively, calculated at PBE0/6-31G(d) level.

As shown in Fig. S7a and b, the transition energies of the lowest excited state in S_0 (3.20 eV) and S_1 geometries (1.57 eV) are both very closed to the values calculated at B3LYP level (3.14 eV for S_0 and 1.54 eV for S_1), and the wavefunctions of HOMO and LUMO are also exactly the same (Fig. 1c and d). The emission properties varying with α and β (Fig. S7c and d) show the same trend with that calculated at B3LYP level (Fig. 2b and c) in addition to a small blueshift (6-20 nm) which is attributed to the intrinsic

difference between the two functionals on dealing with the exchange-correlation contribution. In general, the fully consistent transition orbitals and emission relationship indicate that the results calculated by B3LYP is reliable for this system.

11. Cartesian coordinates of the equilibrium geometries of TPPE calculated at B3LYP/6-31G(d) level

TPPE (S_0)

C	-0.47835800	0.21105500	-0.00615200
C	0.20698800	1.39421400	-0.00615100
C	1.69188700	1.46393400	-0.14523700
C	2.45821300	2.27109900	0.71423400
C	2.36432200	0.77805700	-1.17145500
C	3.83948700	2.36190300	0.57497400
H	1.96624300	2.82035100	1.51173700
C	3.74445000	0.87553700	-1.31718700
H	1.79533400	0.17383600	-1.87082900
C	4.51213200	1.66504900	-0.44385600
H	4.40420500	2.96359500	1.28114000
H	4.22729200	0.35633600	-2.13986500
C	-0.47185700	2.71645200	0.13552400
C	-0.15821500	3.78363400	-0.72464900
C	-1.39727400	2.95639700	1.16587700
C	-0.76732000	5.02620300	-0.58125400
H	0.55910700	3.63161300	-1.52598400
C	-2.00030200	4.20116800	1.31556500
H	-1.63458000	2.16071200	1.86488200
C	-1.70201800	5.26116200	0.44210600
H	-0.53004700	5.81673600	-1.28719600
H	-2.68750600	4.35968900	2.14157000
C	-1.96325800	0.14133600	-0.14524000
C	-2.72958400	-0.66582900	0.71423000
C	-2.63569100	0.82721400	-1.17145900
C	-4.11085800	-0.75663300	0.57496700
H	-2.23761500	-1.21508100	1.51173300
C	-4.01581800	0.72973300	-1.31719300
H	-2.06670100	1.43143500	-1.87083200
C	-4.78350200	-0.05977900	-0.44386400
H	-4.67557700	-1.35832500	1.28113200
H	-4.49865800	1.24893400	-2.13987200
C	0.20048700	-1.11118200	0.13552400
C	-0.11315400	-2.17836400	-0.72464900
C	1.12590200	-1.35112700	1.16587900
C	0.49595100	-3.42093300	-0.58125300
H	-0.83047500	-2.02634300	-1.52598500
C	1.72893000	-2.59589800	1.31556700

H	1.36320700	-0.55544200	1.86488400
C	1.43064800	-3.65589300	0.44210800
H	0.25868000	-4.21146500	-1.28719700
H	2.41613200	-2.75441800	2.14157400
C	5.98325600	1.76481000	-0.59758100
C	6.75305300	0.68113500	-1.05072900
C	6.68015200	2.94652500	-0.29763300
C	8.13273000	0.82533600	-1.17850400
H	6.29001100	-0.27334900	-1.28023200
C	8.06343900	2.98678900	-0.45744500
H	6.15274700	3.83526700	0.03407300
N	8.80010300	1.95288500	-0.89085500
H	8.73439900	-0.01334900	-1.52502100
H	8.60767200	3.90206600	-0.23044100
C	2.07566300	-4.98133300	0.59984900
C	3.39494500	-5.10939000	1.06376300
C	1.40064000	-6.17402700	0.29335300
C	3.95610300	-6.37755000	1.19539700
H	3.98984800	-4.23246800	1.29868900
C	2.05335300	-7.39362300	0.45831200
H	0.37037300	-6.15920000	-0.04786500
N	3.31309600	-7.51779400	0.90230400
H	4.98017100	-6.48165300	1.55020300
H	1.53258300	-8.32127900	0.22651900
C	-6.25462600	-0.15954000	-0.59759100
C	-7.02442700	0.92414600	-1.05070500
C	-6.95151900	-1.34126700	-0.29768100
C	-8.40410300	0.77994600	-1.17848300
H	-6.56138900	1.87864000	-1.28017800
C	-8.33480500	-1.38153000	-0.45749300
H	-6.42411100	-2.23001700	0.03399700
N	-9.07147200	-0.34761500	-0.89087000
H	-9.00577600	1.61864000	-1.52497400
H	-8.87903500	-2.29681600	-0.23051800
C	-2.34703200	6.58660300	0.59984600
C	-3.66628800	6.71466400	1.06383100
C	-1.67203200	7.77929200	0.29328000
C	-4.22744600	7.98282500	1.19546100
H	-4.26117200	5.83774500	1.29881600
C	-2.32474300	8.99888900	0.45824100
H	-0.64178500	7.76446000	-0.04799700
N	-3.58446200	9.12306500	0.90230000
H	-5.25149500	8.08693100	1.55032300
H	-1.80399100	9.92654000	0.22639200

TPPE (S_1)

C	-0.50797400	0.16233700	-0.00120100
C	0.23661600	1.44293300	-0.00120100
C	1.54582600	1.48261900	-0.61097800
C	2.55047000	2.42034300	-0.23300200
C	1.91738000	0.52694000	-1.60009000
C	3.80348200	2.41618900	-0.81859100
H	2.35140900	3.11872800	0.57215100
C	3.16875300	0.53589600	-2.18812100
H	1.18477300	-0.20443200	-1.92497800
C	4.14999600	1.48158600	-1.81916400
H	4.54787300	3.12227800	-0.46313400
H	3.38393600	-0.18443600	-2.97155000
C	-0.37844200	2.59959900	0.60913400
C	-0.07610800	3.93709800	0.22117300
C	-1.38048200	2.44620400	1.60983400
C	-0.70347800	5.02159000	0.80748800
H	0.61885300	4.11200200	-0.59258000
C	-1.99467100	3.53570000	2.19935200
H	-1.64048500	1.44708000	1.94397900
C	-1.67461600	4.85726100	1.81955100
H	-0.47144400	6.01791300	0.44334100
H	-2.71625400	3.36338100	2.99211700
C	-1.81718500	0.12265300	-0.61097800
C	-2.82182500	-0.81507600	-0.23300600
C	-2.18874100	1.07833700	-1.60008300
C	-4.07483900	-0.81092100	-0.81859200
H	-2.62276100	-1.51346700	0.57214100
C	-3.44011600	1.06938200	-2.18811100
H	-1.45613600	1.80971200	-1.92496700
C	-4.42135700	0.12368800	-1.81915900
H	-4.81922700	-1.51701300	-0.46313800
H	-3.65530100	1.78971900	-2.97153600
C	0.10708100	-0.99433000	0.60913500
C	-0.19526400	-2.33182800	0.22118000
C	1.10912300	-0.84093800	1.60983100
C	0.43210100	-3.41632200	0.80749700
H	-0.89022900	-2.50673000	-0.59256900
C	1.72330700	-1.93043500	2.19935200
H	1.36913400	0.15818600	1.94397300
C	1.40324300	-3.25199500	1.81955700
H	0.20005900	-4.41264500	0.44335500

H	2.44489300	-1.75811800	2.99211500
C	5.48580300	1.48484200	-2.44217200
C	6.07090400	0.31252400	-2.95692800
C	6.24904300	2.66202900	-2.55822400
C	7.33419000	0.37170700	-3.53819400
H	5.56363400	-0.64382400	-2.88296400
C	7.50406500	2.61251100	-3.15785000
H	5.86159100	3.61461000	-2.21184700
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C	3.36674500	-4.32798800	2.97542800
C	1.43500000	-5.66592300	2.54082600
C	3.94644500	-5.45221200	3.55606400
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C	2.10434000	-6.72842300	3.14110500
H	0.42206400	-5.81092800	2.17953000
N	3.34395200	-6.64798000	3.64993100
H	4.95436400	-5.38997900	3.96322300
H	1.61447300	-7.69739400	3.22305300
C	-5.75716500	0.12043500	-2.44216200
C	-6.34226900	1.29275600	-2.95691000
C	-6.52040400	-1.05675200	-2.55822000
C	-7.60555600	1.23357500	-3.53817300
H	-5.83500000	2.24910400	-2.88294200
C	-7.77542800	-1.00723200	-3.15784200
H	-6.13295100	-2.00933500	-2.21184900
N	-8.33272600	0.11076500	-3.64921000
H	-8.06158000	2.14084600	-3.93119200
H	-8.36379200	-1.91835200	-3.25410100
C	-2.33773100	6.01681700	2.44266200
C	-3.63812400	5.93324400	2.97542000
C	-1.70638900	7.27119100	2.54081200
C	-4.21783200	7.05746700	3.55605300
H	-4.20781200	5.01168200	2.91613000
C	-2.37573500	8.33368900	3.14108700
H	-0.69345400	7.41620100	2.17951400
N	-3.61534700	8.25323900	3.64991500
H	-5.22575000	6.99522800	3.96321200
H	-1.88587500	9.30266300	3.22303100

Reference

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